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AN INVESTIGATION OF THE STRUCTURE AND PHASE RELATIONS OF
C-S-H GELS

by

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Goals

Solid state NMR was used to obtain data on the atomic level structure of calcium silicate hydrate (C-S-H) that formed from a variety of starting materials under a variety of conditions. Because C-S-H is the major component of hydrated portland cement, a knowledge of its structure and of its structural evolution will ultimately allow users of cement containing materials such as mortars and concrete to more accurately predict the physical and mechanical behavior of these materials once they are placed into service. From the outset, the goal of the work was to observe the hydration process on the atomic level, integrate the findings with existing data in the literature, and refine hydration models as necessary to accommodate the newly acquired data.

Background

C-S-H is a complex material for a number of reasons, the most salient are that it is extremely fine grained and that it has a very high surface area. Although solid state NMR data are revealing the fact that C-S-H has a remarkable amount of order on the atomic-level, C-S-H's general lack of long range order makes it extremely difficult to study using more conventional techniques such as X-ray diffraction.

Because of its X-ray amorphous character, and the additional facts that it also has a wide range of chemical composition and seemingly contains both molecular water and hydroxyl groups, C-S-H has often been described using terms such as poorly crystallized, ill-defined, highly disordered, and partially polymerized. For lack of a better descriptor, C-S-H has been equated with gels in order to explain its gel-like properties (C-S-H gel). Historically, C-S-H has been thought of as a mixture of silicate anions (predominantly dimer) that slowly undergo time and temperature dependent polymerization; the dimers bond to each other to form silicate chains known as dreierkette [(SiO₃)n] where n typically equals 5 to 8. With time, certain C-S-H gels (mainly those containing finely divided silica) often develop poorly crystalline "tobermorite-like" features (C-S-H I). This observation, more than any other, has been offered as "proof" that a "polymerization model" was in fact correct and appropriate to describe all C-S-H phases, regardless of their composition.

Evidence now suggests, however, that there are two C-S-H phases, one contains silicate chains (Ca/Si = 0.6 to 1.0) and the other contains silicate dimers (Ca/Si ≥1.1). The initial C-S-H that forms when tricalcium and/or dicalcium silicate come in contact with water equilibrates rapidly with the solution phase (minutes to hours) and is accordingly rather quickly defined on the atomic level. Processes take place through solution. The structure moves towards "equilibrium" very early in the hydration process. It has a Ca/Si ratio ≥ 2 and it is fully dimeric. Most likely it changes from an "active" to an "inactive" form as the sorosilicate structure sheds its excess calcium and in the process attains a Ca/Si ratio of ~2.0. However, the dimeric structure is extremely unstable and therefore sensitive to localized as well as global variations in composition and temperature (localized calcium deficiency due to precipitation of Ca(OH)₂ and self-heating due to exothermic reaction). The changes that occur as "equilibrium" is reestablished after such a change manifest themselves in terms of weeks and years. Once these facts were realized, the structural evolution of C-S-H could be modeled in a very straight forward fashion.
Existing Models

Until quite recently, most models for C-S-H have been based on the concept that equilibration of cementitious systems was very slow and as a result portland cement based materials continued to polymerize over very long periods of time. For example, it is accepted that the initial C-S-H that forms when tricalcium silicate (Ca$_3$SiO$_5$) is placed in water has a rather high Ca/Si ratio (>2) and that it is composed nearly entirely of (Si$_2$O$_7$)$^{6-}$ silicate ions (dimers). It is also known that the dimeric C-S-H slowly changes into one that is composed of approximately equal amounts of dimer (Si$_2$O$_7$) and silicate chains [(SiO$_3$)$_n$-dreierketten] after a very long time (up to 26 years). Finally, it has been observed that small amounts of poorly crystalline tobermorite-like material would sometimes form in hydrated pozzolanic cements especially at elevated temperatures. Collectively, these observations led to the belief that C-S-H must also have a tobermorite-like structure, albeit a poorly organized precursor structure that might eventually crystallize given the proper conditions.

Taylor (1990) acknowledges the fact that the composition of C-S-H is such that afwillite (Ca$_3$Si$_2$O$_7$·3H$_2$O) may be the stable phase in contact with calcium hydroxide and a solution phase, but the afwillite that has been synthesized shows no similarity to C-S-H found in hydrated cement. In fact, the only crystalline calcium silicate hydrates that form at ≤100°C are tobermorite (Ca$_5$Si$_6$O$_{17}$·9H$_2$O) and/or jennite (Ca$_9$Si$_6$O$_{21}$·11H$_2$O) and because these phases are sometimes found in hydrated cement, they have long served as structural models for C-S-H. See for example Taylor (1990).

New Model

Because of the difficulty of integrating solid state NMR data with a single phase C-S-H model, it became necessary to develop an alternate model based upon a rapidly equilibrating calcium sorosilicate hydrate structure having an initial Ca/Si molar ratio of ~2.0 [e.g. (Ca$_3$Si$_2$O$_7$·Ca(OH)$_2$·xH$_2$O)]. As calcium hydroxide begins to precipitate in size, the monophasic C-S-H associated with these crystals becomes unstable and gradually phase separates. The new diphasic C-S-H contains a sorosilicate-like C-S-H (Ca/Si = 1.7) and a tobermorite-like C-S-H (Ca/Si = 1.0). The phase separation process is suggested to be similar to that observed in glasses (spinodal decomposition). Because the process is diffusion controlled, the amount of the tobermorite-like phase increases as a function of increasing time and temperature. Note that the proposed model breaks with tradition, it does not purport the development of a slowly equilibrating, slowly polymerizing gel-like material, rather, it purports the formation of a rapidly equilibrating material which undergoes time/temperature driven phase separation in response to localized variations in calcium ion concentration and temperature.

Accomplishments

The work completed during the current funding period can be divided into three parts. Each part relied heavily upon structural information derived using solid state NMR and more conventional characterization techniques. First, C-S-H itself was studied using pH control and solution-based syntheses to study its structural evolution as a function of starting materials, alumina content, Ca/Si ratio and time. Second, the structure and properties of the phases that formed in equilibrium with C-S-H were studied (strätlingite and zeolites). And, third, a unified model for C-S-H structural development was developed based on current and already published data. Details are given below.
Part One: C-S-H Studies

- Studies confirmed the fact that the pH of the solution phase played a major role in determining the degree of silicate connectivity of the C-S-H structure. The study confirmed the fact that two structurally distinct phases existed: one stable above pH ~11.5 and one stable below pH of ~11.5. The phase stable in more acidic solutions was tobermorite-like, whereas the one more closely associated with hydrating portland cement appeared to consist of both dimer and dreierkette. These phases have been termed Q^2 and Q^1Q^2, respectively.
- Studies dealt with solution based syntheses of C-S-H with and without added alumina. Mixtures were made at close intervals (~1 wt%) and the pH of the solution was monitored as a way of determining phase behavior. Analyses of selected phases confirmed the fact that the Q^2 and Q^1Q^2 C-S-H phases continued to exist as Al_2O_3 was added to the structure. When excess Al_2O_3 was added other phases such as hydrogarnet, strätlingite and zeolites tended to form. It was found that both Q^2 and Q^1Q^2 structures could routinely accommodate a total of about 5-10 wt% Al_2O_3 divided between tetrahedrally and octahedrally coordinated sites. In the case of hydrothermally cured C-S-H, alumina substitution was observed to reach 25 wt% or more.
- Data suggested that the two structures were separated from each other by an invariancy (Q^1, Q^1Q^2, strätlingite and solution) which accounted for the observed discontinuity in C-S-H chemistry at Ca/Si = 1.
- Physical properties of the two C-S-H phases were studied. It was found that the properties of the C-S-H phases on either side of the invariancy varied in a continuos fashion but they were separated from one another by a first order discontinuity in surface area and combined water content.

Part Two: Other Phases

- Hydrogarnet, strätlingite and zeolites were found to coexist with C-S-H. Hydrogarnet and strätlingite are typically associated with the hydration products found in ordinary portland cement as well as blended cements. A detailed study of strätlingite provided new structural data showing that its silicate connectivity was chain-like consisting of Q^2, Q^2(1Al) and Q^2(2Al) silica tetrahedra. It was also observed that sodium was able to fill vacancies in the structure and thus significantly reduced the observed AI^4/Al^VI ratio.
- Zeolites tended to coexist with the silica-rich C-S-H (Q^2) phase. They were found to form readily from a mixture of Class F fly ash or metakaolinite and concentrated NaOH solutions. Typical zeolite phases that form are Na-P1, X, and Y. When additional calcium was added to the system (portland cement, lime, cement kiln dust) as a partial replacement for fly ash, zeolite-like sodalite and cancrinite formed in equilibrium with tobermorite. This phase assemblages suggests the possibility of using mixtures of this type for autoclaved building materials and/or hazardous waste forms.

Part Three: New Model for C-S-H Evolution

- A new model was developed based on a number of observations made during the study: the fact that a discontinuity existed in NMR and other intensive properties, the fact that ^29Si and ^27Al NMR data suggested a mix of 4 and 6 coordinated aluminum in C-S-H (not rigorously allowed in tobermorite-like structures), the fact that C-S-H sometimes had total aluminum contents well
beyond a generally accepted 10 wt%, and the fact that Stade and Wieker\textsuperscript{1} as well as Young\textsuperscript{2} had both reported that they were able to synthesize a C-S-H composed nearly entirely of dimer only at low temperatures (\(-0^\circ\text{C}\)); the dimer was unstable and tended to develop a chain-like component with increasing time and temperature.

- If one approaches the modeling process starting with the premise that a dimeric structure analogs to a calcium sorosilicate \([\text{Ca}_3\text{Si}_2\text{O}_7\cdot\text{Ca(OH)}_2\cdot\text{xH}_2\text{O}]\) is stable and then undergoes phase separation, the end results of the modeling exercise are the same, but the model allows for a number of factors not possible with a tobermorite-based model. First, calcium sorosilicates are the most common sorosilicate found in nature\textsuperscript{3}. Second, they can accommodate both aluminum and calcium in their central octahedral layers. Third, the structure contains both molecular water and Ca(OH)\(_2\) between the sorosilicate units, which better explains their leaching behavior. Forth, the Ca/Si ratio for a sorosilicate is 2, thus it is possible to have a wide range of Ca/Si ratios (1.1 to 2 and even higher for disordered initial hydrates) without evoking "other" structures such as AFm, portlandite or jennite. Fifth, the molecular water and Ca(OH)\(_2\) are very mobile because they are held with weak hydrogen/van der Waal's bonds. Thus the structure is much more sensitive to temperature, pressure and starting material compositions, which better reflects the actual behavior of the C-S-H associated with hydrating portland cement, much more so than a tobermorite model.

- It has been found that the atomic level structure of C-S-H with a Ca/Si ratio \(\geq 1.1\) is actually very well organized and NMR data are quite reproducible. Thus it seems that the system is thermodynamically controlled from the start and the hydrates that form are continually responding to variations in PTX conditions in order to maintain the lowest possible free energy state. Initial "equilibration" occurs in a matter of minutes to hours rather than the more generally accepted months to years. If anything, the structural evolution of C-S-H is more appropriately described as a gel-like material having a sorosilicate-like structure which ripens and then undergoes phase separation much like a glass undergoes spinodal decomposition as a result of local and global variations in temperature and calcium ion concentration. The exsolution process accounts for the slow development of tobermorite-like characteristics of the C-S-H. As is the case with spinodal decomposition, the process is diffusion controlled and takes months and even years to complete.

- A final paper describing the model in detail has been submitted for publication. A copy is appended in Appendix I.

Publications resulting from the Grant (DE-FG02-91ER45456)


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Talks Given at Major Meetings


Talks To be Given

M.W. Grutzeck, "A New Structural Model for C-S-H" to be given at Engineering Foundation Meeting, Banff Canada, June 1998

Students and Theses supported by the Grant

Stephen Kwan, Ph.D. Materials, Structure and Phase Relations of Calcium Silicate Hydrate and Related Phases in the System: Calcium Oxide-Aluminum Oxide-silicon oxide-water, Penn State University, May 1995.


Visitors Supported by the Grant

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