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DISCUSSION

A DISCUSSION OF THE PAPER "A PROPOSED MECHANISM FOR THE GROWTH OF C-S-H DURING THE HYDRATION OF TRICALCIUM SILICATE" BY E.M. GARTNER[1]

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Introduction

Dr. Gartner (1) has postulated an interesting possible mechanism involving C-S-H growing as wavy or buckled sheets or ribbons with growth arising mainly at the edges of the sheets or at the ends of ribbons, except when new sheets can nucleate on top of an existing sheet only in certain well-ordered flat regions. The three-dimensional aspects of growth and the influence of foreign chemical ions upon the relative nucleation and growth processes are clearly stated. This mechanism is used to explain early exponentially increasing growth before steric hindrance becomes significant, as well as the occurrence of nanocrystalline regions of different compositions that allow for a wide range of Ca/Si ratios within C-S-H as a function of the solution composition during growth.

The underlying problem of C-S-H formation is its considerable complexity. The various theories of C_3S (alite) and Portland cement hydration, whether they be of the protective layer or delayed nucleation type, mostly contain important points of commonality. A plausible theory has been produced (1) that can reconcile at least some of the physically observed effects with the kinetics of hydration in C_3S and, by inference, in Portland cement as well.

One of the difficulties in seeking to explain precisely what happens during the hydration of Portland cement paste relates directly to basic shortcomings in the postulations within the existing theories (2).

For instance, C_3S tends to be treated purely as a silicate, whereas in reality it is a mixed oxide-silicate. In the C_3S lattice there are no discrete SiO_5^{6-} ions, but orthosilicate SiO_4^{4-} and oxide O^{2-} ions. Upon contact with water the key initial step in the dissociation and dissolution of the oxide ions is: $O^{2-} + H_2O \rightarrow 2OH^-$. The hydrolysis of the oxide into hydroxide, which is "swept away" into the aqueous phase is instrumental in destabilising the Ca^{2+} ions in the erstwhile C_3S lattice. The Ca^{2+} ions tend to move away from their original positions, with some, at least, dissolving in the aqueous phase to give an apparently saturated, or even supersaturated, solution of calcium hydroxide. This leaves behind an essentially

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[1] Cem. Concr. Res. 27, 665–672 (1997).

denuded amorphous silicate structure with some Ca^{2+} ions remaining behind, although in an effectively loosened state with respect to the original C_3S.

Silicate dissolution is in quantitative terms very slight (at the parts per million level) but critical in that it has a substantial bearing upon the rate of early hydration. The observation mentioned (1), that the addition of C-S-H generally accelerates C_3S hydration whilst the addition of CH does not, can be understood on the basis that the solubility of the silicate is very low, whereas that of the OH^- is much higher and is in significant quantities that are often supersaturated with respect to CH. Thus, additions of C-S-H, when one takes into account the law of mass action and its ramifications, have a relatively greater effect than corresponding additions of CH, because they can increase the silicate solubility in a relative sense (although it still stays very low), since this is rate-determining in the production of C-S-H. It should not be forgotten that in C_3S hydration C-S-H and CH form concomitantly–you cannot have one without the other. Additions of OH^- ions do not significantly affect the silicate solubility, hence they are less effective when added as CH than C-S-H additions are in raising the rate of C_3S hydration.

The overall effect of the O^{2-} ions from C_3S on the Portland cement hydration process can best be understood by comparing the hydration of C_3S with that of C_2S, since the latter only involves orthosilicate ions $SiO_4{}^{4-}$ hydrating, and produces a similar type of C-S-H to that in C_3S hydration, albeit at a much slower rate (2). By comparing these two overall hydration reactions, it can be seen that the oxide dissociation and hydrolysis is of paramount importance for initiating the early hydration of C_3S.

In a Portland cement, the main clinker phases are impure due to the effects of solid solution and are more thermodynamically unstable in the presence of water, and thus of greater hydraulicity than the pure phases. Hence, in a Portland cement the breakdown of the C_3S by oxide dissociation and dissolution should be intrinsically greater than in pure C_3S, and so should be the subsequent rearrangement of the Ca^{2+} ions brought about by their loosening up in the crumbling C_3S lattice relative to the $SiO_4{}^{4-}$ ions by the dissolution and hydrolysis of the O^{2-} ions. Some, at least, of the loosened Ca^{2+} ions dissolve in the aqueous phase to give what is commonly regarded as being an effectively saturated and thence a supersaturated solution of CH. However, it should not be forgotten that there are other ions dissolved in the aqueous phase, particularly Na^+, K^+, and $SO_4{}^{2-}$, which have an important effect on the overall solubility relationships.

Nevertheless, the benefits of the presence of impurity ions in Portland cement for hydraulic reactivity in comparison with the situation of pure C_3S are at least partially offset by the early surge in amorphous/poorly crystalline ettringite forming substantially within the first 2 min. or so of hydration, which physically impedes much of the ensuing early C_3S hydration by a physical blocking effect on the clinker surfaces. Thus ettringite formation, mostly from C_3A rather than C_4AF at this early stage of the hydration process, would slow down the overall initial rate of C_3S (alite) hydration and, to some extent at least, compensate for the solid solution effects of the impurity ions, which would encourage hydration in a qualitative sense.

Furthermore, the effect of amorphous/poorly crystalline CH needs to be taken into account when assessing early Portland cement hydration. Differential thermal analysis (DTA) can readily differentiate between this type of CH and the more crystalline variety formed upon hydration of C_3S concomitant with significant C-S-H after a few hours under normal hydration conditions at ambient temperature (3). The amorphous/poorly crystalline form of CH may even be present before hydration, as a consequence of moisturisation hydrating some of the cement free lime content. DTA monitoring suggests that this form of CH is present during the first few hours of hydration, covering the “dormant or induction period.” Amorphous/poorly crystalline CH would also coat the alite and other hydrating clinker surfaces unlike a well crystalline CH, which would obstruct further hydration at this stage of the hydration process.

Therefore the development of amorphous/poorly crystalline CH and ettringite at the beginning of hydration, which would obstruct the early hydraulic activity of C_3S (alite) in particular, would be highly likely to have a bearing upon the development of the dormant period during early hydration (2). Past work by Brunauer et al. suggested that amorphous CH was present to the extent of about 0.2 moles per C_3S mole in hydrated C_3S pastes, based upon detailed chemical extraction studies (4). It is of interest to note that the significance of amorphous/poorly crystalline CH in its effect on the overall Portland cement hydration process appears to have been largely neglected in recent years. Indeed, little is known of the precise effects upon the overall hydration pattern of amorphous/poorly crystalline CH, which, as mentioned above, is present from the very beginning of the Portland cement hydration process.

In the consideration of active sites at which C_3S hydration takes place, more appreciation needs to be given to the lattice defect approach of Fierens, where thermoluminesence studies provided evidence of active sites on the C_3S surfaces for hydration to ensue (2). It should be emphasised how many of the theories of Portland cement hydration, be they protective layer or delayed nucleation types, do have quite a lot of commonality (2). In regard to C_3S hydration, the Stein hydrates theory (5), although considered controversial in some quarters, actually does offer a useful framework for understanding and getting to grips with the fundamental basis of C_3S (and by inference) Portland cement hydration. This theory considers the end of the dormant period to be the cause rather than the effect of the CH crystallisation that arises. The end of the dormant period always arises on a regular basis in normal Portland cement hydration. Were it to be merely an effect of CH crystallisation, then it might have been expected to be more influenced by “impurity poisoning” effects than what is actually seen to exist in practice.

Another area that has presented an enigma in the hydration of C_3S and of Portland cements is the polymerisation process for C-S-H formation and its development over many months and years. Trimethylsilylation studies have indicated that for hydration under normal conditions C-S-H normally forms dimers at first and hence with the passage of time further polymerisation with preferences that appear to follow an arithmetic progression for the number of bridged silicate units of 2, 5, 8, 11, 14, etc., with much smaller quantities of 3, 4, 6, 7, etc. silicate units being produced. This suggests that, following initial hydration to a dimer, the next preferred stage of catenation is two dimers reacting with a monomer to form a pentamer, and thereafter a pentamer reacting with a dimer and monomer to form an octamer, etc. The monomer would normally be still unreacted C_3S or alite, or, with Portland cements C_2S (belite), although there might be some monomers produced by debridging, as with the onset of carbonation before it becomes too destructive, or from chain weaknesses caused by foreign ions in the C-S-H structures.

In reaction kinetics there is a very low probability for three molecular components to collide and then react, which would explain the obvious slowness of the overall polymerisation process. However, much C-S-H still remains in the dimeric form after many years. This is probably due to the aforementioned slow dimer + dimer + monomer interaction and to the relative scarcity of monomer for this purpose after many months in most instances. All these polymeric silicate units are essentially amorphous/poorly crystalline chains with the nonstoichiometry of the hydrates giving rise to unsatisfied surface forces of high binding potential. The proposals propounded (1) could provide a way forward in taking into account the 3-dimensional nature of the C-S-H, whereby two dimers and a monomer (2–2-1), for instance, could come together in a stereochemical and thermodynamically favourable situation to undergo a condensation polymerisation to form a pentamer. Because of the difficulties in achieving a suitable orientation, such a condensation would be very slow to arise. Similar condensations that achieve greater silicate chain polymerisation, like the 5–2-1 to give an octomer, would also be very slow. The steric orientation and thermodynamic difficulties for achieving good polymeric reaction conditions would explain why much C-S-H remains as dimer after many years.

The paper by Dr. Gartner (1) usefully contributes to our understanding of the complexities of C_3S hydration and, in turn, of the alite hydration in Portland cement by concentrating on the three-dimensional aspects of C-S-H growth. It also enables others to think in more depth about other factors, some of which have been discussed here, that can influence the course of C_3S hydration and thus of Portland cement hydration. Only by understanding in greater detail what is happening physically and chemically during C_3S hydration, can the basis for better control of the cementing properties of Portland cement type systems under various practical conditions be substantially improved for the end users.

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