

# REACTION MECHANISMS OF ORGANIC ADMIXTURES WITH HYDRATING CEMENT COMPOUNDS

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This paper discusses the possible mechanisms by which organic compounds influence the setting properties of portland cement. From a consideration of the hydration mechanisms of tricalcium silicate and tricalcium aluminate, it is concluded that organic compounds influence the hydration of these compounds by their effect on the hydration products through complexing and nucleation processes. It is hypothesized that the hydration of tricalcium silicate is controlled by the nucleation and growth of calcium hydroxide. The poisoning of nuclei by soluble silica is responsible for the induction period. Adsorption of organic compounds onto calcium hydroxide nuclei, through a chelation process, inhibits crystal growth even more effectively and prolongs the induction period. Tricalcium aluminate is considered to hydrate rapidly because the protective hydrate layer is destroyed by conversion to the hydrate of tricalcium aluminate. Organic retarders enter the interlayer region of the hexagonal hydrates to inhibit this conversion reaction and therefore maintain the integrity of the hydration barrier. A similar mechanism may hold in the presence of sulfate ions. In portland cement, adsorption of admixtures by the hydration products of tricalcium aluminate controls the supply of admixture to tricalcium silicate. This explains the enhanced retardation when the addition of admixtures is delayed after the first addition of water.

•AN important aspect of portland cement and concrete technology is the use of admixtures to control the setting and hardening times of the fresh mix. The delay of several hours after mixing with water before concrete will start to gain cohesiveness and strength is essential to the production of high-quality concrete. There are many occasions when it is desirable to either shorten or prolong the setting time of concrete. Set accelerators are generally soluble calcium salts, such as calcium chloride or calcium formate. Many organic compounds act as retarders, but commercial products are generally complex, polydisperse, by-product materials such as lignosulfonates, wood resins, and petroleum by-products.

Such organic admixtures have been used for many years, and their consumption is increasing. Although the knowledge about their interaction with cement is mainly empirical, relevant experimental data can be found in the literature. In spite of studies dealing with simple organic compounds (1, 2, 3), we still do not know with certainty the chemical and physical bases for the observed behaviors. This paper discusses the existing knowledge in the context of possible hydration mechanisms of the individual cement compounds. For this paper, the standard shorthand notation of cement chemistry used is as follows: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O, and S = SO<sub>3</sub>.

Portland cement is a complex mixture of the four principal compounds: tricalcium silicate (C<sub>3</sub>S), dicalcium silicate (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A), and tetracalcium aluminoferrite (C<sub>4</sub>AF). For simplification of the discussion, it is assumed that the compounds hydrate independently of each other and that only the most reactive compounds, C<sub>3</sub>S and C<sub>3</sub>A, control the early reaction kinetics of cement hydration. It has been amply demonstrated that the acceleration or retardation of cement setting times is primarily due to the acceleration or retardation of C<sub>3</sub>S hydration. This compound is, of course, primarily responsible for early strength, but the hydration of C<sub>3</sub>A plays an important role in the early stiffening of the cement-water system. A knowledge of the

behavior of  $C_3A$  is necessary to explain the abnormal setting behavior that sometimes occurs when admixtures are used.

## MECHANISMS OF RETARDATION

A number of theories have been proposed by various investigators to explain the retarding action of organic admixtures. These are as follows:

1. The interference with reactions of anhydrous compounds is caused by adsorption onto surfaces and precipitation of insoluble materials; and
2. The interference with the growth of hydration compounds is brought about by nucleation, the adsorption of admixtures onto the growth surface of nuclei, and complexing, the incorporation of admixtures into crystal lattices.

### Adsorption

Adsorption of admixtures onto anhydrous cement particles, as first demonstrated by Ernsberger and France (4), was proposed by Hansen (5) as a general theory in 1952 and is an often-quoted explanation. The adsorbed molecules were considered to protect surfaces from initial attack by water. This theory is discussed in detail elsewhere (6); it does not adequately explain the observed behavior of retarders. There is, however, some evidence (7, 8) that at very high concentrations Hansen's ideas may be correct but that at the concentrations used in practice the opposite seems to hold true; i.e., retarders may actually increase reactivity on first contact with water. This aspect will be considered in more detail during the discussion of the hydration of  $C_3A$ .

### Insolubility

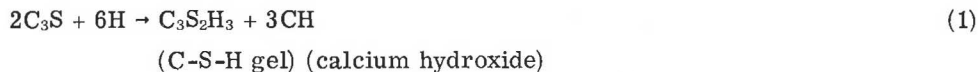
The formation of insoluble calcium salts that precipitate onto anhydrous surfaces was a hypothesis advanced by Suzuki and Nishi (1). An examination of Table 1 indicates that there is not a good correlation between solubility and retarding behavior for the carboxylic acids. This can be readily seen by comparing the solubilities of the calcium salts of maleic and fumaric, gluconic and succinic, and malonic and tartaric acids. Nevertheless, there may be times when precipitation may be important, such as when it effectively removes a potential retarder from the system. This may happen in the case of oxalic acid. Some inorganic retarders, e.g., zinc and lead salts, probably act through precipitation of insoluble compounds.

### Complexing and Nucleation

Admixture behavior seems to be best described by complexing and nucleation, and various aspects of these phenomena will be discussed in the remainder of the paper. The concepts embodied in these mechanisms will be more clearly grasped in the context of a discussion of hydration mechanisms of  $C_3S$  and  $C_3A$ . It should be noted that these mechanisms involve principally the hydration products rather than the anhydrous compounds.

## HYDRATION OF TRICALCIUM SILICATE

The hydration of  $C_3S$  can be approximately represented by equation 1:



The familiar heat liberation curve (Figure 1), obtained from isothermal conduction calorimetry, is a useful starting point in the discussion of  $\text{C}_3\text{S}$  hydration mechanisms. Several distinct stages of the reaction have been identified from this curve by Kondo and Daimon (9):

1. Stage 1 is a brief initial period of reactivity, occupying the first 10 to 15 min after the contact of  $\text{C}_3\text{S}$  with water.
2. Stage 2 is the dormant period following stage 1 when the reaction has become very slow. The term induction period seems to be preferable since reaction does continue although at a very slow rate. It may last several hours.
3. Stage 3 is the acceleration period when there is renewed reaction and rapid hydration of  $\text{C}_3\text{S}$ . It generally begins 2 to 6 hours after  $\text{C}_3\text{S}$  is first mixed with water.
4. Stage 4 is the deceleration period following stage 3 when the reaction slows down and starts to become controlled by the diffusion about 8 to 12 hours after the mixing.
5. Stage 5, the final stage, starts at about 12 to 16 hours and continues throughout the remainder of the reaction period. The system has now settled down to a slow reaction controlled by diffusion.

Figure 2a shows the rate of heat evolution for hydrating  $\text{C}_3\text{S}$  paste. Schematic changes of the liquid phase in contact with hydrating  $\text{C}_3\text{S}$  are shown in Figure 2b. Results of this kind (10) show that in stage 1 there is an initial hydrolysis of  $\text{C}_3\text{S}$  to form calcium hydroxide ions, which move rapidly into solution. Saturation with respect to calcium hydroxide is quickly achieved or surpassed. During the induction period, hydrolysis slows down and supersaturation gradually builds up until, at the beginning of stage 3, the calcium ion concentration drops and the hydration reactions proceed rapidly again.

It can be seen from Figure 2c that the decrease of the calcium ion concentration in solution and the onset of renewed hydration coincide with the crystallization of calcium hydroxide. At the same time the C-S-H gel (Figure 2d) changes its composition and properties and forms the characteristic acicular morphology observed (11) by electron microscopy. The first C-S-H product, designated as the first hydration product by Stein, de Jong, and Stevels (12), was identified by transmission electron microscopy as thin foils. This may well be a pseudo- $\text{C}_3\text{S}$  structure in which little atomic rearrangement has occurred apart from the leaching of lime into the solution. Such a product would be low in bound water and have little silica polymerization.

Stein, de Jong, and Stevels considered the first hydration product to be a diffusion barrier to water and hence the cause of the induction period. An alternative explanation is that this is not the rate-controlling aspect but rather that the rate of hydrolysis is controlled by the increasing calcium ion concentration in solution since calcium ions released from the structure have to move into a solution of increasing chemical potential. This thermodynamic barrier can only be overcome by removing calcium ions from solution, and this occurs when calcium hydroxide behaves as a calcium sink, which keeps the hydrolysis of  $\text{C}_3\text{S}$  relatively rapid during stage 3 until diffusion through the built-up layer of C-S-H gel (Figure 3) becomes the rate-controlling step during stage 4. Large crystals of CH are also formed.

Any compound that hastens the nucleation and growth of calcium hydroxide will act as an accelerator, and any compound that delays this will act as a retarder. Soluble calcium salts will act as accelerators because they will both raise the initial calcium ion concentration and lower the solubility product of calcium hydroxide. Both effects may act to accelerate the nucleation of calcium hydroxide as manifested in the shorter induction period (Figure 4). Calcium chloride is the most effective accelerator because it supplies more calcium ions for a given weight. At equal molarities, different calcium salts have similar accelerating powers. Calcium hydroxide itself may not be

Table 1. Solubilities and retarding power of calcium salts and carboxylic acids.

Calcium Salt	Solubility		Retardation <sup>a</sup>
	g/100 g	mMoles/liter	
Formate	35	127	None <sup>b</sup>
Acetate	40	220	None <sup>b</sup>
Maleate	2.5	16	Moderate
Fumarate	1.5	10	Slight
Gluconate	3.5	8	Very strong
Succinate	1.3	8	Weak
Malonate	0.4	2.5	Negligible
Tartrate	0.35	2	Very strong
Oxalate	0.006	0.005	None

<sup>a</sup>(1, 2, 3).

<sup>b</sup>Accelerated set.

Figure 1. Heat liberation curve for a hydrating C<sub>3</sub>S paste.

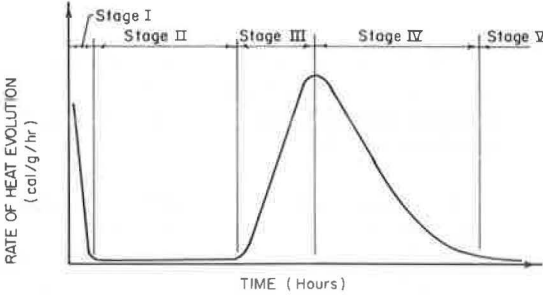


Figure 2. Analysis of hydrating C<sub>3</sub>S paste.

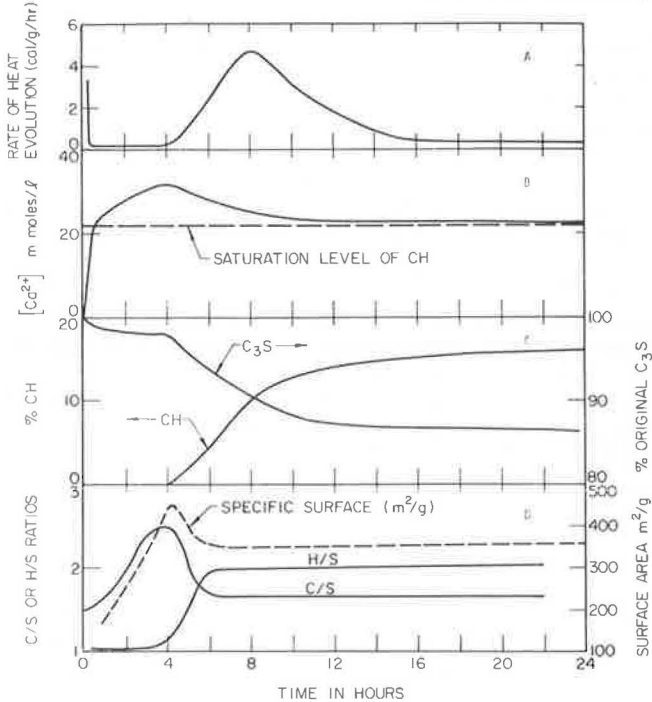


Figure 3. Possible mechanism of reaction of C<sub>3</sub>S with water in paste hydration.

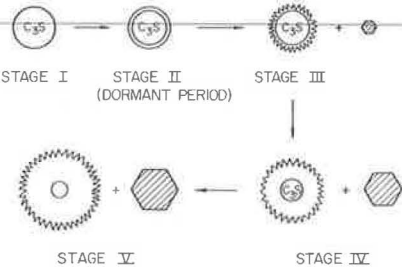
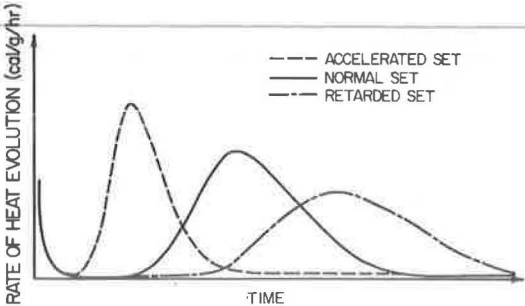


Figure 4. Heat liberation curves for C<sub>3</sub>S pastes hydrated with admixtures.



so effective in this regard because of superficial carbonation.

Why does this high level of supersaturation occur? N. R. Greening has hypothesized that soluble silica precipitates adsorb onto the calcium hydroxide nuclei, thereby poisoning their growth. Supersaturation is needed to overcome this poisoning effect and to continue crystal growth. It is suggested that adsorption may be even more effective with organic species that have the ability to chelate with calcium. Anions like malate, tartrate, and gluconate are strong retarders because of their chelating properties that outweigh the potential accelerating properties of the soluble salts. In fact, all organic compounds classed as strong retarders by Taplin (2) have strong chelator properties. A strong chelation will be irreversibly held at the surface and require new nuclei to form. Thus, higher levels of supersaturation are attained before critical nuclei, free of impurities, can start to grow, and this is manifested in a longer induction period (Figure 4). From Table 1, it can be seen that differences in retarding power between members of couples such as maleate and fumarate and tartrate and succinate can be explained by differences in chelating properties (Figure 5). An excess (e.g., 1 percent by weight) of a good chelator can inhibit  $C_3S$  indefinitely.

The retardation of  $C_3S$  can thus be regarded as a problem of forming nuclei capable of continued growth as a consequence of a complexing process. Silica may be particularly effective through a precipitation process that turns embryonic calcium hydroxide nuclei into an embryonic C-S-H gel. Complexing to calcium in a solid need not have, and probably does not have, the same energetics as measured in solution. Therefore, it is not appropriate to try to correlate retarding properties with formation constants measured for complexes in solution.

## HYDRATION OF TRICALCIUM ALUMINATE

### Without Sulfate

When no sulfate ions are present,  $C_3A$  hydrates according to equations 2 and 3



(hexagonal hydrates)



(cubic hydrate)

The hexagonal hydrates, which form characteristic, thin hexagonal plates, are thermodynamically unstable with respect to  $C_3AH_6$  and slowly convert to the cubic hydrate (according to equation 3) at room temperature. They convert more rapidly above room temperature. It has been shown (13, 14, 15) that  $C_3A$  hydration is retarded when the hexagonal hydrates are stabilized with respect to their conversion to  $C_3AH_6$ . It is assumed that the conversion reaction prevents the hexagonal hydrates from forming efficient diffusion barriers around the  $C_3A$  grain. The conversion reaction (second peak) can be followed by isothermal conduction calorimetry (16 and Figure 6, 14) or by differential thermal analysis (17).

The crystal structure of the hexagonal hydrates ( $C_3A \cdot CX \cdot H_x$ ), shown in Figure 7, can be regarded as a negative clay with exchangeable anions X in the interlayer region. Dosch (18) showed that, like clays, when  $X = OH$  (i.e.,  $C_4AH_{13}$ ) organic molecules can enter between the layers and are tightly held when extensive hydrogen bonding can occur. In paste hydration (15), organic compounds can enter the interlayer region, not necessarily to form distinct complexes but to disrupt the crystal structure and stabilize the hexagonal hydrates. Some X-ray evidence for distinct complexes has been found (15). More recently it has been shown (19, 20) that the very high apparent

adsorption of organic species onto  $C_3A$  from aqueous solution does not occur when non-aqueous solvents are used. Only  $C_4AH_{13}$  shows large and irreversible adsorption under nonaqueous conditions.

The more hydrogen bonding capabilities an organic molecule has, the more effective it appears to be in preventing conversion to  $C_3AH_6$  and retarding the hydration of  $C_3A$ . Strong retarders (e.g., sugars) alter the crystal growth of the hexagonal hydrates (14) and the resulting products seem to form an effective barrier to further hydration. Sugars can hold the hydration of  $C_3A$  to about 35 percent (15) (Figure 8) even up to 122 F (50 C) at which temperature new hydration mechanisms occur (21).

This may not be the complete story, however, since analyses of the liquid phase in the early hydration of cement (1, 22) and of  $C_3A$  (6) in the presence of retarders show high soluble alumina concentrations on first contact with water. This suggests that some complexing between the aluminum hydroxyl ions and retarder molecules may be occurring. At high concentrations of admixture, direct evidence has been obtained for complexes between alumina and salicylic acid (7) or lignosulfonates (8). The formation of soluble complexes of aluminum may explain the accelerating effects of small additions of sugars and the flash set phenomena that sometimes occur (1, 15).

It thus appears that retarder activity may be a balance between potential rapid hydration due to aluminum complexing balanced by retardation arising from stabilization of the hexagonal hydrates. It may be noted that the well-known accelerator triethanolamine accelerates  $C_3A$  hydration but not  $C_3S$  hydration (23) and is a particularly good chelator for aluminum. Another good chelator, 8-hydroxyquinoline, has recently been patented (24) as an accelerator for cements high in  $C_3A$ .

### With Sulfate

More relevant to portland cement hydration is the interaction of  $C_3A$  with the sulfate ions present as gypsum, which are added to control the flash-setting potential of  $C_3A$ . The reactions in these circumstances are



The conversion of ettringite to monosulfate (equation 5) occurs when all sulfate ions have been consumed and can be identified by calorimetry (main peak, Figure 9). The presence of set-retarding admixtures slows down the formation of ettringite and also changes the crystal morphology (14). The mechanism of sulfate retardation is shown in Figure 10 (25). The protective coating of ettringite is considered to rupture repeatedly (stage 2) due to the expansive nature of its formation but is continually healed (stage 3) as long as sulfate ions are present. It may be that the change in crystal morphology changes the expansion characteristics of ettringite formation and slows down rupture of the protective coating.

The possibility also exists that ettringite can interact with the organic compounds and be stabilized with respect to the monosulfate. Ettringite has a columnar structure (Figure 11, 26) with the sulfate ions and most water molecules located in the intercolumnar region. It may be that organic molecules can enter the intercolumnar region, but this possibility has not been investigated. Indeed the effect of admixtures on the  $C_3A-\bar{S}-H$  system in general has not been adequately studied. This is surprising because wherever admixtures have been implicated in problems of abnormal set, the cause has been traced to changes in the reaction kinetics of the sulfate phases.

Figure 5. Chelating properties of carboxylate ions with calcium ion.

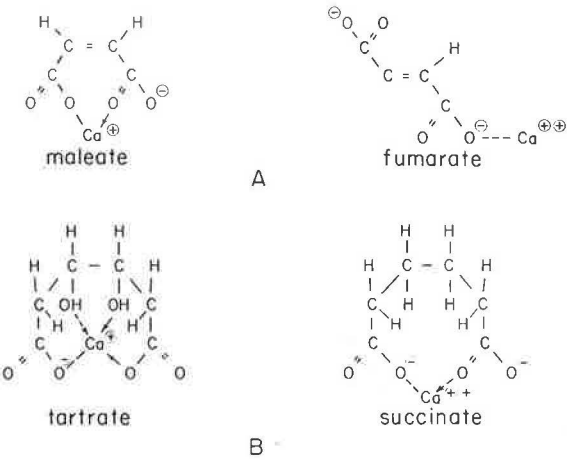


Figure 6. Heat liberation curve for hydrating C<sub>3</sub>A pastes.

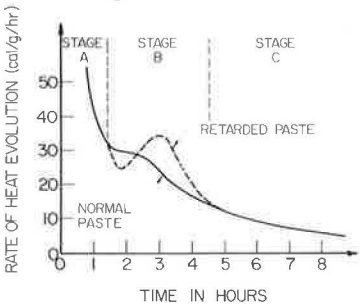


Figure 7. Crystal structure of the hexagonal hydrates.

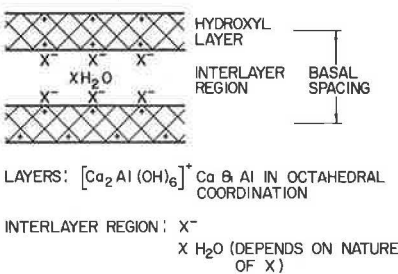


Figure 8. Hydration kinetics of C<sub>3</sub>A pastes: (A) no retarder and complete conversion to C<sub>3</sub>AH<sub>6</sub>; (B) no retarder and partial conversion of the hexagonal hydrates; (C) retarder and no formation of C<sub>3</sub>AH<sub>6</sub>.

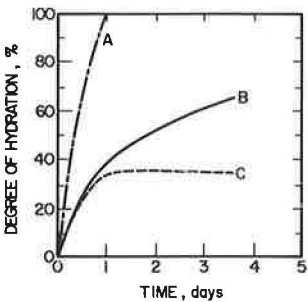


Figure 9. Heat liberation curve for C<sub>3</sub>A pastes hydrated with gypsum.

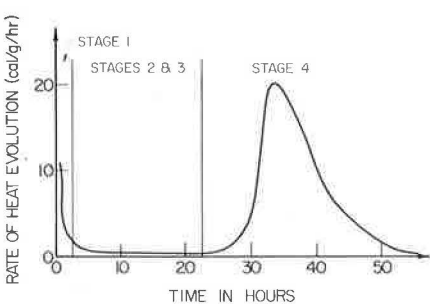


Figure 10. Proposed mechanism for reaction of C<sub>3</sub>A with gypsum in paste hydration.

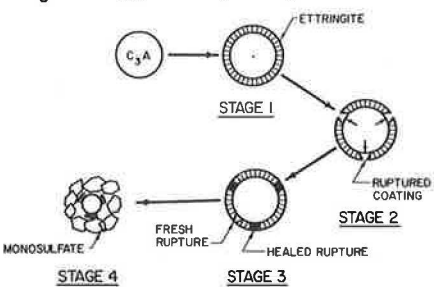


Figure 11. Crystal structure of ettringite.

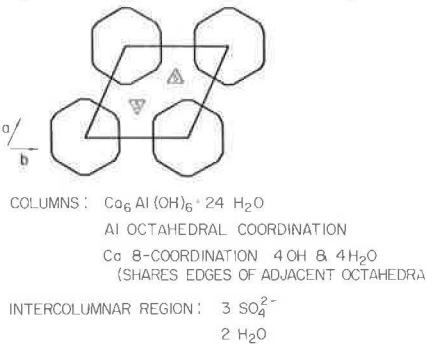


Figure 12. Extra retardation of set due to delayed addition of retarding admixture.





## HYDRATION OF TRICALCIUM SILICATE WITH TRICALCIUM ALUMINATE

It was assumed at the beginning of this paper that the cement compounds hydrate independently of each other. This assumption is not completely true and gives rise to an important phenomenon in the interaction of admixtures with hydrating cement. It has already been noted that hydrating  $C_3A$  pastes adsorb large amounts of retarding molecules from aqueous solution because of interlayer complexing. If  $C_3A$  first reacts with water before it is exposed to the retarder, then the apparent adsorption is reduced. This suggests that complexing occurs most efficiently during crystal growth. This behavior explains why the delayed addition of a retarder to fresh concrete increases its retarding power (27,28) as in Figure 12. The  $C_3A$ -H system and presumably also the  $C_3A$ -S-H system control the supply of retarder to the  $C_3S$  phase (29) and are important in determining the effectiveness of retarders. Indeed the presence of  $C_3A$  in portland cement may be important for suppressing the effects of overdoses of retarders to fresh concrete.

## CONCLUSIONS

This paper has discussed what are considered to be the most important aspects of the mechanisms by which organic compounds influence the setting properties of concrete. It has not been possible to discuss the relevant supporting data in detail, but this has been done elsewhere (6). However, current experimental data do seem to support the hypothesis that the effect of organic compounds on the hydration of cement depends on their interaction with the hydration products rather than the anhydrous compounds per se.

Much more experimental work is still needed to test and refine the ideas presented here, which are put forward to promote further research. There is a particular need for more complete analyses of the liquid phase in contact with hydrating  $C_3S$  and  $C_3A$ . Knowledge of the influence of admixtures on the  $C_3A$ -S-H system is surprisingly sparse and must be expanded. Eventually, it will be necessary to study the neglected phases,  $C_2S$  and  $C_4AF$ , and the synthetic mixtures approximating model cements. Ultimately, it should be possible to precisely control the setting of cement under all circumstances.

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