

# Early-Age Cement Hydration Reactions

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The chemistry of the early reactions that occur during the hydration of the phases in portland cement concrete are considered. Desirable concrete properties are gained because of hydration of the cement. If pozzolanic or latent hydraulic admixtures are present, additional hydration reactions will contribute to strength development. The rate and products of cement hydration may be influenced by the presence of these or of chemical admixtures. Although emphasis is placed on portland cement concrete, reactions in other cements are briefly discussed.

At the time of mixing, fresh concrete contains cement, fine aggregate, coarse aggregate, and water. In addition, chemical and mineral admixtures may be present. Chemical admixtures include accelerating, retarding, water-reducing, or air-entraining admixtures; mineral admixtures include pozzolans, such as fly ash and silica fume, and blast furnace-slag.

Concrete gains desirable mechanical properties principally as a result of the hydration of the cement present. However, if pozzolanic or latent hydraulic admixtures are present, additional hydration reactions will contribute to strength development.

The rate of cement hydration, the composition of the products of hydration, and the morphologies of these hydration products may be influenced by the presence of such mineral admixtures as well as by the presence of chemical admixtures.

The chemistry of the early reactions that occur during the hydration of the phases in portland cement concrete are considered. Early reactions are considered to be those that begin in the first 28 days after mixing. Although emphasis is placed on portland cements, reactions in blended cements, regulated set cements, shrinkage-compensating cements, and high-alumina cements are briefly discussed.

## PORTLAND CEMENTS

Five types (I–V) of portland cement are designated in ASTM C 150 (1). These contain five major compounds whose proportions vary with cement type. Four of the compounds, which include impure forms of tricalcium silicate and dicalcium silicate, an aluminate phase, and a ferrite phase, are formed during the pyroprocessing of cement. A fifth compound, calcium sulfate, is added during the grinding of portland cement clinker. This compound may be present as anhydrite,  $\text{CaSO}_4$ ; as calcium sulfate hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; or as dihydrate or gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

## BLENDED CEMENTS

Eight types of blended cement, containing pozzolan or slag, along with portland cement are designated in ASTM C 595. Pozzolans are a source of reactive silica and, although they are not typically hydraulic in themselves, pozzolans consume calcium hydroxide liberated during cement hydration with the formation of additional binder phase. Commonly used pozzolanic materials include power plant fly ash, silica fume, and certain natural pozzolans. Granulated blast furnace slag is vitrified by rapid quenching and is a latent hydraulic material. The highly alkaline environment of concrete pore solution activates the hydration of slag.

## HYDRATION REACTIONS IN MODEL SYSTEMS SIMULATING PORTLAND-BASED CEMENTS

### Very Early Reactions

Although the consumption of all the anhydrous phases present in cement initiates at the time of mixing, some hydration reactions end very early. This may occur as a result of the rapidity of these reactions, because the reacting anhydrous solids are finely ground and immediately available to react with the liquid phase or because only a minor amount of the reacting phase is present. Hydration of calcium oxide, reaction of calcium sulfate hemihydrate to form gypsum, and the formation of syngenite may be categorized in this way.

### *Hydration of Free Lime*

Virtually all portland cement contains minor amounts of anhydrous calcium oxide,  $\text{CaO}$ . Calcium oxide is present as a result of both the proportioning of the raw materials in the manufacture of cement and the nature of the pyroprocessing process. In the manufacture of cement, sources of calcium oxide and silica are finely ground, mixed, and pyroprocessed. During the pyroprocessing step, the calcium oxide and silica initially react to form dicalcium silicate, leaving excess calcium oxide. Tricalcium silicate forms as a result of the reaction of dicalcium silicate with calcium oxide. Often this reaction does not completely consume all the calcium oxide available. The calcium oxide present in cement is called “free lime” and reacts rapidly with water to form calcium hydroxide according to



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This reaction is expansive in that the solid volume of a mole of calcium hydroxide exceeds that of a mole of calcium oxide by a factor of about 2. The occurrence of this reaction while concrete is in a plastic stage is of little consequence in terms of the dimensional stability of the structure in question. However, in improperly pyroprocessed cements containing high amounts of free lime, undesirable expansion is possible. If all the free lime in a cement is not immediately available to the mixing water, its hydration cannot occur until the anhydrous phases surrounding the grains of free lime have been consumed. Should this occur to a significant extent after the concrete has hardened, the expansion associated with the hydration of the free lime could lead to crack development.

#### Hydration of Calcium Sulfates

One or more forms of calcium sulfate (anhydrous, hemihydrate, or dihydrate) are interground with cement clinker to control the rate at which the aluminate phases in portland cement hydrate. The chemical formulas for these compounds are as follows:

Type	Formula	Compound
Anhydrous	$\text{CaSO}_4$	Anhydrite
Hemihydrate	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Plaster of Paris
Dihydrate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum

Anhydrous calcium sulfate is classified into two types according to its dissolution rate. The terms "soluble anhydrite" and "insoluble anhydrite" have come to be used to indicate the rate at which a particular anhydrous  $\text{CaSO}_4$  dissolves. In some instances naturally occurring anhydrite or anhydrite formed by the dehydration of gypsum or hemihydrate may dissolve very slowly. If the anhydrite dissolution rate is less than that necessary to control the rate of aluminate hydration, the anhydrite is considered to be insoluble.

Even if gypsum is interground with cement clinker, the heat generated during grinding is frequently sufficient to cause the gypsum to dehydrate to hemihydrate. In extreme instances dehydration may also result in anhydrite formation. During the batching of concrete, both soluble anhydrite and hemihydrate will react with the mixing water to form gypsum as follows:



Figure 1 shows relative rates at which hemihydrate converts to gypsum, depending on temperature (2). At the fineness of hemihydrate used in this experiment, the conversion is virtually complete by 30 min at 25 and 41°C, and by about 1 hr at 5°C. Because calcium sulfates are relatively soft, they are easily ground and tend to occur as fine particles or as layers on the surfaces of the cement particles. Thus, the hydration of hemihydrate tends to be complete at shorter times than those typically required for initial set of concrete. In some instances the conversion of hemihydrate to gypsum can result in a phenomenon called "false set," which occurs when the gypsum crystals that have formed result in an apparent set of the mix. Gypsum crystals tend to form as hexagonal needles and their needlelike shape contributes to the occurrence of

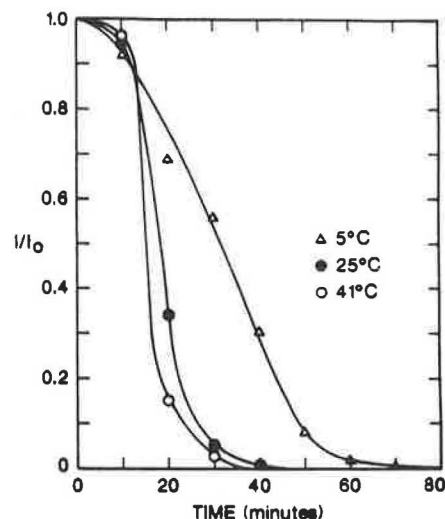
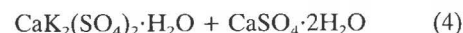


FIGURE 1 Relative rates of conversion of hemihydrate to gypsum depending on temperature.

false set. However, if the mixing process is continued beyond the completion of the hemihydrate-to-gypsum conversion process, the viscosity of the mixture decreases. This is called mixing through false set.

#### Syngenite Formation

Syngenite is a potassium sulfate–calcium sulfate double salt having the formula  $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ . Syngenite formation may rapidly occur in cements containing calcium langbeinite,  $2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4$ , according to (3)



and lead to accelerated set. Flash set has, for example, been observed in cements to which  $\text{K}_2\text{CO}_3$  has been added (4). Syngenite formation is favorable in pore solutions where the concentration of potassium exceeds 0.35 molar (5). This is not uncommon in cements produced in the United States, especially in those containing alkali sulfates.

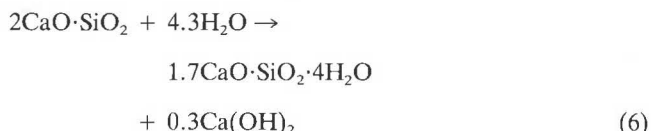
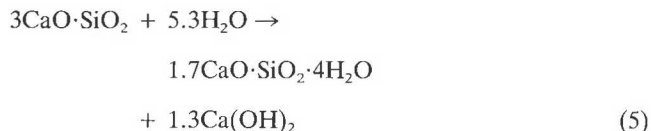
The occurrence of set associated with syngenite formation is, as in the case of gypsum formation, in part a result of the morphology of syngenite. Syngenite has a needlelike habit and syngenite crystals are capable of causing a loss in plasticity by bridging water-filled spaces. It is not unreasonable that syngenite has sometimes been confused for ettringite; both have generally similar morphologies and strong x-ray diffraction peaks over the same angular ranges (6). Syngenite should persist as a stable phase in concrete until the concentration of sulfate in solution becomes depleted through the formation of ettringite.

#### Silicate Hydration

The silicate phases collectively constitute about 80 weight percent of portland cement. These phases are impure trical-

cium silicate,  $3\text{CaO}\cdot\text{SiO}_2$ , called alite, and impure dicalcium silicate,  $2\text{CaO}\cdot\text{SiO}_2$ , called belite. It is the hydration reactions of these silicate phases that are primarily responsible for the development of concrete strength. Alite and belite hydrate to form the same hydration products, calcium silicate hydrate (C-S-H) and calcium hydroxide. However, both the rates of reaction and the relative proportions of the hydration products formed are quite different. The rate of alite hydration is significantly more rapid than that of belite. The relative rates of hydration of the various phases in portland cement are qualitatively shown in Figure 2 (7).

The hydration reactions for these phases may be expressed as follows, once calcium hydroxide has precipitated:



During the early stages of alite or belite hydration, the stoichiometry of the calcium silicate hydrate varies as shown in Figure 3 (8). [First-formed C-S-H will have a lime-to-silica ratio near 0.8. Because this ratio is less than 3, the solution will become enriched in calcium. C-S-H formed subsequently will have higher lime-to-silica ratios. These are determined

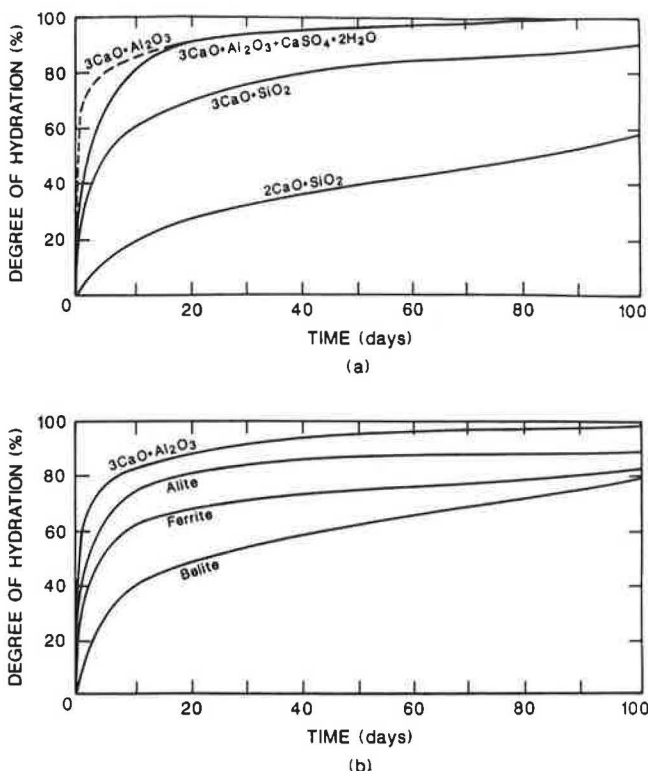


FIGURE 2 Degree of hydration versus time for (a) pure cement phases and (b) those phases in portland cement.

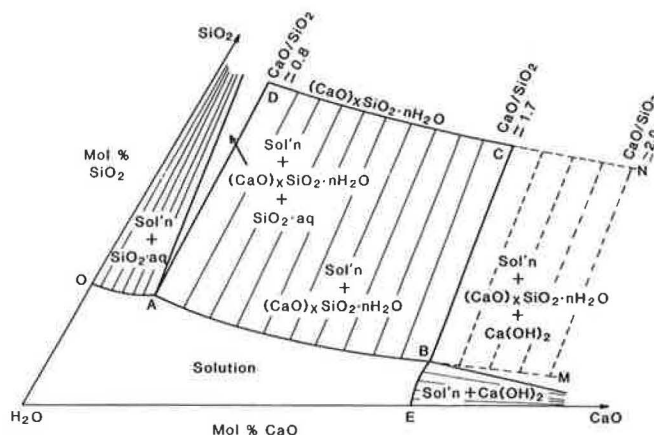
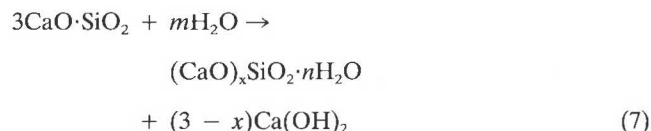


FIGURE 3 Water-rich portion of the ternary system  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ .

by the equilibria with the solution. Eventually the solution composition will reach Point B. When this invariant point is reached, the C-S-H forming will be at equilibrium with a solution also saturated with respect to  $\text{Ca}(\text{OH})_2$  and will have a lime-to-silica ratio of about 1.7.] Dissolution of tricalcium silicate or dicalcium silicate continues until the solution becomes supersaturated with respect to calcium silicate hydrate. The calcium silicate hydrate that initially precipitates has a calcium-to-silica ratio near 0.83. This is far lower than the value of 1.7 shown in Equations 5 and 6. Because the calcium-to-silica ratio of the calcium silicate hydrate is always less than that in the anhydrous dicalcium silicate or tricalcium silicate, the solution becomes enriched with calcium as hydration proceeds. To maintain equilibrium, the calcium-to-silica ratio in the C-S-H also increases. Eventually, the solution becomes supersaturated with respect to calcium hydroxide. However, the initial precipitation of this phase does not occur until the calcium hydroxide concentration in solution is about 1.5 times saturation. The calcium-to-silica ratio of the C-S-H responds to the calcium hydroxide supersaturation by reaching a value possibly as high as 2. Eventually, as calcium hydroxide does precipitate and its concentration in solution approaches saturation, the system shown in Figure 3 approaches the invariant Point B, and the calcium-to-silica ratio of the C-S-H reaches about 1.7. Thus, the values for the calcium-to-silica ratio given in Equations 5 and 6 assume that this invariant point has been reached.

Using tricalcium silicate as an example, a more general equation describing silicate hydration may be written as follows:



This equation indicates the variability in the composition of the C-S-H in response to the prevailing solution composition and, along with a companion equation for the hydration of dicalcium silicate, is more relevant to the hydration of the silicate phases in cement than are Equations 5 and 6. Variation in solution composition may be expected during cement

hydration depending on the amount of free lime present, the presence of pozzolans or slag, as well as the concentration of the alkalis, sodium, and potassium in solution.

In addition to the compositional changes that occur during the hydration of the silicate phases in cement, mechanistic and morphological changes occur. Indeed, the latter two changes are closely related. From a mechanistic standpoint, tricalcium silicate hydration occurs in three stages. The first of these is responsible for the onset of the induction period and is the result of the formation of a layer of C-S-H on the surfaces of the hydrating particles. The formation of this layer causes hydration to become diffusionally controlled, with the rate of tricalcium silicate hydration depending on the rate of diffusional transport through this layer. The rate of hydration during this stage is slow and does not appear to be strongly dependent on fineness (9). This period of hydration is called the "induction period." Eventually this layer becomes unstable and a morphological transformation to an acicular, cauliflower-like, C-S-H hydration product occurs (10). The specific reason for this transformation remains a matter of speculation; however, there is evidence to suggest that it is associated with a polymerization reaction in which monomeric silicate tetrahedra in the C-S-H condense to form dimers (11).

Once the initial layer of C-S-H has undergone the transformation to an acicular product, the anhydrous tricalcium silicate particle surfaces are again exposed to the solution. This results in the onset of a period of rapid hydration, referred to as the "acceleratory period." A significant fraction of the alite in cement is consumed during the acceleratory period with the actual amount consumed depending on the fineness of the cement. However, the acceleratory period eventually comes to an end and the rate of hydration decreases again as the small particles of tricalcium silicate are consumed and as the layers of hydration products around the larger particles thicken. A transition to a "postacceleratory period" is complete when the layers of C-S-H surrounding the hydrating particles are sufficiently thick to cause hydration to again become diffusionally controlled. It appears that the hydration rate during this period is independent of fineness (12). Thus, in the hydration of cement, it appears that the primary difference in behavior between a Type I or a Type II and a Type III cement lies in the amount of hydration that occurs during the acceleratory period and that grinding to higher fineness contributes principally to the amount of hydration occurring during the acceleratory period.

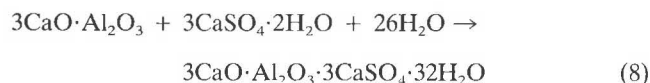
### Aluminate Hydration

The percentage of the aluminate phase in portland cements may vary from essentially zero in so-called "zero C<sub>3</sub>A cements" to as high as 14 percent or more.

The aluminate phase in cement is generally considered to be an impure form of tricalcium aluminate. The principal substitution that affects the stoichiometry of the aluminate phase is that of sodium for calcium. However, in cements the composition of the aluminate phase may also depart significantly from that of tricalcium aluminate because of the quenching of nonequilibrium compositions during cooling.

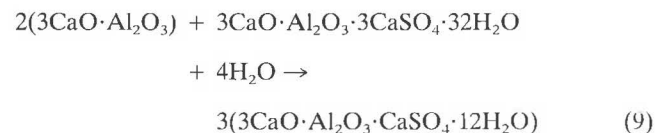
Tricalcium aluminate is a highly reactive phase. If tricalcium aluminate is mixed with water at room temperature, the rate

of heat evolution associated with its rapid hydration may be sufficient to cause the water to boil. The rapidity of this reaction leads to a phenomenon in concrete called "flash set." Flash set results because the products of aluminate phase hydration cause a stiffening of the fresh concrete. Premature stiffening associated with aluminate hydration makes placement and finishing difficult. The use of gypsum to control flash set goes back over a century to the studies of Michaelis in 1870 (13). The mechanism by which the hydration of the aluminate phase in cement is retarded in the presence of gypsum has remained a matter of debate (14). However, it is generally recognized that retardation is associated with the formation of ettringite,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$ . The reaction of tricalcium aluminate in the presence of gypsum to form ettringite may be written as follows:



The amount of calcium sulfate interground with cement clinker is carefully proportioned to ensure that ettringite formation does not continue to any significant extent after about one day, when the concrete has started to gain strength. The formation of ettringite is an expansive reaction. The expansion associated with ettringite formation is acceptable when concrete is in a plastic state and the formation of ettringite needles may indeed contribute to set. It is usually undesirable that an expansive reaction occur in hardening concrete because dimensional instability and cracking may result. There are two reasons why ettringite formation is expansive. First, the solid volume of the ettringite product phase exceeds the sum of the solid volumes of the tricalcium aluminate and gypsum reactant phases. Second, ettringite needles tend to bridge pores in the hardening concrete. Once an ettringite needle has bridged a pore, its continued growth will generate a tensile stress on the pore walls. These internal tensile stresses may eventually lead to crack formation.

A mechanism proposed for the retardation of tricalcium aluminate hydration in the presence of gypsum involves the rapid formation of a layer of ettringite around the hydrating tricalcium aluminate grain. However, the molar volume of the ettringite is much larger than that of the tricalcium aluminate from which it has formed. This results in stresses that lead to cracking of the ettringite layer. As the cracks are filled by additional reaction product, more cracks form. Eventually all the gypsum is consumed. When this occurs, ettringite reacts with the remaining unhydrated tricalcium aluminate to form the monosulfate phase,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$ , according to

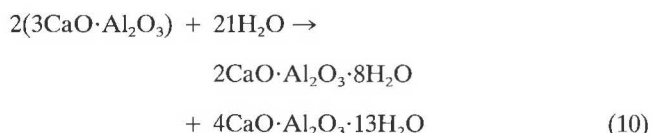


Supporting this mechanism is the observation that tricalcium aluminate hydration is not effectively retarded in the absence of ettringite formation (15). On the other hand, the needlelike morphology of ettringite is not in accord with that of a phase that forms an effective diffusion barrier and thereby controls

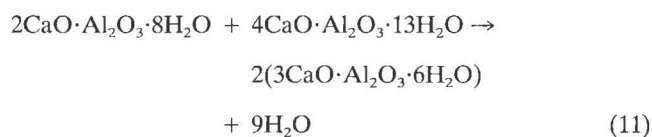


the rate of tricalcium aluminate hydration. Recent work elucidating the phase relationships in the system  $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4\text{-H}_2\text{O}$  may reconcile this (8,16). Formation of ettringite from tricalcium aluminate results in the existence of local equilibria in the interfacial region between the hydrating particle and the solution. At the exterior of the interfacial region ettringite is in equilibrium with the solution. Inside the ettringite layer is a layer of the monosulfate phase. Inside that is a layer of calcium aluminate hydrates, and inside that, on the anhydrous surface, is a layer of alumina gel. It is suggested that, in analogy with the induction period in the hydration of tricalcium silicate, it is the transport processes across the alumina gel layer that control the rate of tricalcium aluminate hydration. Although an ettringite layer exists at the surface of the hydrating particle, it in itself is not a diffusional barrier; rather its existence allows the formation of an alumina gel diffusional barrier at the tricalcium aluminate interface.

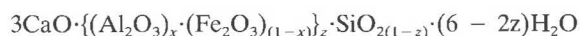
If the hydration of one mole of tricalcium aluminate is carried out in the presence of three moles of gypsum, the reaction proceeds according to Equation 8 and the final product is ettringite. If hydration is carried out in the presence of one mole of gypsum, the reaction proceeds according to Equation 9 and the final product is monosulfate. At gypsum-to-tricalcium aluminate mole ratios greater than 1 but less than 3, a mixture of ettringite and monosulfate forms. At gypsum-to-tricalcium-aluminate mole ratios less than unity, all the available sulfate in the system will have reacted to form monosulfate according to Equation 9 before the anhydrous tricalcium aluminate has been consumed. In this case a third set of hydration reactions involving the formation of calcium aluminate hydrates will occur as follows:



Because all the available sulfate has already been consumed, the hydration reaction represented by Equation 10 involves only the formation of calcium aluminate hydrates. Although the formation of the hydrates  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$  and  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$  is kinetically favored, these hydrates are metastable with respect to the hydrate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$  at above about  $15^\circ\text{C}$ . As a consequence,  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$  and  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$  will eventually transform to the stable phase  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$  according to



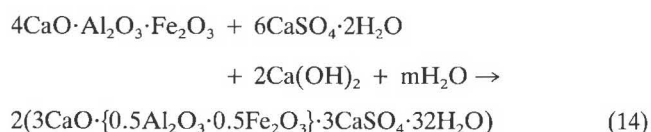
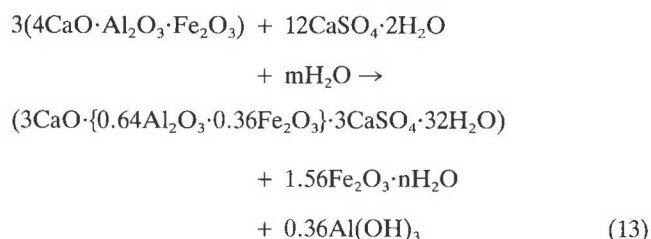
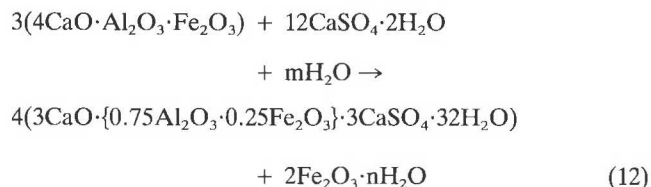
The situation is somewhat different for portland cement when silica and ferric oxide are available. In cement, the calcium aluminate hydrate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$  may form solid solutions with a calcium ferrite hydrate and silica. The general formula for this solid solution may be written as



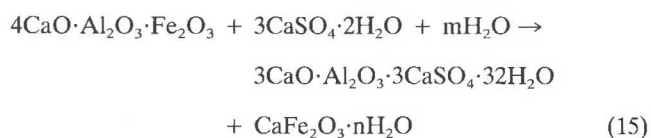
## Ferrite Phase Hydration

The relative abundance of the ferrite phase in portland cements is in the same range as that of the aluminate phase or slightly lower. In the pure system,  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ , the ferrite phase is actually a solid solution having a generalized composition of  $\text{Ca}_2\text{Fe}_{(2-x)}\text{Al}_x\text{O}_5$  where  $x$  varies between 0 and 0.6. The hydration behavior of the compound tetracalcium aluminoferrite,  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ , has often been regarded as representative of the behavior of ferrite solid solutions in general. However, in cement, as with the aluminate phase, a variety of substitutions may occur in the ferrite phase, and this, coupled with quenching-in of nonequilibrium compositions, can result in ferrite phase compositions remote from tetracalcium aluminoferrite.

Of the four major phases in portland cement, the hydration of the ferrite phase is the least well understood. Investigations (17-19) of the hydration of tetracalcium aluminoferrite in the presence of gypsum have reported the following hydration reactions, respectively:



These reactions suggest a variable stoichiometry for the ettringite-like hydration product. However, a recent investigation (20) has shown that early hydration of  $\text{C}_4\text{AF}$  in gypsum and lime-gypsum solutions results in the formation of iron-free ettringite and a calcium ferrite gel according to



## HYDRATION REACTIONS IN PORTLAND CEMENTS

The reactions described for the pure phases or their combinations to a large extent also occur in portland cements. There are, however, important differences both in the rates of reac-

tion and in the compositions and morphologies of the hydration products.

None of the major phases in portland cement are pure; all are solid solutions. Although the nature of the substitutions varies, all these solid solutions contain alkalis. As a consequence, except for the very earliest reactions, hydration in cement occurs at pH values higher than would occur in the model systems. This affects both the stabilities and the compositions of the hydration products that form. For example, if a cement pore solution contains alkali hydroxides in sufficient concentration, the alkali-silica reaction will occur. However, hydration of a mixture of pure phases in the presence of reactive aggregate will not lead to the alkali-silica reaction.

Although the hydration of cement produces significant amounts of calcium hydroxide, very little is observed in the pore solutions extracted from cements. This is because the common ion effect with potassium and sodium hydroxides depresses the calcium ion concentration. On the other hand, there is sufficient calcium present to preclude the formation of the hydrated calcium aluminate phase,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ . Rather, the phase  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$  forms. Other effects associated with elevated alkali hydroxide concentrations in solution include a decrease in the stability of ettringite and, as discussed previously, a tendency for syngenite to form.

Major differences may occur in the hydration of the aluminate and ferrite phases when the behavior of the pure phases and the analogous phases in portland cement are compared. Figure 2 suggests that the ferrite phase in cement is rather slow to react. On the other hand, it has been observed that the hydration of the phase tetracalcium aluminoferrite with gypsum occurs at a higher rate than that of tricalcium aluminate with gypsum (P. W. Brown, unpublished data). The reason for this difference is that the hydration reaction of the ferrite phase is strongly retarded in the presence of calcium hydroxide, whereas that of the aluminate phase is only mildly retarded.

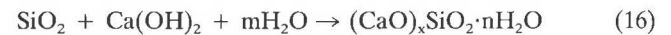
The hydration of both the ferrite and the aluminate phases in cement is affected by the competition of the C-S-H for sulfate. In cement the molar ratio of calcium sulfate-to-(aluminate + ferrite) is about 0.7. Thus, monosulfate phases and hydrated calcium aluminate/ferrite phases would be expected to be the terminal phases associated with aluminate and ferrite phase hydration. However, a small percentage of the silicate in C-S-H can be replaced by sulfate (21), and the formation of a sulfate substituted C-S-H results in the decomposition of the monosulfate phases in cements. Finally, as mentioned above, silicate also substitutes in the hydrated calcium aluminate/ferrite phases. As a consequence, the terminal aluminate and ferrite phases in portland cement are hydrogarnets.

## EARLY HYDRATION REACTIONS IN MODIFIED PORTLAND CEMENTS AND NONPORTLAND CEMENTS

### Blended Cements

The principal difference between the hydration of portland and blended cements is that the calcium hydroxide liberated during silicate hydration reacts with the additives containing

reactive silica to produce additional C-S-H. This reaction is called the pozzolanic reaction, which can be described by the following equation:

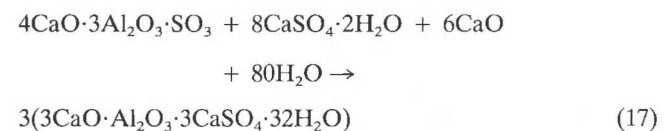


It is not possible to predict the stoichiometry of the C-S-H while the pozzolanic reaction is occurring, but compositional analyses of C-S-H in the vicinity of reacting fly ash particles indicate the C/S ratio to be in the range of 1.2 to 1.4. This represents an averaged value because the C/S ratio at the ash particle-(C-S-H) interface is probably near 0.83, as Figure 3 would suggest, whereas the C/S ratio of the C-S-H at the (C-S-H)-pore solution interface is probably near 1.7. If, when the pozzolanic reaction has reached completion (i.e., the source of reactive silica has been completely consumed) there is calcium hydroxide remaining, the C/S ratio of the C-S-H should eventually reach about 1.7. If, on the other hand, the available calcium hydroxide is consumed and there is still unreacted silica present, the C/S ratio of the C-S-H formed because of the pozzolanic reaction will be less than 1.7.

### Shrinkage-Compensating and Regulated-Set Cements

It was mentioned that the amount of calcium sulfate interground with portland cement clinker is proportioned to preclude ettringite formation after about the first day of hydration. Although the expansive reaction associated with ettringite formation can be accommodated while concrete is in a plastic state, the occurrence of an expansive reaction in hardened concrete used in ordinary construction is undesirable. There are, however, exceptions to this and cements have been formulated based, in part, on the formation of ettringite. These cements fall into two general categories—shrinkage-compensating and regulated-set cements.

Shrinkage-compensating cements are formulated so that an expansive reaction compensates for the drying shrinkage typical in portland cement concretes. In cements of this type, ettringite is formed as a result of the reaction between gypsum and the compound  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$  according to the reaction



Shrinkage-compensating cements are also referred to as expansive cements or self-stressing cements.

Regulated-set cements contain the compounds that react rapidly with sources of calcium sulfate to form ettringite. The early strength gain in regulated-set cements is associated with ettringite formation. After ettringite formation has reached virtual completion, reaction of the silicate phases results in continued strength gain. In one class of regulated-set cements,  $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$  is added. This compound is rapidly hydraulic and ettringite is rapidly formed when a source of calcium sulfate is present. In a second class, the compound  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$  is present but in higher proportion than that used in shrinkage-compensating cements.

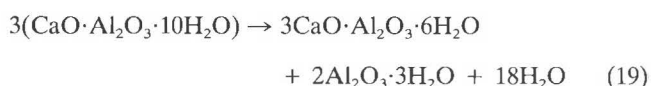
## High-Alumina Cement

High-alumina cement is a nonportland cement composed essentially of monocalcium aluminate,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The hydration reaction in this cement is



High-alumina cement offers the desirable features of high early strength and resistance to chemical attack. The source of resistance to chemical attack is the fact that the calcium aluminate hydrate formed is of low basicity and is not attacked by mild acids.

High-alumina cements perform adequately providing the exposure condition does not promote the conversion of the monocalcium aluminate hydrate to tricalcium aluminate hexahydrate. This conversion reaction may be written as follows:



The monocalcium aluminate hydrate phase becomes increasingly unstable with respect to tricalcium aluminate hexahydrate as the temperature is increased above room temperature. This conversion reaction leads to a loss of strength that has resulted in structural failures (22).

## Miscellaneous Cements

A variety of cements used for specialized applications, such as white cements, oil well cements, alinite cements, and so forth have not been considered in this paper. In addition, the above discussion of blended, shrinkage-compensating, regulated-set, and high-alumina cements is not intended to be comprehensive and reference may be made to a variety of sources regarding these types of cements (19,23–26).

## ACKNOWLEDGMENT

The author gratefully acknowledges the support of the Air Force Office of Scientific Research, Electronic and Materials Science Directorate.

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Publication of this paper sponsored by Committee on Mechanical Properties of Concrete.