

# Studies of Early Hydration Reactions of Portland Cement by X-Ray Diffraction

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Monitoring by X-ray diffraction of hydration of tricalcium aluminate in pastes containing calcium hydroxide and gypsum has demonstrated successive formation of the high-sulfate form of calcium sulfoaluminate hydrate (ettringite), the low-sulfate form of that compound, and finally, a solid solution of the low-sulfated hydrate and tetracalcium aluminate hydrate. These reactions and effects of various factors on them correspond very closely to the early hydration behavior of  $C_3A$  in portland cement. Diffraction studies of hydrating sintered tricalcium aluminate slabs have demonstrated the retarding effect of the initially formed ettringite film. X-ray and dilatometer studies have shown that the hydrating  $C_3A$  pastes undergo large increases in volume because of a tendency to imbibe large quantities of water. The individual effects of other portland cement constituents on these hydration reactions have been investigated.

A study of hydration of combinations of the various constituents has led to a fairly complete picture of the early hydration reactions of portland cement. Examination of a few well-known accelerating and retarding materials has shown them to affect primarily the hydration rate of  $C_3S$ . They may affect the rates but not the nature of the early  $C_3A$  reactions. Retarders can produce a large initial acceleration of  $C_3A$  hydration. When considered in relation to the state of the calcium sulfate in the cement, this previously unrecognized effect can account for many instances of abnormal setting of concrete. Optimum  $SO_3$  content is characterized by gypsum depletion at 18 to 24 hr after gaging. Higher  $SO_3$  contents cause water imbibition to produce excessive expansion and lowered strength. This water imbibition is a major factor in the behavior of shrinkage-compensating and expansive cements.

•MANY MODERN methods of concrete construction involve conditions of use affecting the early hydration reactions of portland cement. Various means are used to produce acceleration or retardation of set, enhancement of rate of early strength development, and variations in workability and water requirement of concretes made from a given cement. These practices result from the increasing production of concrete under unusual conditions such as extremes of temperature and also from the ever-increasing interest in the use of chemical admixtures to modify concrete characteristics (1).

Accompanying these practices, there are developing an increasing number of problems relating to the performance of the concrete. Some of these are caused by improper use of concreting materials. Others appear to result from unusual and unexpected behavior exhibited by particular cement-admixture combinations. In numerous instances the causes of the observed behavior are not understood, and corrective measures must be developed empirically.

A fundamental approach to solutions of these problems requires a knowledge not only of the early hydration reactions of portland cement but also of the effects of various factors on these reactions and, further, of the effects of variations in these reactions on the ultimate properties of the concrete. The work of Lerch (2) on the effect of  $\text{SO}_3$  content on the properties of hydrated cement is a landmark in this area. The existing scientific knowledge of pure cement components was applied to a study of the effects of cement composition on the rates of early hydration and also on some of the important engineering properties of concrete. The effect of variations of  $\text{SO}_3$  content on the early hydration of cements with various compositions was clearly demonstrated. Equally clear was the demonstration that changes in  $\text{SO}_3$  content and in the rates of hydration affected the engineering properties studied. A more recent paper by Klieger (3) demonstrates analogous results as regards the effect of placing and curing temperature on strength development.

The implications of Lerch's work have not yet been fully explored. For instance, it seems reasonable to suppose that the use of chemical admixtures known to have an effect on the rates of early hydration would, as in the case of gypsum, affect the ultimate concrete performance. Because of the problems encountered in recent years, there is presently a definite need for a better understanding both of the early hydration reactions and of the effects of deliberate changes in the early reaction rates. Lerch based his conclusions primarily on the effects of cement composition on the early reaction rates as measured by rates of heat evolution. He was thus able to avoid involvement in the existing uncertainties concerning the nature of the hydration reactions and reaction products occurring in cement pastes with the water contents used in concrete. Resolution of these uncertainties would add greatly to the ability to control and interpret concrete performance.

The present paper is a progress report covering a large volume of work on the application of specially developed X-ray diffraction techniques (4) to supplement the earlier results of calorimetry, microscopy, and chemical analysis by direct observations of changes in composition and structure of hydrating solid phases.

A detailed examination was made of the hydration of tricalcium aluminate in low-water-content pastes containing solid calcium hydroxide and gypsum.

## MATERIALS AND TECHNIQUES

### Aluminates

Various methods of preparing tricalcium aluminate have been compared. The method found most effective was based on an observation by Schneider and Thorvaldson (5). In this method, an appropriately proportioned mixture of calcium hydroxide and aluminum hydroxide was autoclaved to produce the cubic  $\text{C}_3\text{AH}_6$ . (Symbols used in cement chemistry are as follows: C =  $\text{CaO}$ , A =  $\text{Al}_2\text{O}_3$ , S =  $\text{SiO}_2$ , F =  $\text{Fe}_2\text{O}_3$ , N =  $\text{Na}_2\text{O}$ , H =  $\text{H}_2\text{O}$ .) The product was then fused at 1410 C. The free lime content of the product was 0.2 percent. It is thus possible to produce this material with only one fusion. The fineness of grinding and possibly the method of preparation have a profound effect on the reactivity of the product. The rates of reaction for different batches varied widely. As a consequence, the behavior of complex mixtures was correspondingly variable in time of development of new phases, in rate of heat development, and in setting time. The results reported here are necessarily limited to comparisons between hydration stages of the same materials or between different compositions made from portions of the same batch of  $\text{C}_3\text{A}$ .

For the preparation of sodium calcium aluminate ( $\text{NC}_3\text{A}_3$ ), a mixture of calcium oxide and aluminum oxide in a mole ratio of 5:3 was heated to its melting point. A mixture of the product with appropriate proportions of tricalcium aluminate and sodium carbonate was then fused. The resulting solid was ground to pass a 200-mesh screen and then heated to fusion again. The heat treatment resulted in a loss of alkali by volatilization. The final product, therefore, contained only 6.6 percent  $\text{Na}_2\text{O}$  as compared with the theoretical 7.6 percent. For the purposes of this study, this deficiency of alkali is unimportant.

### Ferrites

The ferrites  $C_2F$ ,  $C_6AF_2$ , and  $C_6A_2F$  were prepared as described in the literature (6). The compound  $C_4AF$  was prepared in the same way as the tricalcium aluminate described previously, except for inclusion of an appropriate quantity of ferric hydroxide in the raw material.

### Tricalcium Silicate

The tricalcium silicate was prepared by a method described in the literature (7).

### X-Ray Diffraction

All X-ray diffraction work was carried out with copper  $K\alpha$  radiation on a Norelco Geiger counter diffractometer modified to provide temperature and ambient atmosphere control of the sample, as has been described in a previous paper (4) that also describes the monitor techniques used. Most X-ray scanning was done at a rate of  $1^\circ 2\theta/\text{min}$  with  $1^\circ$  divergence and receiving slits, a  $0.003^\circ$  scatter slit, and a time constant of 4 sec.

No special precautions were taken to avoid preferred orientation of the powdered samples. As a result, individual lines in patterns of duplicate samples of the same material exhibit small random variations in intensity. This random variation is necessarily a component of changes observed in diffraction patterns of different hydration stages, either of different samples of the same material or of the same sample after smoothing, such as are shown in the figures. These variations could be clearly distinguished from the intensity changes described in the text as indicating changes in compositions only after examination of large numbers of individual patterns.

In some instances it became necessary to distinguish between di- and tetracalcium aluminate hydrates. At water saturation, these phases are present as  $C_2AH_6$  and  $C_4AH_{19}$ , both of which have a first order diffraction at  $2\theta = 8.3^\circ$ . A method of identification was developed, based on work of Roberts (8). In this method, dry nitrogen is admitted to the diffractometer scatter shield through the atmosphere control system. The ensuing dehydration of the sample produces line shifts from  $8.3^\circ$  for saturation compounds to  $10.2^\circ$  and  $11.2^\circ$  for  $C_2AH_5$  and  $C_4AH_{13}$ , respectively.

### Temperature Control

All work was carried out at room temperature unless otherwise indicated. Initially, reaction mixtures were frequently stored at 40 F to prevent conversion of the hexagonal tetracalcium aluminate hydrates to the cubic  $C_3AH_6$ . This precaution was later found to be necessary only for compositions free of sulfate ion. It has been verified that a very small quantity of sulfate ion stabilizes the hexagonal hydrates at temperatures up to 100 F. Previous investigators have uniformly found that  $C_3AH_6$  crystallizes with difficulty, if at all, in compositions containing  $SO_3$  (9). The relationship between the thermodynamic stability of the phases and the temperature has been demonstrated (4).

### Volume Change

Tendencies toward volume changes during early hydration were measured with a dilatometer adapted from the osmotic cells previously used for studies of alkali-reactive aggregates (10). For this purpose, a cement membrane with a water-cement ratio of 0.75 was inserted into the cell in the usual way. A pat of the paste to be studied was trowelled on one side of the membrane. The cell was then assembled so that the half-cell containing the pat was full of mercury, while the other half-cell was full of water. If the pat imbibed water through the membrane, the mercury level rose and the water level fell. If, on the other hand, the pat contained excess water, the mercury pressure forced the water through the membrane, with a corresponding drop in mercury level and rise in water level. The results obtained were not quantitatively reproducible because the swelling tendency could be counteracted by the small mercury pressure present and because of the dependence of the water imbibition rate on the shape of the pat

and the area exposed to the membrane. The reliance placed on the results obtained depends on the constancy of the levels after the reactions have ceased. This stability of the system indicates the absence of leaks and of extraneous reactions causing flow through the membrane.

### Hydration of Sintered Slabs

A novel technique was developed for investigating the nature of hydration reactions on the surface of tricalcium aluminate. For this purpose aggregations of the powdered mineral were prepared by compaction and subsequent sintering at about 1400 C. The pats were formed as little slabs that fit into the diffractometer sample holder. After the surface was smoothed by filing, the pat was hydrated by immersion for some appropriate length of time. X-ray diffraction patterns were then made of the hydrated surface and of the surfaces remaining after thin layers of hydrated material were removed by grinding. By this technique, the nature and sequence of the hydration products could be ascertained.

### Chemical Analysis

The conventional methods of chemical analysis of portland cement (11) were used in these studies. However, determinations of alumina in compositions high in both lime and alumina gave inaccurate results because of precipitation of part of the lime as calcium hydroxide in the  $R_2O_3$  precipitate. This error was detected from analyses of pure compounds that yielded  $CaO/Al_2O_3$  ratios consistently less than stoichiometric. Even a triple precipitation of aluminum hydroxide by the classical ammonia method carried down a considerable quantity of calcium. Successful separations were obtained by precipitation of the aluminum as the basic succinate (12).

The concentration of sucrose in solution was determined by a published method (13).

Lignosulfonate concentration in solution was determined by a modification of the spectrophotometric method of Ernsberger and France (14), whereby the final pH of the solution was adjusted to a value of 3.0 to avoid effects of acidity on optical density (15). Measurements were made at  $360\text{ m}\mu$  for low concentrations of  $410\text{ m}\mu$  for the higher range.

## BASE MIXTURES AND THEIR HYDRATION

### Purpose and Composition of Base Mixtures

In these studies, the fundamental reference point is the hydration behavior of a particular series of mixtures of synthetic compounds designated as base mixtures. All mixtures in the series contain tricalcium aluminate, calcium hydroxide, gypsum, and distilled water. In these mixtures, the  $C_3A$  and  $Ca(OH)_2$  are present in equimolar quantities and the gypsum content is varied. The water-to-solids ratio is 0.4.

The compositions of the base mixtures were selected after a number of exploratory studies. The unit mole ratio for  $Ca(OH)_2/C_3A$  stemmed from an observed enhancement of the retarding effect of gypsum by calcium hydroxide and also from a desire to allow formation of the highest limed hydrate,  $C_4AH_{19}$ . The water content was chosen low enough to produce a diffraction surface that would not be materially distorted by sedimentation.

The previously described special sample holders (4) were devised when it was found that the water-to-solids ratio of 0.4 frequently provided insufficient water for completion of the hydration reactions. The imbibition of water from the reservoirs in these holders caused distortion of the diffracting surface as the sample swelled. Restoration of the surface was accomplished by frequent manual smoothing.

The general hydration behavior of the base mixtures and the techniques used in interpreting the diffraction patterns can be most easily described by means of specific examples (Figs. 1 and 2). These illustrations, typical of the general pattern, show diffraction patterns at various ages for base mixtures with  $SO_3/Al_2O_3$  mole ratios of  $1/4$  and  $3/4$ , respectively, for a sample of  $C_3A$  with a specific surface of 3,100 sq cm/g (Blaine). The actual patterns shown here were not, however, produced by continuous

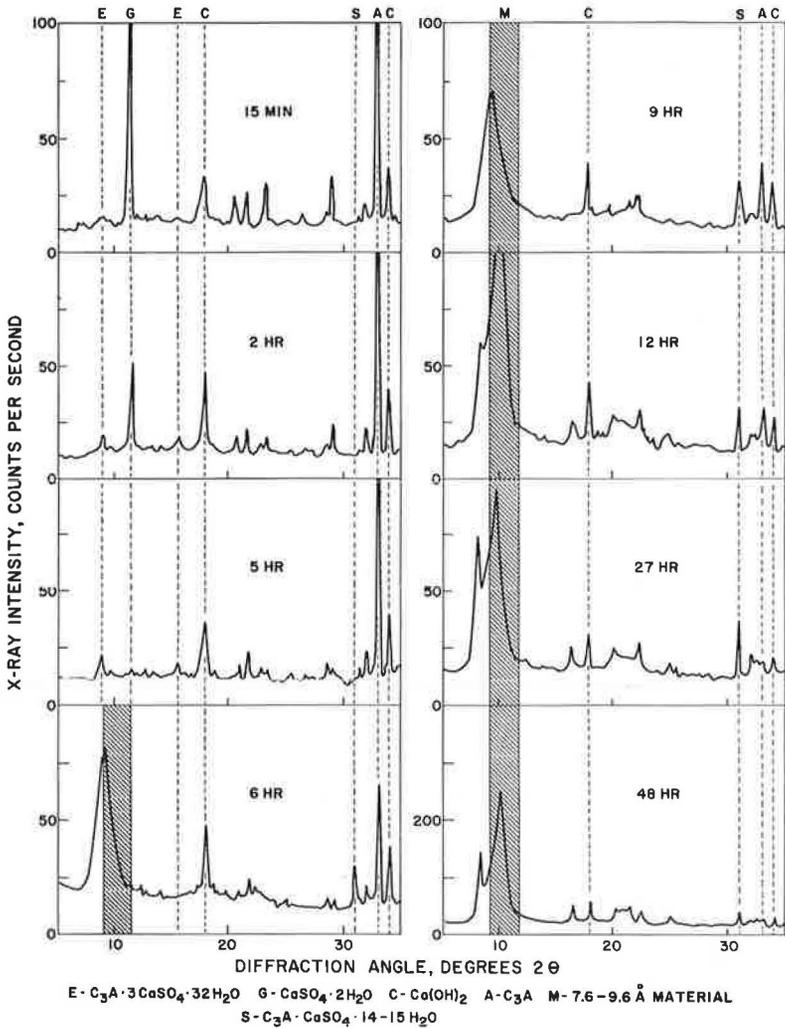


Figure 1. Diffraction patterns of base mixture with 1/4 mole  $SO_3$  per mole alumina.

monitoring, because excessive carbonation would have resulted in distortion of the results at later ages. Several identical samples were hydrated simultaneously in the special sample holders in a sealed container, and care was taken to transfer only relatively uncarbonated samples to the diffractometer at the appropriate times. It has been found that continuous monitoring of samples for more than a few hours is feasible only during periods of rapid expansion; under these conditions the manual smoothing results in removal of carbonation products from the diffracting surface. In the following descriptions, as in the figures, locations of diffraction lines are designated in terms of degrees  $2\theta$ .

#### Hydration at Low Gypsum Content

In Figure 1 the pattern at 15 min indicates the presence of the raw materials by a very large  $C_3A$  peak at  $33.1^\circ$ , a gypsum peak at  $11.6^\circ$ , and a calcium hydroxide peak at  $18.1^\circ$ . In addition, slight lines are seen at  $9.1^\circ$  and  $15.7^\circ$  for the high-sulfate form of calcium sulfoaluminate hydrate ( $C_3A \cdot 3CaSO_4 \cdot 31-33H_2O$ ) which, for simplicity, will be consistently referred to as ettringite. The pattern at 5 hr represents a transition

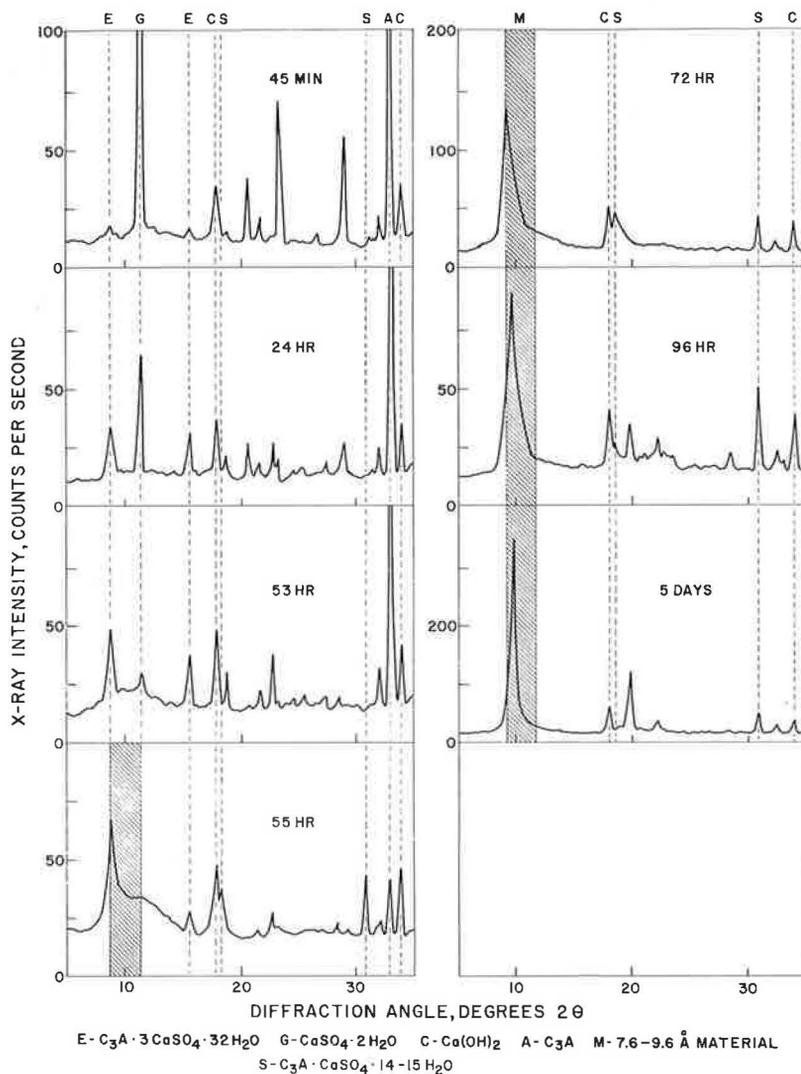


Figure 2. Diffraction patterns of base mixture with  $3/4$  mole  $SO_3$  per mole alumina.

stage at which the gypsum has reached final depletion and a new set of reaction products shown more clearly in the 6-hr pattern is forming. The temperature rises noticeably at this stage. Peaks at  $9.2^\circ$  and  $31.0^\circ$  appear, indicating formation of the low-sulfate form of calcium sulfoaluminate hydrate,  $C_3A \cdot CaSO_4 \cdot 14-15H_2O$ , by reaction of ettringite with more of the tricalcium aluminate. Turriziani (16) also has obtained evidence of this reaction. The intensity of the calcium hydroxide peak shows a slight decrease. Between 6 and 48 hr, the low-angle peak of the low-sulfate form of calcium sulfoaluminate hydrate continues to increase in intensity and to shift toward higher angles. The peak for calcium hydroxide continues to decrease in intensity. The low-sulfate form of calcium sulfoaluminate hydrate reacts with more  $C_3A$  and calcium hydroxide to form a solid solution. This reaction is accompanied by a decrease in intensity and the ultimate disappearance of the  $31.0^\circ$  peak. Earlier evidence for solid solution formation had been obtained by chemical analysis of the liquid phase (17). At 12 hr, a peak for  $C_4AH_{19}$  has appeared at  $8.3^\circ$  and continues to increase in intensity as the calcium hydroxide and tricalcium aluminate continue to react. At 48 hr, the  $C_3A$  has es-

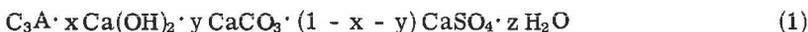
entially hydrated completely. The final 48-hr pattern indicates that the  $C_4AH_{19}$  and the sulfate-hydroxide solid solution are essentially the only hydration products.

X-Ray Patterns of Complex Calcium Aluminate Salts

As indicated previously, complex solid solutions of varying composition and structure are formed during and after the later stages of hydration of the  $C_3A$  in the base mixtures. These hydration products introduce uncertainties into the stoichiometry of the reactions and also into interpretation of the X-ray patterns.

The situation is further complicated by the virtual impossibility of completely excluding carbon dioxide from the reaction mixtures. Carbonation is most intense at the surface exposed to the atmosphere, which is necessarily also the diffracting surface. As a result, marked distortion of the solid solution patterns is quite common, especially in samples subject to lengthy monitoring.

Under ordinary monitoring conditions sharp peaks, or broad bands with peaks, may be found anywhere in the angular range  $9.2$  to  $11.8^\circ$ , corresponding to a composition range



subject to the limitation that  $x + y$  cannot exceed unity. This angular range corresponds to a range of d spacing of  $7.6$  to  $9.6 \text{ \AA}$ . Because of the frequent uncertainty in composition and structure of the material exhibiting spacings in this range, the entire angular range is consistently presented here as a shaded area in the diffraction patterns of later hydration stages. The hydration product with spacings in this range will henceforth be termed  $7.6$  to  $9.6 \text{ \AA}$  material unless reference is made to identifiable specific phases. Table 1 lists known compounds in this range of composition, together with the angles or angular ranges in which they have been observed in studies of the base mixtures hydrated for various periods and at various temperatures. Examination of the second-order diffraction in an angular range at approximately double the diffrac-

TABLE 1  
FIRST-ORDER DIFFRACTION PEAKS OF  
COMPLEX CALCIUM ALUMINATE  
HYDRATES<sup>a</sup>

Hydrate	x	y	Diffraction Angle, 2θ (deg)
Hydroxyaluminate	1	0	8.3
Monosulfate <sup>b</sup>			
i form	0	0	9.8-10
j form	0	0	9.1-9.3
z form	0	0	8.5-8.7
Solid solution	0-0.4	0	9.8-10.1
Monocarbonate	0	1	11.6
Hemicarbonate	0.5	1 - x	10.5-10.9

<sup>a</sup>Of the form  $C_3A \cdot x Ca(OH)_2 \cdot y CaCO_3 \cdot (1 - x - y) CaSO_4 \cdot z H_2O$ .

<sup>b</sup>Nomenclature of Turriani (16).

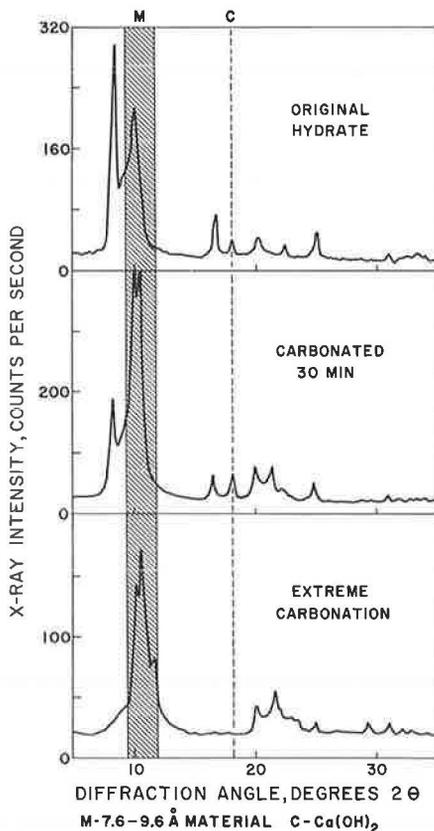


Figure 3. Changes in diffraction pattern of  $7.6$  to  $9.6 \text{ \AA}$  material caused by exposure of fully hydrated base mixture to atmospheric carbon dioxide.

tion angles discussed previously is sometimes useful in revealing the identity of the phases present.

The effect of carbonation is illustrated in Figure 3. Here the top pattern is that for the material before exposure and after 8 days of storage in a sealed container. The storage period has resulted in a recrystallization of the  $C_4AH_{19}$ , as reflected by the sharpening and narrowing of the  $8.3^\circ$  peak. The second pattern shows the effect of exposure to laboratory air for 30 min with the surface kept moist. The first-order peak for the hemicarboaluminate is clearly visible. The peak for  $C_4AH_{19}$  has decreased in intensity.

The bottom pattern in Figure 3 shows the effect of extreme carbonation of the material. The  $C_4AH_{19}$  in the original hydration product has been completely carbonated. The first-order lines for both hemi- and monocarbonate have appeared. The absence of any clearly defined new sulfate-containing material indicates that the calcium sulfate present remains in the 7.6 to 9.6 Å material.

Numerous studies of equilibrium mixtures in the range covered in Formula 1 have only partially resolved the problem of identification of phases. The crystalline state of the monosulfate depends not only on temperature but also on previous history of the sample in a manner not yet understood. If calcium hydroxide enters the phase, the solid solution pattern is obtained uniquely. With sufficient lime,  $C_4AH_{19}$  and the solid solution can coexist, thus indicating some upper limit for  $x$  when  $y$  is zero in Formula 1. It might thus be expected, and has in fact been experimentally verified, that hydration of base mixtures containing high gypsum contents will not produce a sulfate-free phase. Base mixtures with a  $SO_3/Al_2O_3$  mole ratio of about 0.7 or higher exhibit this behavior. This result corresponds to an upper limit of about 0.3 for  $x$  when  $y$  is zero in Formula 1. In the absence of  $CO_2$ , modified base mixtures, with calcium hydroxide contents adjusted to give  $CaSO_4/Ca(OH)_2$  mole ratio a value of  $(1-x)/x$  in Formula 1, hydrate with complete consumption of calcium hydroxide. In sulfate-free compositions, the hemicarbonate can coexist with either  $C_4AH_{19}$  or with the monocarbonate in the appropriate composition ranges. The data indicate that the previously assumed (4) value of 0.5 for  $y$  when  $x$  is  $1-y$  in Formula 1 is essentially correct.

### Stages of Hydration

Figure 1 indicates that the hydration of  $C_3A$  in a base mixture takes place in three stages. In stage I, the  $C_3A$  combines with the gypsum to form ettringite. Stage I terminates and the next stage of hydration begins when the gypsum is depleted. Stage II is characterized by reaction of the ettringite with more  $C_3A$  to produce the low-sulfate form of calcium sulfoaluminate hydrate and is terminated when the ettringite has completely reacted. Consumption of  $C_3A$  is much more rapid than in the first stage and is accompanied by considerable evolution of heat. During the last stage of hydration, stage III, the remaining  $C_3A$  reacts with calcium hydroxide and with the low-sulfate form of calcium sulfoaluminate hydrate to form 7.6 to 9.6 Å material. The times of termination of these stages can be used as convenient qualitative measures of the average rates of the respective hydration reactions. Instantaneous reaction rates are difficult to ascertain quantitatively by measurements of diffraction line intensities in these systems because of the distortions of the specimen surface produced by volume changes and because of the preferred orientations produced by smoothing of the specimens.

### Hydration at Moderate Gypsum Content

Figure 2 demonstrates essentially the same sequence of events as Figure 1, but at the slower rate expected from the higher gypsum content. The initial pattern at 45 min reflects the change in composition; the gypsum diffraction intensity is much higher and the  $C_3A$  diffraction intensity somewhat lower than at a correspondingly early hydration stage in Figure 1. The sequence of events and the reaction products are essentially the same as before and can be seen more clearly because of the lower rates and higher intensities. Stage I hydration is complete at 53 hr. The pattern at 55 hr shows that stage II is almost terminated; it actually terminated less than an hour later. Stage III terminated at 72 hr. The succeeding patterns show continuing recrystallization in the 9 to  $10^\circ$  range. No  $C_4AH_{19}$  was formed at this higher  $SO_3$  content.

These descriptions demonstrate the feasibility of direct observation of the chemical reactions occurring in the hydration of the base mixtures and the techniques used for this purpose. Further studies have been made to determine the effects of various factors on the rates of hydration.

### Effect of Water Content

Comparisons have been made of the hydration behavior of base mixtures at various water contents, even though slurries with high water contents cannot be monitored directly and require filtration. It was found that at least stage I hydration was accelerated by the presence of excess water. Significantly, in numerous experiments in which excess water was used, only the rates of reaction were affected. The chemical nature and the sequence of the reactions remained unchanged. These facts make it possible to study a particular stage of reaction by determination of the nature of the solid phase of a slurry by X-ray diffraction and the composition of the corresponding liquid phase by chemical analysis. The slurry must be filtered only when the desired degree of reaction has been attained. For study of various hydration stages of the same mixture, either filtration of duplicate mixtures at various times or successive sampling of a large quantity of slurry has proven equally satisfactory.

### Effect of Fineness

Reference has already been made to the effect of fineness on the hydration characteristics of  $C_3A$ . Table 2 gives results for base mixtures made from various grinds of a particular batch of tricalcium aluminate at a  $SO_3/Al_2O_3$  mole ratio of  $1/4$ . The results show that hydration rates at stage I and II increase with fineness.

### Auxiliary Experiments

Two sets of experiments using other techniques have been made to assist in the understanding and application of the X-ray results.

Nature of the Hydrated Surface.—An indication of the texture and location of products of base mixture hydration has been obtained by an auxiliary experiment using sintered slabs of tricalcium aluminate, prepared as described earlier. In these studies, a  $C_3A$  slab was positioned  $1/4$  in. from the surface of a slab of compacted powdered gypsum. In the first test, a pair of slabs was covered with a saturated solution of gypsum. Little if any visible change occurred on the  $C_3A$  slab. Diffraction revealed a thin layer of ettringite, formed at the surface of this slab and apparently sufficiently impermeable to prevent further reaction. In a second test, a pair of slabs was covered with a saturated calcium hydroxide solution. The hydration in this configuration was the same as in the first one. When a pair of slabs was covered with distilled water, a gel-like white layer formed rapidly on the  $C_3A$  surface and continued to thicken for 17 hr. X-ray diffraction revealed the presence of three layers, containing, successively, ettringite, the  $\alpha_1$  form of monosulfate, and finally, dicalcium aluminate octahydrate adjacent to the unhydrated  $C_3A$ .

The results obtained in these experiments are readily explained on the basis of the chemical reactions already observed in base mixtures. The following comments are numbered in the order of the slab pairs to which they apply:

1. If calcium sulfate is present in the original contact solution, a tightly adhering and relatively impermeable thin layer of ettringite is rapidly formed at the tricalcium aluminate surface.
2. The presence of calcium hydroxide initially in the absence of the sulfate is known to retard hydration (2). After the calcium sulfate entering the solution reaches the  $C_3A$  surface, the hydration process is similar to that in the gypsum solution.
3. In the absence of a retarder, the initial hydra-

TABLE 2  
EFFECT OF PARTICLE SIZE OF TRICALCIUM ALUMINATE ON RATE OF HYDRATION OF BASE MIXTURE

Sample No.	$C_3A$ Fineness (mesh)	Hydration Time (hr)	
		Stage I	Stage II
1	325-400	54	20
2	- 400	4.8	6.3
3	- 400*	1.0	1.4

\*Sample 2 reground to a specific surface of 4,100 sq cm/g (Blaine).

tion reaction penetrates more deeply. Auxiliary experiments using the drying procedure described in the section on X-ray techniques have clearly verified that the initial reaction product in the absence of appreciable sulfate ion is a mixture of the hexagonal hydrates,  $C_2AH_6$  and  $C_4AH_{19}$ . As the calcium sulfate from the gypsum slab reaches the surface, a layer of ettringite ultimately forms. The thinness of the ettringite layer indicates retardation of further reaction of the calcium sulfate in solution. This situation differs from the others in that the layer covers hydrated rather than unhydrated material and also in that the hydration continues. It must, therefore, be assumed that in this case the ettringite layer allows permeation of the liquid phase. Low mobility of the calcium sulfate through the ettringite layer results in further reaction of the  $C_3A$  surface with water to produce the di- and tetracalcium aluminate hydrates. The hydrated layer below the ettringite then provides a medium for formation of the low-sulfate calcium sulfoaluminate hydrate by migration of calcium sulfate out of the ettringite structure. Finally, the  $C_4AH_{19}$  combines with the monosulfate above it, leaving a layer of  $C_2AH_6$ . This reaction should produce a layer of solid solution immediately below the monosulfate. No such layer was observed, perhaps because it was thinner than the increment of grinding. Apparently sufficient sulfate ion is present in all layers to prevent formation of the cubic  $C_3AH_6$ .

These results throw light on the mechanisms of the reactions occurring in the hydration of the base mixtures. As long as the calcium sulfate concentration in solution is sufficiently high, only ettringite can form. When the depletion of gypsum causes a reduction in the calcium sulfate concentration, the calcium sulfate from the ettringite reacts with further unhydrated solid material and the ettringite decomposes to produce the low-sulfate form of calcium sulfoaluminate hydrate. The accompanying increase in rate of heat evolution indicates that the layer becomes more permeable as the ettringite reacts. When the ettringite is depleted, the calcium sulfate concentration in solution decreases to a point that permits calcium hydroxide and further  $C_3A$  to combine with the reaction product to form the solid solution.

**Volume Changes During Water Imbibition.**—The observed imbibition of water by base mixtures in the X-ray sample holder was investigated further by the osmotic cell dilatometers described earlier. Figure 4 gives observed expansions for a series of base mixtures with  $SO_3/Al_2O_3$  mole ratios varying from  $1/8$  to 1. The reported expansions are based on the initial volume of the reaction mixture as calculated from densities given by Lea (18, p. 227).

Calculation of the water requirement for the formation of ettringite during stage I hydration shows that the water-to-solids ratio of 0.4 in base mixtures provides sufficient water over the range of gypsum contents used. This conclusion is confirmed by results of base mixture hydration in the absence of a water reservoir. Stoppage of hydration by water deficiency occurs only after stage I hydration reaction has gone to completion. Only a slight expansion of the mass in the X-ray sample holder is observed.

The data show, on the other hand, that initial access to water results in large-scale imbibition and expansion even against the slight mercury pressure. This effect cannot be caused by the chemical requirement for water and must be associated with crystal growth. The expansion continues during stage II and III hydration and increases the water content to a level sufficient for completion of the later hydration reactions.

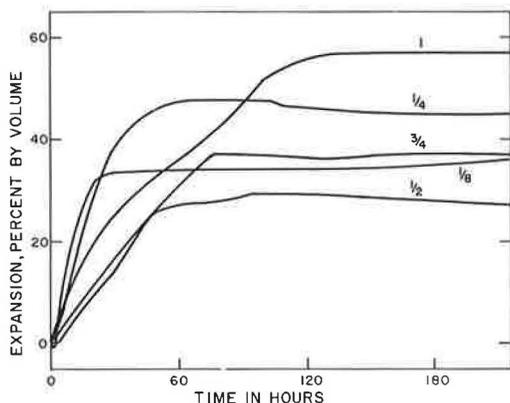


Figure 4. Volume increase from imbibition of water during base mixture hydration for varying  $SO_3/Al_2O_3$  mole ratios.

### Hydration at Lower Lime Contents

In the course of various exploratory and auxiliary studies, a considerable body of information has been obtained concerning the hydration reactions of mixtures of tricalcium aluminate, calcium hydroxide, and gypsum containing less than 1 mole of calcium hydroxide per mole of alumina. Although not directly applicable to cement hydration, the results obtained are necessary as background for portions of the present paper and are, therefore, given in the Appendix.

### EARLY HYDRATION REACTIONS OF PORTLAND CEMENT

X-ray diffraction studies have previously been reported on aged hydrated cement pastes (19), predried and enriched pastes (16, 20), dried fresh pastes (21), and fresh pastes with an indeterminate moisture content (20). The published literature contains no reports of studies on fresh pastes deliberately maintained in a saturated condition.

Attempts to use the controlled atmosphere and temperature diffractometer for direct observation of the hydration of cement-water pastes met with numerous difficulties, as might be anticipated from earlier work (16). The most active ingredients at very early ages are present in such small quantity that identification of the hydration products is very difficult. The overlap of lines of the cement constituents is such that rates of hydration reactions cannot be readily estimated by observation of decreases in peak heights of individual compounds.

The present investigation is based on the observed similarity in hydration behavior between base mixtures and portland cement pastes, which indicates that the hydration reactions in the two systems are similar. It must be borne in mind, however, that the diffuseness of the diffraction patterns obtained from hydrated portland cement is definite evidence that the reaction products are structurally different from those of the base mixtures.

### Comparison of Base Mixture and Cement Hydration

The sequence of chemical reactions in the base mixtures, leading first to a high-sulfate form and then to a low-sulfate form of calcium sulfoaluminate hydrate, is identical with the sequence that has been postulated for early cement hydration reactions. Transformation from high- to low-sulfate form of sulfoaluminate phase is generally agreed on (18, pp. 205-208; 22). Special mention must be made here of the work of Turriziani (16) who failed to find the low-sulfate form in fractionated pastes that had undergone considerable manipulation before examination with the result that the  $\text{SO}_3$  and  $\text{R}_2\text{O}_3$  were no longer together in the same fractions. He reports lines in the range  $10.7^\circ$  to  $11^\circ$ , which could be interpreted as calcium hemicalcium aluminate hydrate resulting from carbonation, or possibly a dehydrated form of the low-sulfate form of calcium sulfoaluminate hydrate (17) which has been observed at spacings as low as the reported range.

The phase equilibrium studies of Jones (22) had indicated the possibility of forma-

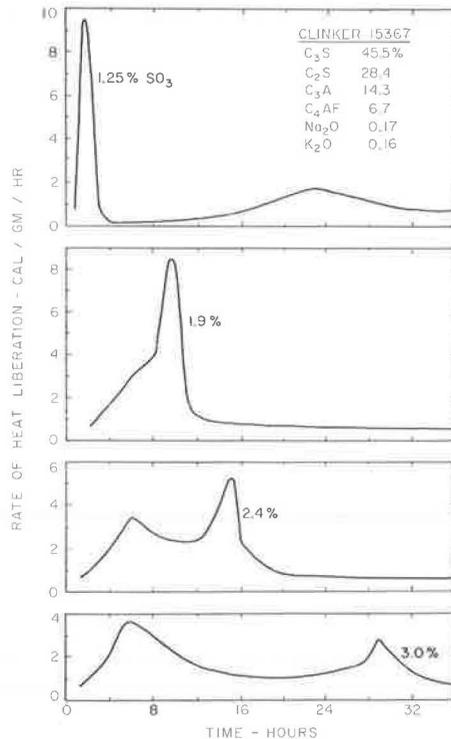


Figure 5. Increasing gypsum content delays final period of rapid cement hydration.

tion of solid solution. In addition, Steinour (23) had suggested the formation of a sulfate-free hydrate. The variations in gypsum content produce changes in reaction rate corresponding to the known retarding effect of gypsum on cement hydration. The effect of greater specific surface in accelerating the reactions also corresponds to well-known characteristics of cement hydration. In addition, the behavior of the sintered  $C_3A$  slabs corresponds precisely to a widely accepted mechanism for retardation of clinker hydration by gypsum which assumes an impermeable ettringite coating on the  $C_3A$  particles (24).

Further evidence of the similarity is provided by Figure 5 which has been reproduced from the earlier work of Lerch (2). These curves represent rates of heat evolution during hydration of a clinker ground with various quantities of gypsum to produce the indicated  $SO_3$  contents. The initial heats of hydration are not shown in the figure; only the second and, where they exist, the third cycles of increasing reaction rate are shown. The effect of  $SO_3$  content on the time of occurrence of the third cycle of increasing reaction rate in cement hydration can be unambiguously associated with the observed increases in duration of stage I hydration and the increases in rate of hydration of the base mixtures at the beginning of stage II.

The observed similarity between the hydration of the base mixtures and cement-water pastes can be readily explained on the basis that the calcium silicate phases of cement are relatively inert during the very early stages (25) and act only as sources of calcium hydroxide. The base mixtures thus contain most of the active components of fresh cement pastes.

It must be emphasized that the water-to-solids ratio of 0.4 used in the base mixtures provides considerably less water for hydration than is present in concrete at the earliest stages of hydration of cement. In the latter situation, all water present is available to the gypsum,  $C_3A$ , and ferrite phases because of the inertness of the calcium silicate phases. Thus, in a cement containing a total of 35 percent of the active components ( $C_3A$  + ferrite + gypsum), a water-cement ratio of 0.5 would yield a water-to-solids ratio of 1.43 for the active solids, until the rate of hydration of the  $C_3S$  becomes appreciable. The observed imbibition of water by the samples of base mixtures and the resulting expansion of the samples thus cannot be directly related to early volume changes in cement hydration or to the well-known expansion in water of cements with excess gypsum.

Studies on the effects of the other cement components on the hydration behavior of the base mixtures have led to further insight regarding the nature of the early cement hydration reactions. The results obtained on selected combinations of cement constituents have served to demonstrate clearly the role of tricalcium aluminate in the hydration of portland cement and to lay a foundation for the studies of the effects of admixtures and other applications.

#### Hydration of Ferrite Phase

Pastes have been monitored in which the  $C_3A$  of the base mixtures was partially or completely replaced by a ferrite phase. In these studies, the design of the mixtures was based on essentially the same principles that governed the design of the base mixtures. The existence had to be considered of a set of calcium ferrite and sulfoferrite hydrates completely analogous to the calcium aluminate and sulfoaluminate hydrates (16). Just as the  $Ca(OH)_2$  content of the base mixtures was determined on the basis of possible formation of  $C_4AH_{13}$ , so the calcium hydroxide content should, theoretically, have been increased to give the mole ratio,  $CaO/(Fe_2O_3 + Al_2O_3)$ , a value of 4. It was found, however, that such a degree of dilution of the other reactants was not necessary; the rates of reaction encountered were so low that the theoretically required quantities of lime proved to be excessive for the observation periods used. The mole ratios actually used varied from 2.5 to 3.5.

Hydration Rates.—Studies were made on modified base mixtures in which the  $C_3A$  was replaced by the compositions  $C_2F$ ,  $C_6AF_2$ ,  $C_4AF$ , or  $C_6A_2F$ , thus covering both end members,  $C_2F$  and  $C_6A_2F$ , of the aluminoferrite solid solution series, as well as materials representative of those found in cements. In all instances, the hydration rates of the modified base mixtures proved to be relatively low, even when the  $SO_3/(Al_2O_3 + Fe_2O_3)$  mole ratio was as low as  $\frac{1}{8}$ .

Further studies were made on these mixtures in slurries containing an excess of water and agitated continuously in plastic bottles on a rotating wheel. Although the excess water tends to speed hydration, the rates were still markedly lower than in the corresponding unmodified base mixtures.

In one test, a mixture of  $C_3A$  and a ferrite phase was tested. The molar composition was  $\frac{2}{3}C_3A + \frac{1}{3}C_4AF + Ca(OH)_2 + \frac{1}{3}CaSO_4 \cdot 2H_2O$ . After 17-days hydration in an excess of water, the diffraction pattern showed that considerable gypsum was still present and that stage II had not been initiated. Thus, not only did the ferrite hydrate much more slowly than the aluminate, but the presence of the ferrite phase actually retarded the normal stage I hydration reaction.

**Hydration Products.**—The hydration of mixtures containing the alumina-free phase, dicalcium ferrite, unlike that of the other mixtures, produced no observable reaction products even after 13-days hydration.

In all instances, the hydration behavior of the mixtures containing  $C_6AF_2$ ,  $C_4AF$ , or  $C_6A_2F$  corresponded to the three stages of base mixture hydration, but at the lower rates already indicated. Diffraction patterns of these mixtures are indistinguishable from those obtained at a corresponding stage in base mixture hydration, except for stage III, where the absorption of calcium hydroxide is not accompanied by the usual changes in the pattern in the 7.6 to 9.6 Å range. It has been established that the calcium ferrite hydrates have diffraction patterns almost identical with calcium aluminate hydrates (16). However, the presence of a red material in the hydrated mixtures in the present study indicates that some amorphous ferric hydroxide was formed. It has not been possible to determine at any particular stage the extent to which the observed crystalline hydrates contain ferric oxide as well as alumina. Over a period of weeks or months, the red color gradually fades. No change in diffraction pattern accompanies the color change. It is, therefore, reasonable to assume that the ferric hydroxide enters the crystalline phases present. However, with respect to ferrite hydration, the presence of the red ferric hydroxide indicates that simulation of cement hydration has not been as successful as in many other instances.

### Effect of Alkalies

Previous work has shown that the alkalies are released rapidly (18, p. 478) during cement hydration. They must thus be added to the list of the active constituents present during the very early hydration. The known great chemical activity of these constituents would point to a considerable effect from their release.

Replacement of water by sodium or potassium hydroxide solutions in the base mixtures resulted in an acceleration of all reactions without any discernible change in the nature of the reaction products. However, in portland cement hydration the alkali release is not instantaneous, so that these observations cannot be considered necessarily representative of the actual situation.

To provide a closer simulation of cement hydration, base mixtures were made with sodium calcium aluminate in place of the  $C_3A$ . Under these conditions the alkali had a slight accelerating effect on the rates of reaction without any change in the reaction products. This can be seen by comparing samples 1 and 3 of Table 3 with the results already discussed in Figures 1 and 2. At a specific surface of 2,100 sq cm/g (Blaine), the alkali-containing samples in Table 3 hydrate at least as fast as the alkali-free samples of the figures at 3,100 sq cm/g (Blaine) at the same  $SO_3/Al_2O_3$  mole ratios. The data in Table 3 also indicate the characteristic effect of changes in gypsum content.

An interesting result obtained with these mixtures containing sodium calcium aluminate has provided a basis for quantitative measurements. The mixtures were hydrated in an excess of water, and chemical analyses of the liquid phase were compared with X-ray

TABLE 3  
HYDRATION OF BASE MIXTURES  
WITH  $C_3A$  REPLACED BY SODIUM  
CALCIUM ALUMINATE<sup>a</sup>

Sample No.	$SO_3/Al_2O_3$ Mole Ratio	Hydration Time (hr)	
		Stage I	Stage II
1	0.25	2.5	0.8
2	0.50	18.5	8.5
3	0.75	55	7

<sup>a</sup>Sodium calcium aluminate with specific surface, 2,100 sq cm/g (Blaine).

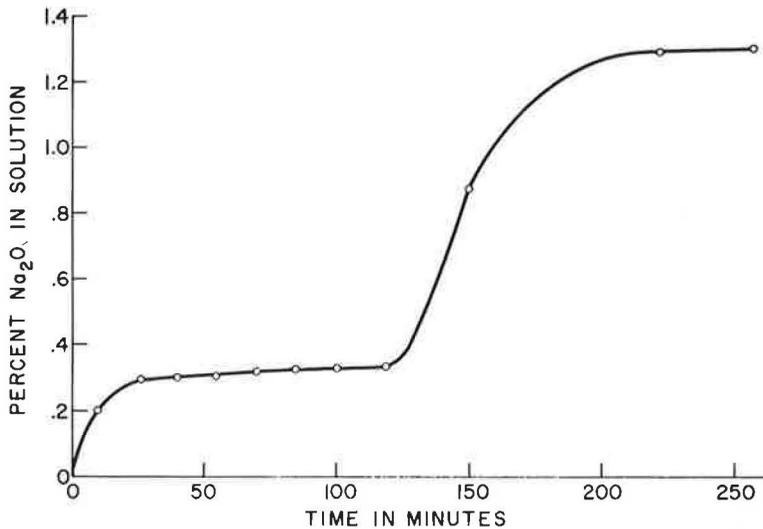


Figure 6 Release of  $\text{Na}_2\text{O}$  to liquid phase as quantitative measure of degree of hydration of sodium calcium aluminate.

patterns of the solid. The results indicated that the rate of release of the alkali into solution was equivalent to the rate of hydration of the aluminate phase itself. Figure 6 illustrates this phenomenon. In this particular instance the sodium calcium aluminate, calcium hydroxide, and gypsum were mixed in a mole ratio of 1:3:0.75. The water-to-solids ratio was about 6. The presence of the excess water allowed periodic withdrawals of the liquid phase for analysis. Stage I hydration is represented by an initial rapid release of alkali followed by a very slow release. Finally a very rapid reaction occurs, as indicated by the sharp rise in alkali concentration to a point indicative of complete hydration. This last stage of the reaction corresponds to stages II and III of base mixture hydration.

Attempts were made to use alkalis to increase the rate of ferrite hydration to a value comparable to that of  $\text{C}_3\text{A}$  in base mixtures. Slurry hydration tests of the various ferrites in mixtures with gypsum and calcium hydroxide in 3 percent sodium hydroxide solution demonstrated that the alkalis increased the hydration rate but not to the anticipated degree.

#### Effect of Tricalcium Silicate

Studies of the effect of tricalcium silicate on the reactions of the base mixtures demonstrated that the resulting hydration behavior more nearly approaches that of portland cement. In these studies the synthetic mixtures contained  $\text{C}_3\text{S}$  as a replacement for the calcium hydroxide of the base mixture.

Reaction Mixture Composition.—To determine compositions suitable for comparison with base mixtures, a study was made of the hydration stoichiometry of mixtures of various amounts of  $\text{C}_3\text{S}$  with tricalcium aluminate and gypsum in a mole ratio of  $\text{SO}_3/\text{Al}_2\text{O}_3$  of 0.25. A water-to-solids ratio of 0.4 was again found adequate for maintenance of an adequate diffraction surface.

Free calcium hydroxide was observed in the final reaction product from these mixtures when the quantity of  $\text{C}_3\text{S}$  originally present was increased from 0.50 to 0.75 mole per mole of alumina. The Appendix describes similar tests in which calcium hydroxide was used. It can be seen in Figure 7 that a line,  $g = 0.25$ , intersects the boundary between regions B and C at  $h = 0.75$ . This means that when the mole ratio  $\text{SO}_3/\text{Al}_2\text{O}_3$  is 0.25, formation of calcium hydroxide occurs only when the  $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$  mole ratio is greater than 0.75. The experimental result indicates that  $\text{C}_3\text{S}$  releases 1.0 to 1.5

mole lime during early hydration and that suitable comparisons with base mixtures can be obtained by replacement of calcium hydroxide by at least 0.75 mole  $C_3S$  per mole  $Ca(OH)_2$ . In practice, an equimolar quantity was usually used.

**Stage I Hydration.**—Stage I hydration was somewhat accelerated when  $C_3S$  replaced calcium hydroxide in the base mixtures. This effect may be simply a result of the added water per unit  $C_3A$  during initial hydration or may also be an effect of the initial absence of calcium hydroxide. A physical setting (stiffening) resembling that of cement occurred during stage I hydration but did not affect the nature of the ettringite-producing hydration reaction.

**Later Hydration.**—The presence of tricalcium silicate produced marked changes in stages II and III hydration. The setting of the pastes restrained markedly the imbibition of water and the resulting expansion. There was a corresponding decrease in rates of reaction. Finally, it was found that the reaction products were relatively poorly crystallized.

Figure 8 shows the effects on reaction rates and products. Here a comparison is made between a base mixture and two pastes in which the calcium hydroxide of the base mixture was replaced by increasing amounts of  $C_3S$ . The patterns represent the hydration states at 24 hr. All three pastes became somewhat carbonated during the monitoring, but the essential features are clearly shown. In the interpretation of the patterns, consideration must be given to the lower  $C_3A$  and gypsum contents in the  $C_3S$ -containing compositions.

The retarding effect of  $C_3S$  on stage II hydration can be seen from the slight  $15.7^\circ$  ettringite line in the bottom pattern, which represents a paste in which 3 moles of  $C_3S$  replaced a mole of  $Ca(OH)_2$ . The relatively low intensities of the  $C_3A$  and  $Ca(OH)_2$  lines in the top pattern, for the base mixture, indicate that stage III hydration is well under way. The middle pattern represents a stage III hydration condition less advanced than that for the top pattern, as shown particularly by the intense peak for the as-yet-unhydrated tricalcium aluminate.

Comparison of the patterns for the 7.6 to 9.6 A material in Figure 8 shows decreasing peak height and increasing line broadening as the  $C_3S$  content increases. This phase thus becomes progressively less well crystallized as the  $C_3S$  content increases and approaches the state occurring in cement. The effect is especially clear in the second-order diffractions at  $20^\circ$  to  $23^\circ$ .

For comparison, Figure 9 shows a pattern of a Type I cement containing 13.2 percent  $C_3A$  after 24-hr hydration. The essential features are seen to be present, even though the  $C_3A$  content is lower than in the bottom chart of Figure 8 and additional peaks for other anhydrous clinker components are present.

A closely related effect of the  $C_3S$  shown in Figure 8 is the absence of  $C_4AH_{19}$  in the hydration product from mixtures with low gypsum contents. Various auxiliary experiments in which both the gypsum and  $C_3S$  contents have been varied show that the excess of  $C_3A$  over that required for production of the 7.6 to 9.6 A material hydrates without producing a distinctive diffraction pattern. In the absence of gypsum, the effect shown in Figure 8 is accentuated to a point where no macrocrystalline material can be detected and it may be assumed that the hydration product enters the hydrous calcium silicate gel. This effect does not invalidate the reasoning on  $C_3S$  reaction mixture composition unless a mole of alumina carries more than 3 moles of lime into the gel.

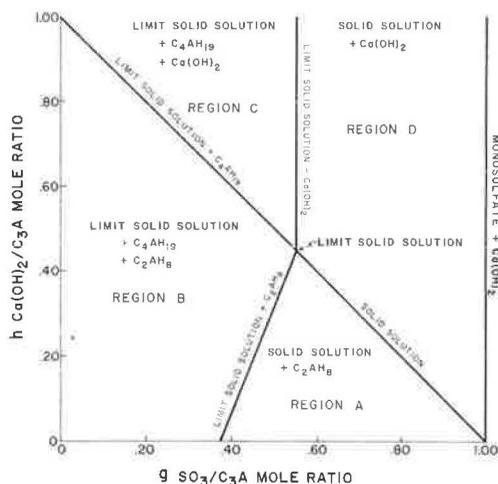


Figure 7. Nature of final hydration products of reaction mixtures containing  $C_3A$  varies with composition range. Final solid phases obtained from the hydration of  $C_3A$  depend on  $Ca(OH)_2$  and gypsum content of reaction mixture.

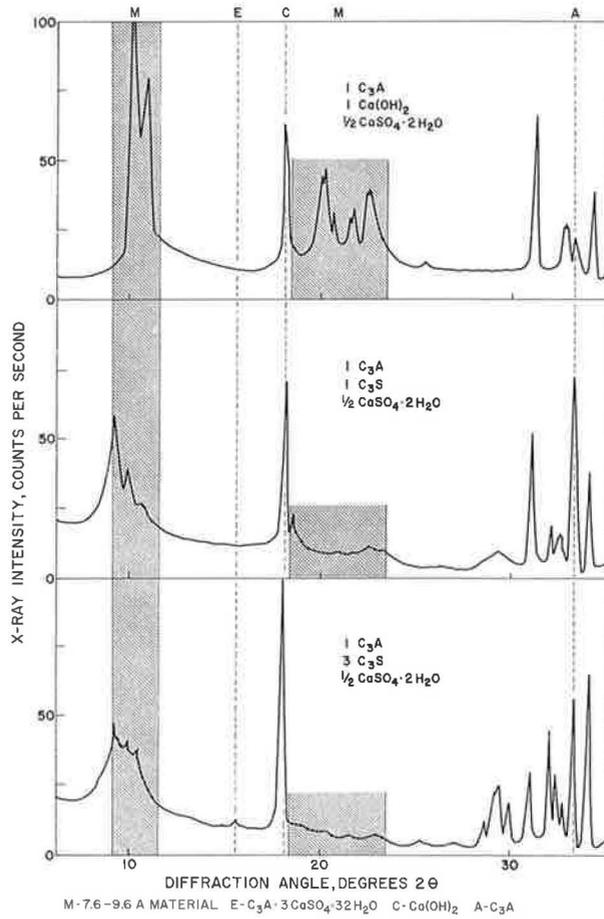


Figure 8. Replacement of calcium hydroxide by increasing amounts of  $C_3S$  retards hydration of base mixture and causes formation of poorly crystallized products.

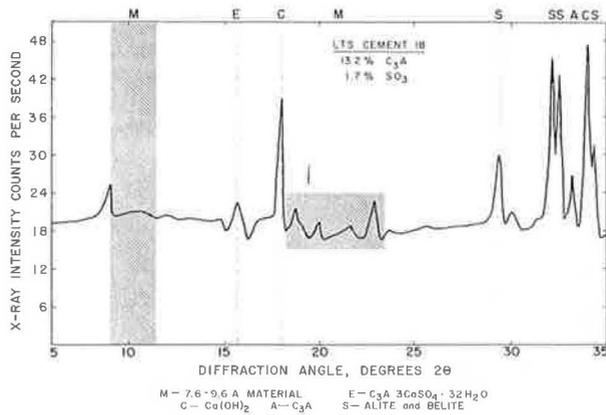


Figure 9. High  $C_3S$  Type I cement 24-hr diffraction pattern shows features illustrated in Figure 8 as modified by lower  $C_3A$  content and presence of additional clinker residues.

These results establish the relationship between the hydration behavior of portland cement and that of the base mixtures. They further provide an indication of the stoichiometry of early cement hydration reactions.

**Volume Change.**—The restraining effect of  $C_3S$  was investigated by use of the osmotic cell dilatometers. In this series of tests, the high  $C_3S$  contents used required a reduction of the water-to-solids ratio to 0.25 for formation of a paste of suitable consistency. The quantity of water per unit  $C_3A$  in the compositions is significantly greater than in base mixtures, so that smaller expansion was expected. For a mixture with 77 percent  $C_3S$  and a mole ratio  $SO_3/Al_2O_3$  of  $1/8$ , Figure 10 shows that a relatively slight expansion occurred. Addition of gypsum to increase the mole ratio  $SO_3/Al_2O_3$  to  $3/4$  reduced the  $C_3S$  content to 71 percent and resulted in a significant expansion. For the same  $SO_3/Al_2O_3$  ratio, addition of sufficient  $C_3S$  to raise its content to 83 percent produced the marked restraint shown. The expansion continues during the entire hydration process. Because the increase in  $C_3S$  content is accompanied by a corresponding decrease in  $C_3A$ , there appears to be some critical relationship between these quantities and the gypsum content which determines whether excessive expansions can occur.

**Effect of Other Cement Constituents.**—The effect of  $C_3S$  on hydration of base mixtures containing alkali is similar to that discussed previously. Further details of the behavior of this combination of materials will be considered in a later section on lignosulfonate admixtures.

In sulfate-free mixtures of  $C_3S$  and  $C_4AF$ , hydration of the ferrite phase retarded hydration of the  $C_3S$ . This result is a confirmation that the observed delay in  $C_3S$  hydration of undersulfated cements can be attributed to hydration of the ferrite phase (2).

**Conclusions.**—The early hydration of portland cement resembles closely the hydration behavior of base mixtures up to the time at which the cement sets. Setting, produced by hydration of the tricalcium silicate, retards further hydration of the tricalcium aluminate. The presence of the hydrous calcium silicate gel in hydrated cement causes a change in the stage III hydration reaction. The excess of  $C_3A$  over the quantity that can enter the sulfate-containing crystalline phase hydrates to become part of the gel rather than forming a crystalline  $C_4AH_{19}$  as in base mixture hydration.

## EFFECTS OF CHEMICAL ADMIXTURES

The work described previously has yielded detailed information on the chemical reactions occurring in portland cement hydration during the period before setting and also on the role of tricalcium aluminate during the entire cement hydration process. The results obtained have been directly applied to clarification and solution of problems of practical interest arising from unusual hydration behavior of cement or from hydration under unusual conditions. Many of the applications provided additional confirmation of the conclusions already described and, in some instances, provided data that were used in arriving at these conclusions.

The present section deals specifically with the effects of chemical admixtures on the early chemical reactions and the interpretation of admixture activity in terms of the observed effects. Only relatively pure chemicals were used as additives in these initial studies to simplify interpretation. The techniques developed and the results obtained appear readily applicable to more complex situations.

### Calcium Chloride

Though calcium chloride is known to form a complex hydrate with tricalcium aluminate, previous work (25) has indicated that this admixture has little effect on  $C_3A$  hydration reactions and that the observed acceleration of set and of strength development in cement paste or concrete results from an increase in the rate of

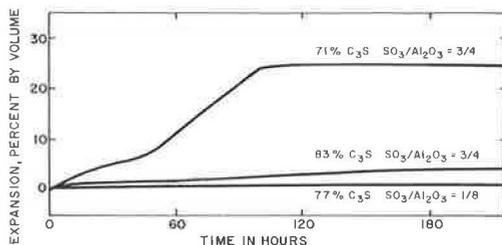


Figure 10. Water imbibition and resultant expansion at high  $C_3S$  contents.

TABLE 4  
EFFECT OF DELAYED ADDITION  
OF SUCROSE<sup>a</sup>

Sample No.	Additive (%)	Hydration Time (hr)	
		Stage I	Stage II
1	—	17	3
2	0.7	1.5	> 288
3	0.7 <sup>b</sup>	60	>> 264

<sup>a</sup>Base mixture  $\text{SO}_3/\text{Al}_2\text{O}_3$  mole ratio of 0.5, water-to-solids ratio of 2.0.

<sup>b</sup>Initially, 75 percent water added; sucrose dissolved in remainder of water and added after 1 min.

$\text{C}_3\text{S}$  hydration. These results are supported by the present study. An addition of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  to a base mixture, in the amount of 10 percent by weight of  $\text{C}_3\text{A}$  and corresponding to a 1 percent addition to a cement containing 10 percent  $\text{C}_3\text{A}$ , produced only a slight retardation of the hydration reactions.

### Sucrose

It is well known that sugar (sucrose) is an extremely effective retarder of the setting of portland cement pastes, although an initial rapid stiffening may occur (18, p. 253). The studies described here were undertaken primarily because of these properties and also because of the availability of the material as a pure chemical compound.

The initial effect observed in base mixtures containing sucrose was a very rapid acceleration of the reaction between the gypsum and the  $\text{C}_3\text{A}$  phase. A large ettringite peak was observed in the diffraction pattern at the earliest age of observation. Auxiliary studies established the reason for this behavior. The solid  $\text{C}_3\text{A}$  sorbs sucrose to produce a surface that does not permit the formation of the characteristically thin and relatively impermeable layer of ettringite. Thus, the reaction with gypsum could proceed to a greater degree before sufficient ettringite was produced to cause the usual retarding effect. No evidence of formation of unusual solid phases was observed. Further, the initial stiffening occurred in portland cement pastes containing sugar at very low water-cement ratios. Under these conditions the ettringite formed must act as a binder to stiffen the paste.

In demonstrating the effect of the sugar, it was found that one gram of  $\text{C}_3\text{A}$  could remove 99 percent of the sugar from 5 cc of 1 percent sucrose solution within 7 min. The presence of gypsum or calcium hydroxide did not interfere with this process. If  $\text{C}_3\text{A}$  was allowed to hydrate for a minute or two before the sugar was added, sorption was much less, whether gypsum was present or not. Thus, very early reaction of the  $\text{C}_3\text{A}$  surface with water altered the capacity of the surface for sugar. The effect of the immediate sorption on the nature of the ettringite coating was demonstrated by hydration studies of base mixtures; delayed addition of the sugar did not cause the initial rapid reaction (Table 4). After the immediate accelerated hydration reaction, the further reaction with gypsum in stage I when sugar was added initially was somewhat retarded and the subsequent reactions of stages II and III were greatly retarded. The decline in intensity of the  $\text{C}_3\text{A}$  pattern was exceedingly slow.

Subsequent experiments confirmed that the primary effect of sucrose in the hydration of cement is a great retardation of the rate of hydration of tricalcium silicate.

### Lignosulfonate

Extensive studies have been made on lignosulfonate admixtures as an example of a widely used water-reducing and set-retarding admixture readily available free of other components that may be present in commercial formulations. Much information has been collected on the effects of lignosulfonates on hydration of the various cement components and on the effects of various cement components on the activities of the admixture.

Experiments on removal of a calcium lignosulfonate from solution show that  $\text{C}_3\text{A}$  rapidly sorbs considerable quantities, whereas  $\text{C}_3\text{S}$  and  $\text{C}_4\text{AF}$  sorb very little. Similar results have recently been reported by other investigators (26). It might thus be expected that the activities of sucrose and lignosulfonate would be very similar. This conclusion, however, proved to be false.

The incorporation of calcium lignosulfonate in base mixtures resulted in very little, if any, acceleration of the initial reaction between tricalcium aluminate and gypsum. Marked retardation of all hydration stages occurred, particularly in stages II and III. Figure 11 shows the effect on a system containing alkali, i. e., the effect of 3 percent sodium lignosulfonate, based on total solids, on the release of soda from the composi-

tion previously shown in Figure 6, the data from which are also shown for comparison. The effect of the admixture here is very similar to the retarding effect on base mixtures without alkali.

Studies with pats of  $C_3S$  and water revealed that additions of small quantities of eight different lignosulfonate admixtures could retard setting indefinitely, even though some of these contained appreciable quantities of  $CaCl_2$ . Diffraction patterns of these pats show no indication of calcium hydroxide formation. In the presence of alkalis, a delayed set ultimately occurs, and the effect of the admixture approaches that observed in cements. Apparently, the alkali reacts chemically with the admixture to destroy its hydration-inhibiting effect.

The behavior of lignosulfonates in more complex mixtures differs markedly from the effects on hydration of base mixtures or on  $C_3S$  alone. Table 5 gives the results of a series of tests in which sodium calcium aluminate replaced the  $C_3A$  in the base mixture to provide a source of alkali and to facilitate measurement of the degree of hydration by chemical analysis. The sodium lignosulfonate solution used is identical to "Admixture Solution QA" (27). Tests were carried out in the absence of a source of lime and also with  $Ca(OH)_2$  or  $C_3S$  as lime sources. Excess water was used in these mixtures as in the tests shown in Figures 6 and 11. All mixtures contained sodium calcium aluminate and gypsum in a mole ratio of  $SO_3/Al_2O_3$  of 0.5. The liquid phase, water or 0.5 percent sodium lignosulfonate solution, was added in a proportion of 5.8 ml/g sodium calcium aluminate. As a source of lime, 1 mole calcium hydroxide or  $C_3S$  per mole alumina was added. Samples of the liquid phase were analyzed after 10 min and after 17 hr of hydration.

Mixtures 1, 2 and 3 were control samples to show behavior in the absence of the admixture. Conclusions drawn earlier could be quantitatively confirmed in this series of tests. Comparison of mixtures 1 and 2 demonstrates the retarding effect of calcium hydroxide. Mixture 3 shows the early retarding effect of  $C_3S$  as a source of lime and the later retarding effect caused by the restraint of water imbibition resulting from the setting of  $C_3S$ .

The remaining mixtures in the table indicate that the effect of the admixture depends on a variety of factors, especially the ability of the admixture to inhibit the release of lime from  $C_3S$  and the effect of agitation. Comparison of mixtures 2 and 4 indicates the early retarding effect of the admixture and the marked retarding effect at longer hydration times. Substitution of tricalcium silicate for calcium hydroxide resulted in a very early acceleration of stage I hydration that could be further accelerated by agitation, as seen in mixtures 5 and 6. This behavior is very similar to the early effect of sucrose on hydration of base mixtures

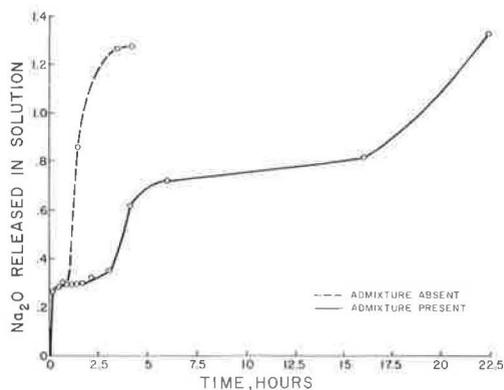


Figure 11. Delayed release of  $Na_2O$  to liquid phase showing retarding effect of lignosulfonate admixture on hydration of sodium calcium aluminate.

TABLE 5  
EFFECT OF LIGNOSULFONATE ON HYDRATION OF SYNTHETIC MIXTURES OF CEMENT COMPONENTS<sup>a</sup>

Mixture No.	Source of Lime	Admixture Present	Analysis of Liquid Phase (%)			
			At 10 Min.		At 17 Hr.	
			$Na_2O$	$SO_3$	$Na_2O$	$SO_3$
1	None	No	0.48	0.19	—	—
2	$Ca(OH)_2$	No	0.27	0.26	0.94	0.02
3	$C_3S$	No	0.27	0.34 <sup>b</sup>	0.87	0.01
4	$Ca(OH)_2$	Yes	0.23	0.20	0.37	0.34
5	$C_3S$	Yes	0.38	0.46 <sup>b</sup>	1.13	0.03
6 <sup>c</sup>	$C_3S$	Yes	0.46	0.09	—	—
7	$C_3S + 0.5$ mole CaO	Yes	0.28	0.21	0.32	0.24

<sup>a</sup> Equimolar mixtures of sodium calcium aluminate and source of lime with enough gypsum to give  $SO_3/Al_2O_3$  ratio of 0.5.

<sup>b</sup> Supersaturated with respect to gypsum (27).

<sup>c</sup> Mixture 6 agitated during first 10 min.

but apparently can occur here only in the virtual absence of calcium hydroxide in solution. The admixture inhibits release of calcium hydroxide from the tricalcium silicate; the highly alkaline solution decreases solubility of any  $\text{Ca}(\text{OH})_2$  present. Calorimetric data confirm that the observed behavior occurs also in cement, as indicated by significant increases in heats of immediate hydration when set-retarding admixtures are present. Mixture 7 indicates that inclusion of calcium oxide in the composition restores the retarded behavior of mixture 4.

The temperature of mixture 6 rose considerably during agitation. The sulfate content of the solution indicates that stage I hydration was completed in 10 min. Apparently, agitation caused exposure of fresh tricalcium aluminate surface to the liquid phase.

As indicated also in a recent report (28), delayed addition of the admixture resulted in decreased sorption with elimination of early acceleration. The resultant greater concentration of the admixture produced a greater retardation of all hydration stages than that produced by immediate addition.

## APPLICATIONS

It is well known that changes in cement composition or the use of chemical admixtures can influence the properties of fresh mortar or concrete. Whereas many factors may contribute to these effects, there are a number of instances where a great similarity exists between the observed changes in concrete and corresponding changes in paste behavior. In these instances it can safely be assumed that the behavior of the cement paste is the primary factor.

### False Set and Other Rheological Anomalies in Fresh Concrete

Results obtained in these studies have been especially useful in analyses of problems involving abnormal rheological behavior of fresh cement paste, mortar or concrete. Some applications to analysis are described in this section. These applications require primarily a knowledge of stage I hydration of  $\text{C}_3\text{A}$  because this stage of hydration continues throughout the period of interest for a normally retarded cement. Stage II hydration normally begins during or after setting.

The variations in the early hydration reactions encountered in specific applications depend not only on the content and activity of the  $\text{C}_3\text{A}$  in the cement, but also on the amount and state of the calcium sulfate. For clarity in the ensuing descriptions, a brief summary of existing information regarding the state and effect of the calcium sulfate during early cement hydration is first presented. For this purpose, the point of view of Gaskin and McGowan (29) has been adopted. The work at these Laboratories on false set (30) and related phenomena have led to the conclusion that, of all the points of view expressed in the literature, this one is outstanding in providing the most satisfactory explanation of the observed facts.

The state of calcium sulfate in a cement depends on both the time and temperature of grinding of the clinker with the gypsum. The resulting product in all cements is characterized not only by some degree of dehydration of the gypsum but also by some degree of disorganization of the crystal structure of any remaining fully hydrated gypsum. The disorganization, as well as the more commonly recognized dehydration, causes an increase in solubility. Thus, the early formation of a supersaturated solution of calcium sulfate is the rule, rather than the exception, during cement hydration.

The time of precipitation of well-crystallized gypsum from the supersaturated solution depends on availability or formation of well-crystallized gypsum crystals as nuclei. For low grinding temperatures and short grinding periods, the fragments of the original gypsum crystals cause sufficiently early precipitation, usually during the mixing of the concrete, and no interference with concrete placing operations occurs. With high grinding temperatures and long grinding periods, no suitable nuclei remain, and the delay in precipitation usually causes a plaster set (false set) after the mixing period.

This background will now be applied, in combination with the results of the X-ray study, to some problems of practical interest:

1. A particular high-capacity ready-mix plant using a 1-min mixing time in the central mixer experienced difficulty apparently caused by variations in cement. The cement usually produced normal concrete, but sometimes stiffened and produced cement balls that prevented proper discharge of concrete from the mixer. X-ray diffraction patterns revealed the gypsum in the "faulty" cement to be relatively well crystallized, whereas that in the "well-behaved" cement was thoroughly disorganized and highly dehydrated. Tests showed the latter cement to be, in fact, false setting, although not causing difficulty under the particular conditions of use. The observed difficulty with the "faulty" cement could thus be attributed to an early precipitation of gypsum at the end of the short mixing time. With the "well-behaved" false-setting cement, the gypsum precipitation occurred at a later time, while the concrete was in the truck mixers, and created no problem. This line of reasoning proved, indeed, to be true.

2. Various instances (31, 32, 33) have been reported of early stiffening of concretes containing normally setting cement when set-retarding and water-reducing admixtures have been used. The present studies indicate these effects to be attributable to two distinct causes, namely, acceleration of stage I hydration of  $C_3A$  and retardation of the precipitation of gypsum. Acceleration of stage I hydration can produce an early stiffening by increasing the quantity of hydration product, as was shown earlier to be an effect of sucrose; the resulting depletion of gypsum, in cements with relatively low  $SO_3/Al_2O_3$  ratios, could cause a flash set. It might be expected that in instances of flash set this stiffening would not be reduced by further agitation and that an increase in sulfate content of the cement (31) would prevent the stiffening. Admixtures may also produce early stiffening by inducing false set. Auxiliary experiments in the present studies have shown that calcium lignosulfonate retards the setting of plaster. Thus, this admixture can, by delay of precipitation of gypsum, induce false set in an otherwise normally setting cement. This type of early stiffening can be reduced by further agitation, just as in other instances of false set. This retardation may be a factor in the reported variations in slump loss resulting from the use of chemical admixtures and may even contribute to plastic shrinkage cracking (34).

3. A case of anomalously slow setting concrete in a tunnel lining was recently described in the literature (27). This concrete, containing a lignosulfonate admixture, remained plastic for hours. The addition of gypsum to the cement resulted in a normally setting concrete. That report provided much of the impetus for the studies on alkalis described earlier. It was because of this interest that the tests reported in Table 5 were made with "Admixture Solution QA." From the results obtained in these studies as described in the following paragraphs, a complete explanation of the various observed effects could be obtained, and a major conclusion could be drawn that the observed excessive retardation resulted from a combination of factors and a chain of events that ultimately caused a lack of sufficient alkali release during the early hydration of the cement.

The cement used was a Type II, low alkali cement. Different shipments of this cement varied slightly in  $SO_3$  content, but in all cases met specifications and exhibited normal setting behavior in the absence of the admixture. The excessive retardation occurred only when the admixture was used with cements of relatively low  $SO_3$  content. Addition of gypsum to the cement restored normal behavior. For the excessively retarded cement-admixture combinations, a previous commentary (31) has noted the early consumption of  $C_3A$ , sulfate, and admixture, which the present studies show to be an adsorption of the admixture on the  $C_3A$ , accompanied by an acceleration of stage I hydration as demonstrated in Table 5. The observed rapid stiffening at 10 min in time-of-set tests and the relatively high initial Proctor needle penetration resistance for mortars containing the abnormally behaving combinations of materials point to an initially accelerated stage I hydration producing an early stiffening accentuated by low  $SO_3$  content.

The remaining hydration of the cement can then be considered typical of an under-sulfated, low  $C_3A$ , low alkali cement. Lerch (2) has shown that, in hydration of cements of this type, there is a high and very early heat release (as for flash set) followed by considerable delay in setting and in further appreciable rate of heat evolution. It is thus not surprising that an unusually long time of set would be observed in the present

instance. However, Lerch's results did not indicate (2, Table 14) an extreme retardation of the type observed.

For an understanding of the extreme retarding effect of the admixture, the chemical composition of the cement must be considered. Chemical analysis showed the alkalis to be present as 0.47 percent soda and 0.03 percent potash. The release of soda, the major alkali, would be expected to follow a course such as that shown in Figure 10, where a considerable delay in alkali release during stage II is evident when a lignosulfonate admixture is present.  $C_3S$  will not set in the presence of a lignosulfonate unless some minimum quantity of alkali is present. The alkali level during the delay in stage II was probably too low to permit setting of the  $C_3S$ . Finally, this line of reasoning provides for the corrective action of additional gypsum. With added gypsum, stage I hydration is somewhat slower and consumes more of the aluminate phase, thus, releasing more alkali before the delayed stage II reaction is initiated. At a sufficiently high alkali level, normal setting of the cement during stage I hydration should occur, even in the presence of the admixture.

4. From the work done on sucrose, it was reasoned that sufficient acceleration of stage I hydration would prevent false set by an increase in the rate of removal of sulfate ion from solution. Because sucrose has no effect on the setting time of plaster (35), this conclusion could be investigated experimentally. Table 6 gives results obtained from the addition of sucrose to a false-setting cement. The results show that as little as 0.05 percent sucrose could prevent the premature stiffening of the paste. It was also found (Table 7) that sucrose was ineffective in preventing false set associated with aeration of the cement. If, as has been postulated, this aeration produces an inactivation of the  $C_3A$  surface, it can be concluded that sucrose is ineffective in reactivating the aerated surface.

#### "Optimum" $SO_3$ Content of Cement

Lerch's work was primarily directed toward evaluation of specification limits for  $SO_3$  content of cement. Although the present studies provide a background for an understanding of many of the calorimetric results, progress has not yet reached the point where the observed effects on the ultimate properties of concrete can be understood. Some interesting conclusions can, however, be drawn from published results of the extraction test, ASTM Test Method C 265.

The marked decreases in sulfate ion concentration in the liquid phase occurring between 18 and 24 hr at the optimum gypsum content (36) must correspond to the termination of stage I hydration in that time interval. For pastes with gypsum contents at or below optimum, the X-ray and calorimetric evidence indicates that stage II and most of stage III hydration occur in 4 to 8 hr. Thus, the bulk of  $C_3A$  hydration at these gypsum contents occurs within approximately 32 hr. Under these conditions, very little expansive tendency remains during later hydration. About 32 hr is the latest age at which the paste structure can accommodate the expansive forces existing at the water contents used. The increased expansion in water at  $SO_3$  contents higher than optimum can be attributed to continued hydration

TABLE 6  
EFFECT OF SUCROSE ON FALSE-SETTING CEMENT<sup>a</sup>

Sample No.	Sucrose (%)	Penetration (mm)					
		Init.	5 Min	8 Min	11 Min	15 Min	Remix
1	—	50 +	50 +	4	3	—	50 +
2	0.025	50 +	50 +	50 +	45	20 <sup>b</sup>	50 +
3	0.05	50 +	50 +	50 +	50	45 <sup>b</sup>	50 +
4	0.1	50 +	50 +	50 +	50 +	50 +	50 +

<sup>a</sup>Cement, Lot 19737, used with indicated quantity of sugar in ASTM Method C 359-56T.

<sup>b</sup>Because of possibility of a delayed false set, test was extended beyond time specified in test method.

TABLE 7  
EFFECT OF SUCROSE ON AERATED FALSE-SETTING CEMENT<sup>a</sup>

Sample No.	Sucrose (%)	Penetration (mm)				
		Init.	5 Min	8 Min	11 Min	Remix
1	—	14	3	1	1	50 +
2	0.025	50 +	50 +	15	3	50 +
3	0.1	50 +	50 +	4	1	50 +

<sup>a</sup>Tests reported in Table 6 repeated after cement had been aerated for 24 hr at 74° F and 50 percent RH.

as indicated in the earlier discussion of Figure 10. This expansion may also account for the decrease in strength at higher  $\text{SO}_3$  contents at later ages, but does not account for the optimum at 1 day.

### Expanding Cements

It was pointed out earlier that the observed imbibition of water with resultant swelling of the base mixtures during stage I hydration could not be directly correlated with volume changes during portland cement hydration. It was also pointed out that in pastes containing sufficient tricalcium silicate, the expansive forces could be restrained. However, a large increase in the proportion of aluminate and sulfate phases, relative to the tricalcium silicate content, could well result in pastes which swell during hydration, as shown in Figure 10. This situation appears to be the basis of shrinkage-compensating or expanding cements. The various formulations studied for these materials have all depended on attainment of this effect by addition to portland cement clinker of admixtures containing calcium aluminates and calcium sulfate, or by blending such materials with portland cement.

### SUMMARY AND CONCLUSIONS

X-ray diffraction studies of the reactions occurring in mixtures of tricalcium aluminate, calcium hydroxide, gypsum, and water have demonstrated that, for compositions corresponding to the sulfate-to-alumina ratios found in portland cements, tricalcium aluminate hydration takes place in three successive stages when excess lime is present:

- I. Some of the tricalcium aluminate reacts with gypsum and water to produce the high-sulfate form of calcium sulfoaluminate hydrate (ettringite).
- II. More of the tricalcium aluminate reacts with the high-sulfate form of calcium sulfoaluminate hydrate and with water to produce the low-sulfate form of calcium sulfoaluminate hydrate.
- III. Still more of the tricalcium aluminate reacts with calcium hydroxide and the low-sulfate form of calcium sulfoaluminate hydrate to form a solid solution. The remainder of the tricalcium aluminate reacts with calcium hydroxide and water to form a tetracalcium aluminate hydrate,  $\text{C}_4\text{AH}_{19}$ .

The effects of the initial solid mixture composition and of fineness correspond very closely to the effects of these same factors during paste hydration of portland cement. Diffraction studies of sintered tricalcium aluminate slabs hydrated in various media have demonstrated the retarding effect of the initially formed ettringite film. X-ray and dilatometer studies have demonstrated that under conditions of access to water, hydrating  $\text{C}_3\text{A}$  pastes undergo large increases in volume because of a tendency to imbibe quantities of water far in excess of the stoichiometric requirements of the hydration reactions.

The individual effects of other portland cement constituents on these hydration reactions have been investigated. Partial or total replacement of  $\text{C}_3\text{A}$  by a ferrite phase, although introducing numerous experimental difficulties, appears to produce a series of analogous reactions in which  $\text{Fe}_2\text{O}_3$  replaces  $\text{Al}_2\text{O}_3$ , occurring at a much slower rate. Addition of alkalis causes slight acceleration of the reactions. Replacement of calcium hydroxide by tricalcium silicate causes, as major effects, decreased crystallinity of the low-sulfate form of calcium sulfoaluminate hydrate and also absorption of excess  $\text{C}_3\text{A}$  by the hydrous calcium silicate gel, in place of formation of the sulfate-hydroxide solid solution. The setting of the  $\text{C}_3\text{S}$  causes retardation of hydration by providing restraint to the water imbibition observed when calcium hydroxide is used.

Study of hydration of combinations of the various constituents has led to a fairly complete picture of the early hydration reactions of portland cement and of the influence of various factors on these reactions.

The effects of a few well-known accelerating and retarding materials have been examined. In low concentrations, none of these materials affects the nature of the hydration reactions; only the rates are influenced. The effect of calcium chloride is almost

exclusively an acceleration of  $C_3S$  hydration. Materials that cause retardation of set, such as sucrose or lignosulfonates, can also produce a large initial acceleration of the hydration reactions. This acceleration may be caused by inhibition of lime release by the silicate phases or by increased reactivity of the  $C_3A$  with gypsum, resulting from the very high sorption of the additive in the  $C_3A$  surface. The early acceleration and high sorption can be avoided by delayed addition of the retarder; the retarding effect is then markedly increased.

Careful consideration has been given to various cases of anomalous rheological behavior during early hydration. Recent results of X-ray diffraction studies of the state of calcium sulfate in cement are summarized. Short mixing times for concretes made from cements with little gypsum dehydration can result in stiffening at time of discharge from the mixer. Retardation of plaster hydration by an admixture can induce false set in an otherwise normally setting cement. Initial admixture-induced acceleration of hydration can lead, in effect, to undersulfating of the cement during later hydration. In high or moderate  $C_3A$  cements, a condition resembling flash set can then occur; in low  $C_3A$ , low  $SO_3$  cements, abnormally long setting times may appear under these conditions. Lignosulfonates can retard the setting of  $C_3S$  indefinitely, but the effect is counteracted by the alkali released during hydration. In cements where the alkali is present predominantly as sodium calcium aluminate, admixture retardation of the hydration of this phase can result in abnormally low alkalinities which will cause marked increases in time of set.

Interpretation of earlier results obtained by ASTM C 265 indicates that the optimum gypsum content of a cement is that for which the formation of ettringite is complete between the ages of 18 and 24 hr. At higher gypsum contents, the moist-cured paste can no longer accommodate the expansive forces accompanying the reaction of ettringite formation so that higher expansions in water and lower strengths occur.

The observed water imbibition accompanying ettringite formation accounts for the behavior of shrinkage-compensating and expansive cements.

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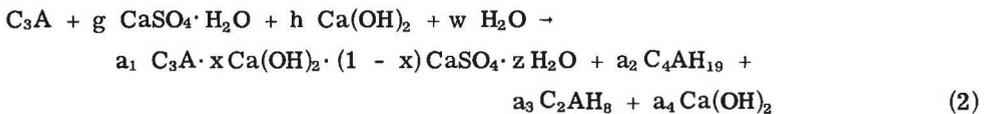
### Appendix

This Appendix contains a brief presentation of the final reaction products obtained in a variety of exploratory and auxiliary tests on relatively low-limed carbonate-free reaction mixtures containing  $\text{C}_3\text{A}$  and gypsum. Though the results obtained could be presented as a conventional phase diagram, the plot shown in Figure 7 is sufficient for present purposes. The abscissa,  $g$ , represents the  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio and the ordinate,  $h$ , the  $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$  ratio. The final hydration products in the four regions and along the four boundaries are shown. It has been assumed, for convenience, that the limiting solid solution contains 0.45 mole calcium hydroxide per mole alumina. This value actually may be as high as 0.5 or as low as 0.35.

The scheme shown is based in the following observations on hydration reactions:

1. The hydrate  $\text{C}_2\text{AH}_8$  cannot coexist with  $\text{Ca}(\text{OH})_2$  but will react to produce  $\text{C}_4\text{AH}_{19}$ ;
2. The hydrate  $\text{C}_4\text{AH}_{19}$  cannot coexist with the monosulfate or with a low-limed solid solution but will react to produce a higher limed solid solution; and
3. The cubic phase,  $\text{C}_3\text{AH}_6$ , never forms in the presence of sulfate.

On this basis the hydration stoichiometry may be represented by the following equation:



in which the coefficients have the values shown in Table 8 for the various regions of Figure 7.

TABLE 8\*  
COEFFICIENTS FOR EQUATION 2

Coefficient	Region			
	A	B	C	D
$a_1$	$\frac{1}{2}(1+g+h)$	$\frac{g}{1-x_0}$	$\frac{g}{1-x_0}$	1
$x$	$\frac{1-g+h}{1+g+h}$	$x_0$	$x_0$	$1-g$
$a_2$	0	$\frac{1}{2} \left[ 1+h-g \left( \frac{1+x_0}{1-x_0} \right) \right]$	$\frac{1-g-x_0}{1-x_0}$	0
$a_3$	$\frac{1}{2}(1-g-h)$	$\frac{1}{2}(1-g-h)$	0	0
$a_4$	0	0	$g+h-1$	$g+h-1$
$w$	$\frac{1}{2} [ 9+z+(z-9)h+(z-13)g ]$	$\frac{1}{4} [ 27+9h+g \left( \frac{z-19-5x_0}{1-x_0} \right) ]$	$18-g \left( \frac{20-2x_0-z}{1-x_0} \right)$	$z-2g$

\* $x_0$  is the upper limit of  $x$ .