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**TRANSPORTATION RESEARCH RECORD**  
**564**

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## **Concrete Admixtures**

**4 reports prepared for the 54th Annual Meeting  
of the Transportation Research Board**

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**TRANSPORTATION  
RESEARCH BOARD**

**NATIONAL RESEARCH  
COUNCIL**

**Washington, D. C., 1976**

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Transportation Research Record 564  
Price \$4.00  
Edited for TRB by Joan B. Silberman

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The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competence and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

The views expressed in this report are those of the authors and do not necessarily reflect the view of the committee, the Transportation Research Board, the National Academy of Sciences, or the sponsors of the project.

#### LIBRARY OF CONGRESS CATALOGING IN PUBLICATION DATA

National Research Council. Transportation Research Board.  
Concrete admixtures.

(Transportation research record; 564)

1. Concrete—Additives—Addresses, essays, lectures. 2. Cement—Additives—Addresses, essays, lectures. I. Title. II. Series.

TE7.H5 no. 564 [TP884.A3] 380.5'08s [666'.89]

ISBN 0-309-02474-9

76-14799

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## FOREWORD

This RECORD will be of interest to engineers and scientists concerned with the theories and performance of admixtures in cement and concrete. Young reviews the mechanism in which organic admixtures react with hydrating cement compounds. The hydration of the calcium silicates that are present in cement is postulated to be controlled by the nucleation and growth of calcium hydroxide. The influence of admixtures of the calcium hydroxide nuclei can inhibit crystal growth and prolong the induction period and thus result in retardation. Among the mechanisms with which organic retarders interact is hydrating tricalcium aluminate. The absorption of admixtures by hydration products of tricalcium aluminate controls the supply of admixtures to tricalcium silicate. This explains the enhanced retardation when the addition of admixture is delayed after the first addition of water.

Daugherty and Kowalewski found that the performance of 30 commercial and laboratory admixtures varied significantly as a function of temperature [70 to 110 F (21.1 to 43.3 C)] when added in normal and above normal concentrations to white and gray cement pastes. The best retarders were tested in concrete batches. Increased dosages would generally be necessary to produce the desired retardation at temperatures >90 F (32.2 C). The admixtures not only controlled the setting time but also influenced strength development and shrinkage. The time of mixing also influenced engineering properties.

Green reports the influence of a water-reducing admixture on the quick setting experienced in certain white cements that contain less than 1.6 percent  $SO_3$ . Although the cements set normally at normal temperatures without admixture, they set rapidly at both normal and high concrete temperatures when the admixture was present. In the quick-setting cements, the consumption of  $SO_3$  was accelerated in the presence of the admixture. This resulted in insufficient  $SO_3$  remaining in solution to properly control the hydration products of C3A.

Skalny and Odler review the use of admixtures in the production of low-porosity cement pastes and concretes. The high-strength, low-porosity cement paste is made by mixing finely ground clinker containing alkali or alkaline earth lignosulfonates with aggregate and water containing alkali carbonate. The use of low-porosity paste resulted in concretes and mortars with improved strength and excellent stability.

—Richard L. Berger



# REACTION MECHANISMS OF ORGANIC ADMIXTURES WITH HYDRATING CEMENT COMPOUNDS

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

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

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

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

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

## MECHANISMS OF RETARDATION

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

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

### Adsorption

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

### Insolubility

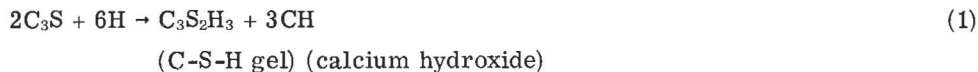
The formation of insoluble calcium salts that precipitate onto anhydrous surfaces was a hypothesis advanced by Suzuki and Nishi (1). An examination of Table 1 indicates that there is not a good correlation between solubility and retarding behavior for the carboxylic acids. This can be readily seen by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

### Complexing and Nucleation

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

## HYDRATION OF TRICALCIUM SILICATE

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



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

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

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

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

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

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

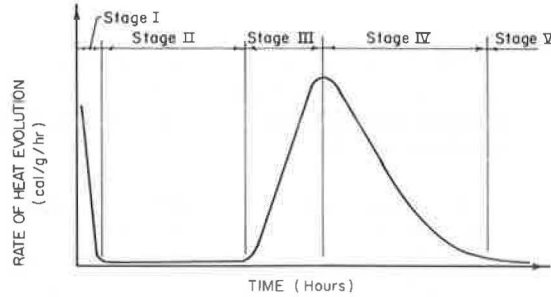
**Table 1. Solubilities and retarding power of calcium salts and carboxylic acids.**

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

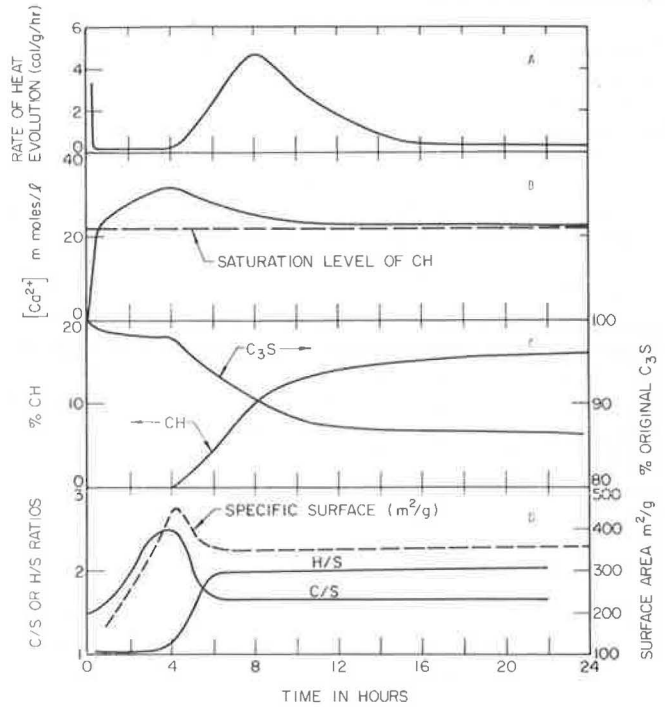
<sup>a</sup>(1, 2, 3).

<sup>b</sup>Accelerated set.

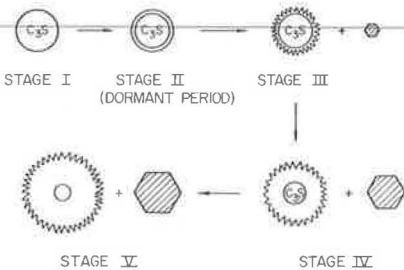
**Figure 1. Heat liberation curve for a hydrating C<sub>3</sub>S paste.**



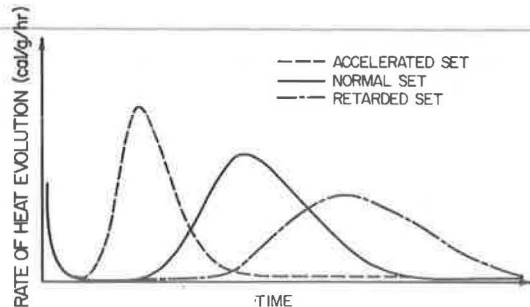
**Figure 2. Analysis of hydrating C<sub>3</sub>S paste.**



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



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



so effective in this regard because of superficial carbonation.

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

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

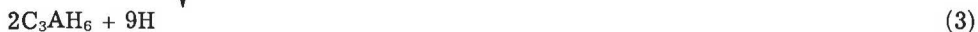
## HYDRATION OF TRICALCIUM ALUMINATE

### Without Sulfate

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



(hexagonal hydrates)



(cubic hydrate)

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

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

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

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

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

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

#### With Sulfate

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



(ettringite)

↓ +  $C_3A$

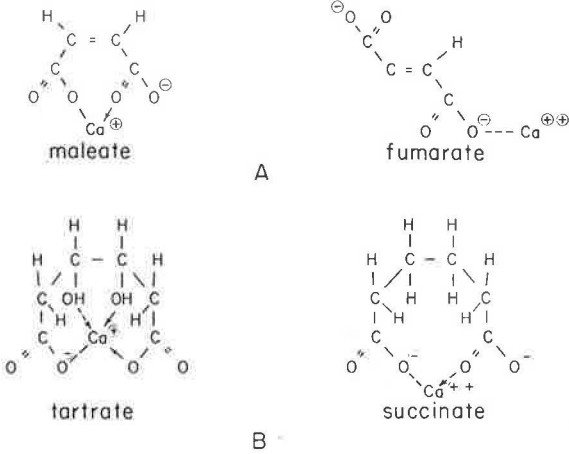


(monosulfate)

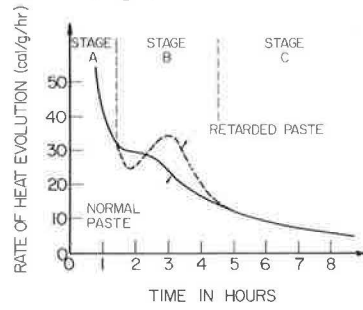
The conversion of ettringite to monosulfate (equation 5) occurs when all sulfate ions have been consumed and can be identified by calorimetry (main peak, Figure 9). The presence of set-retarding admixtures slows down the formation of ettringite and also changes the crystal morphology (14). The mechanism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

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

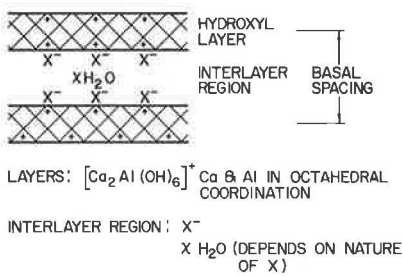
**Figure 5. Chelating properties of carboxylate ions with calcium ion.**



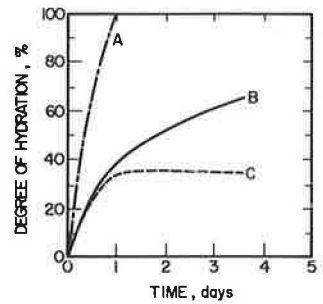
**Figure 6. Heat liberation curve for hydrating C<sub>3</sub>A pastes.**



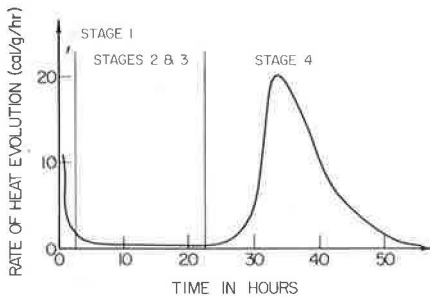
**Figure 7. Crystal structure of the hexagonal hydrates.**



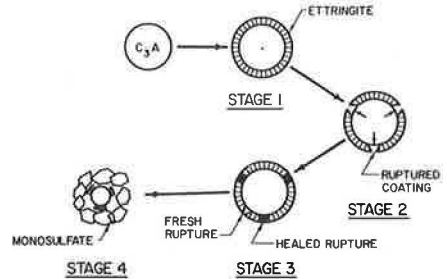
**Figure 8. Hydration kinetics of C<sub>3</sub>A pastes: (A) no retarder and complete conversion to C<sub>3</sub>AH<sub>6</sub>; (B) no retarder and partial conversion of the hexagonal hydrates; (C) retarder and no formation of C<sub>3</sub>AH<sub>6</sub>.**



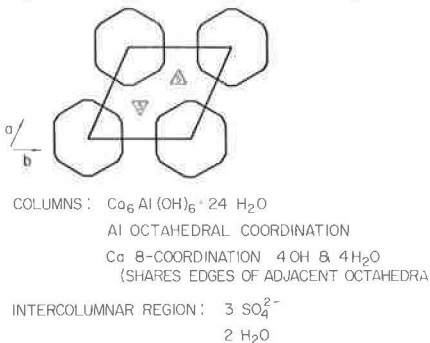
**Figure 9. Heat liberation curve for C<sub>3</sub>A pastes hydrated with gypsum.**



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



**Figure 11. Crystal structure of ettringite.**



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





## HYDRATION OF TRICALCIUM SILICATE WITH TRICALCIUM ALUMINATE

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

## CONCLUSIONS

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

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

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# USE OF ADMIXTURES IN CONCRETE PLACED AT HIGH TEMPERATURES

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The difficulty posed by the high temperatures of concrete batches in areas such as the southwest United States limits the use of concrete. High temperatures and subsequent hot materials are present in the concrete mixers and the concrete poured. This high-temperature condition shortens the setting time and workability time of the concrete. Ice, which can be added to the mixer to reduce the temperature, is costly and sometimes not readily available at the job site. It is possible to lengthen the setting time and workability time by the addition of water-reducing, set-retarding chemical admixtures. This study attempts to determine by cement paste and concrete studies the best commercial and laboratory type of admixtures available for white and gray cement concretes. Thirty admixtures at normal and above-normal concentrations were tried in the paste systems, and the best retarders were tested subsequently in concrete batches. The temperature range used in this study varied from 70 to 110 F (21.1 to 43.3 C).

•THE placement of high-strength structural white concrete at ambient temperatures greater than 90 F (32.2 C) is a major problem in the Southwest and possibly other regions of the United States. The additional water required, sometimes in the form of high-cost ice, for maintaining slump during the 90 min necessary for placement (ASTM C94) results in losses in concrete compressive strengths [16 and 26 percent at 28 and 90 days respectively in our control batch at 90 F (32.2 C)].

The hot-weather concreting practice (ACI 605-59) did not meet the needs of and was not practical for concrete mixing operations in the Southwest. The maximum placement temperature of 85 F (29.4 C) at the completion of the 90-min mixing time during the summer months is lower than the actual temperatures experienced. The normal high temperature of the day during the summer months is 110 F (43.3 C). Random afternoon field inspection of summer concreting operations indicates placement temperatures between 90 and 100 F (32.2 and 37.8 C).

This project was initiated because it was believed that the use of a retarding admixture that would be effective at high ambient temperatures would solve the problems of adequate workability and strength development of white structural concrete. It was also found that the results of this study were applicable to types 2 and 3 gray cement concretes.

## PROJECT SCOPE

### Testing White Concrete

Thirteen laboratory concrete batches proportioned to have 7 sacks or 658 lb/yd<sup>3</sup> (390.4 kg/m<sup>3</sup>) of white cement were used in the test program. The following cylinders, shrinkage bars, and flexure beams were cast (1 in. = 2.54 cm):

<u>Item</u>	<u>Number</u>	<u>Measurement (in.)</u>
Cylinders	560	4 × 8
Shrinkage bars	80	4 × 4 × 12
Flexure beams	100	2 × 2 × 12

The mix sequence involved 5 min at the start, at 45 min, and at 85 min of batch life or a total of 15 min of actual mixing during the 90-min period. The concrete between mixes remained at rest in the Essiz 9-ft<sup>3</sup> (0.26-m<sup>3</sup>) mixing drum. ASTM tests of slump, unit weight, Proctor penetration resistance, setting time, and air content of freshly mixed concrete by the pressure method were conducted on each batch. Temperatures were also measured. Tests for compressive strength, flexural strength, and volume change were performed on cured specimens at intervals from 1 day to 1 year.

### Admixture Testing

This program included tests on white cement pastes, mortars, and concretes at 70 F and at 90 to 110 F (21.1 C and 32.2 to 43.3 C) and involved 30 admixtures (Table 1). Thirteen commercially available admixtures from five companies were chosen as retarders. These have been documented as approved set-retarding or water-reducing admixtures at normal temperatures. The other 17 admixtures, designated as laboratory admixtures, were selected by us from previous studies that indicated particularly good retardation at high temperatures with white cement.

The categories of retarders include liquids and powders that range from high to low solubility in water and from white powders to dark-brown solutions. Liquids were added to the mixing water, and powders were blended into the white cement before water was added. The 13 commercial admixtures tested included lignosulfonates, salts of lignosulfonates and their derivatives, hydroxycarboxylic acids and their derivatives, and hydroxylated polymers. The 17 laboratory admixtures included sugars, heavy metal oxides, salts, and alkaline-alkaline earth hexafluorosilicates. This paper discusses the findings from both the laboratory and commercial admixtures.

### PROCEDURES FOR EVALUATION OF ADMIXTURES IN WHITE CEMENT PASTES

A Japanese automatic vicat setting time recorder was used to determine the initial and final setting times of the white cement pastes with and without admixtures at normal temperatures of 75 F (23.9 C) and 50 percent relative humidity and at 110 F (43.3 C) and 20 percent relative humidity. The high temperatures are characteristic of the hot, dry summertime conditions in the southwest United States.

It was not necessary to test all admixtures at 75 F (23.9 C) to determine whether they retarded white cement. Those not tested were documented by manufacturers and were indicated by a literature search to retard portland cement systems at normal temperatures [75 F (23.9 C)]. The admixtures were added in an attempt to cause more than 60-min retardation of the initial setting time of the cements, as required in ASTM C 494-68, at the high temperature of 110 F (43.3 C).

All admixtures were tested in cement pastes of normal consistency (ASTM C 187) at 110 F (43.3 C) in a temperature-controlled cabinet. Random afternoon field inspection of summer concreting operations indicated placement temperatures between 90 and 100 F (32.2 and 37.8 C). The specified 0.39 ± 0.039-in. (10 ± 1-mm) plunger penetration was broadened to 0.39 ± 0.078 in. (10 ± 2 mm) for the extraordinary high temperatures of the test.

In the initial tests at 110 F (43.3 C) mixes were prepared at 75 F (23.9 C) and then immediately transferred to the 110 F (43.3 C) chamber for setting-time testing. These tests showed significantly different behavior compared to that of mixes prepared at

110 F (43.3 C). Consequently all 110 F (43.3 C) tests were mixed at 110 F (43.3 C) so that the most severe conditions likely to be encountered in high temperature concreting could be simulated.

The study of cement paste time of setting at 110 F (43.3 C) showed only four of the tested admixtures retarded without noticeable discoloration of the white cement pastes.

Admixture dosages from 0.1 to 4.0 percent by weight of cement were used in the admixture trials. Commercial admixture dosages varied from normal manufacturer's recommended dosages to seven times normal.

The admixtures and concentration levels that proved most successful in white cement pastes were

1. Two commercial admixtures of the hydroxycarboxylic acid type (admixtures A and B in Table 2) with a dosage varying from four to seven times normal dosage;
2. By weight, 1.0 percent of cement for the lead monoxide admixture (admixture C in Table 2); and
3. By weight, 0.7 to 1.0 percent of cement for the boron trioxide admixture (admixture D in Table 2).

When the study with cement pastes was completed, the four chosen admixtures as well as Borax (admixture E) and another commercial hydroxycarboxylic acid type of admixture (admixture F) were tested in concrete (Table 2). The first four admixtures (A, B, C, and D) were tested in concrete mixes at temperatures in the 70 F (21.1 C) range, and all six admixtures were tested in the temperature range higher than 90 F (32.2 C).

Because of space limitations, it is impossible to include the data obtained during the course of this study; however, Tables 3 and 4 give examples of the types of data obtained.

#### PROCEDURES FOR EVALUATION OF ADMIXTURES IN WHITE CEMENT CONCRETES

Modifications were made in the quantity of admixtures added to the concrete as compared with the quantity of admixtures added to the cement pastes. Normal concentrations of the commercial admixtures A and B were used in the 70 F (21.2 C) range. One-third of 1 percent by weight of cement was used for admixtures C and D in the 70 F (21.1 C) range.

High concentrations of admixtures (above normal dosages) were used in concrete in the greater than 90 F (32.2 C) range. This included a dosage of 8 to 12 oz (236.6 to 354.9 ml) per sack for the commercial admixtures A, B, and F and 0.4 to 1.5 percent by weight of cement for laboratory admixtures C, D, and E.

Control concrete mixes without admixtures were made at 70 F (21.1 C) and 90 F (32.2 C) at 7 sacks/yd<sup>3</sup> (390.4 kg/m<sup>3</sup>) with a 4-in. (10.16-cm) slump target. A cement content of 7 sacks/yd<sup>3</sup> (390.4 kg/m<sup>3</sup>) was selected because most field problems have occurred in mixes designed for high strength at 28 days. This is considered as the average cement content necessary to produce these high strengths. The mix water was reduced by 10 percent from that of the control when an admixture was used.

Concrete temperatures between 67 and 74 F (19.4 and 23.3 C) were maintained at laboratory conditions. Concrete temperatures higher than 90 F (32.2 C) were attained by preconditioning all components and the mixing drum to 100 F (37.8 C) before mixing. The temperature of the mixing drum was maintained by running hot water [140 F (60 C)] over the drum as needed during the mixing period.

Three times for measuring properties of the concrete were chosen: 5, 45, and 90 min. Slump, unit weight, air content, and temperature were determined after 5 min of mixing at 1, 40, and 85 min; however, specimens were cast only at the 5 and 90-min intervals.

The short time of 5 min was chosen for casting to simulate the conditions of on-site mixing. In some of these trials, the use of an admixture did not prove to be beneficial.



**Table 1. Admixtures tested in concrete placed at high temperatures.**

Commercial		Laboratory	
Daratard H.C.	Borax	Pozzolith MB-HC	Sodium borate concentrates
Daratard Lignin	Boric acid	Sonotard	Sodium hexafluorosilicate
Orzan Al-50	Boron trioxide	Sonotard 6050	Sodium hexametaphosphate
Orzan S	Calcium chloride	Zeecon R	Sodium tetraborate · water
PDA 25-R	Calcium hexafluorosilicate		Sorbitol
Plastiment	Iron sulfate		Sucrose
Pozzolith 8	Lead monoxide		Zinc hexafluorosilicate
Pozzolith 100R	Mannitol		Zinc oxide
Pozzolith 100XR	Potassium hexafluorosilicate		

**Table 2. Admixtures used in concrete studies.**

Admixture	Source	Type	Level of Addition	
			At 70 F	At 90 F
A	Commercial	Hydroxycarboxylic acid	2 to 4 <sup>a</sup>	6 to 12 <sup>a</sup>
B	Commercial	Hydroxycarboxylic acid	2 to 4 <sup>a</sup>	6 to 12 <sup>a</sup>
C	Laboratory	Lead monoxide	0.33 <sup>b</sup>	0.4 to 1.5 <sup>b</sup>
D	Laboratory	Boron trioxide	0.33 <sup>b</sup>	0.4 to 1.5 <sup>b</sup>
E	Laboratory	Borax	—	0.4 to 1.5 <sup>b</sup>
F	Commercial	Hydroxycarboxylic acid	—	6 to 12 <sup>a</sup>

Note: 1 F = 1.8 (C) + 32, 1 oz = 29.6 ml.

<sup>a</sup>In ounces (milliliters) per sack. <sup>b</sup>In percent by weight of cement.

**Table 3. Properties of fresh white cement concrete prepared with commercial admixtures.**

Mix Type	Mix No.	Dosage per Sack (oz)	Mix Temperature (F)	Time of Test* (min)	Slump (in.)	Unit Weight (lb/ft <sup>3</sup> )	Air Content (percent)	Cement Content (lb/yd <sup>3</sup> )	Water-Cement Ratio
	2	70	40	2	146	2.0	646	0.45	
	3	70	85	1	146	2.0	646	0.45	
	4	>90	1	2	146	4.0	640	0.51	
	5	>90	40	1	144	3.5	640	0.50	
	6	>90	85	1	143	3.5	640	0.53	
With admixture A	1	4	70	1	4	153	1.2	678	0.41
	2	4	70	40	4	151	0.9	662	0.47
	3	4	70	85	4	148	1.2	639	0.56
	4	12	>90	1	4	152	1.4	665	0.44
	5	12	>90	40	4	150	1.4	648	0.52
	6	12	>90	85	4	149	1.4	639	0.55
With admixture B	1	3	70	1	6	152	1.2	667	0.43
	2	3	70	40	4	153	1.4	674	0.43
	3	3	70	85	4	152	1.2	664	0.46
	4	9	>90	1	5	153	1.6	679	0.38
	5	9	>90	40	5	151	1.2	665	0.43
	6	9	>90	85	5	151	1.2	660	0.46
With admixture F	1	8	70	1	5	152	1.5	660	0.49
	2	8	70	40	4	150	1.5	641	0.54
	3	8	70	85	4	150	1.4	641	0.56

Note: 1 oz = 29.6 ml, 1 F = 1.8 (C) + 32, 1 in. = 2.54 cm, 1 lb/ft<sup>3</sup> = 16.02 kg/m<sup>3</sup>, 1 lb/yd<sup>3</sup> = 0.69 kg/m<sup>3</sup>.

\*After initial 5-min mixing.

**Table 4. Strength of 4-in. (10.1-cm) slump white cement concrete made with various commercial admixtures mixed at 70 and 90 F (21.1 and 32.2 C) for various times.**

Mix Type	Mix No.	Dosage per Sack (oz)	Mix Temperature (F)	Casting Time (min)	Compressive Strength (psi)						Flexural Strength (psi)			
					1 Day <sup>a</sup>	3 Day <sup>b</sup>	7 Day <sup>c</sup>	28 Day <sup>d</sup>	90 Day <sup>e</sup>	365 Day <sup>e</sup>	3 Day	7 Day	28 Day	90 Day
Control	1		70	5	2,400	3,280	3,790	4,690	5,790	5,800	480	460	560	600
	2		70	90	2,140	2,840	3,460	4,320	5,730	5,760	440	460	540	580
	3		>90	5	3,210	3,280	3,730	4,900	6,600	6,800				
	4		>90	90	1,910	2,230	2,510	4,110	4,880	5,000				
With admixture A	1	4	70	5	3,600	4,210	4,920	6,410	7,980	8,020				
	2	4	70	90	2,230	2,770	2,960	4,430	5,500	5,600				
	3	12	>90	5	1,140	3,780	4,310	5,220	6,070	6,200				
	4	12	>90	90	2,590	3,460	3,560	4,280	4,340	4,700				
With admixture B	1	3	70	5	2,870	4,140	4,450	6,060	7,520	7,600	540	620	680	970
	2	3	70	90	2,750	3,590	3,710	5,250	6,670	6,700	550	620	640	760
	3	9	>90	5	1,050	1,880	2,370	2,800	3,630	3,800				
	4	9	>90	90	2,080	2,340	2,620	4,970	5,260	5,300				
With admixture F	1	8	>90	5	3,590	3,540	4,480	5,350	6,250	6,300	610	610	850	880
	2	8	>90	90	2,930	2,940	3,330	4,010	5,580	5,900				

Note: 1 oz = 29.6 ml, 1 F = 1.8 (C) + 32, 1 psi = 6.9 kPa.

<sup>a</sup>Cured 1 day at mix temperature at 100 percent relative humidity.

<sup>b</sup>Cured 1 day at mix temperature at 100 percent relative humidity, then at 72 F (22.2 C) at 100 percent relative humidity until test.

<sup>c</sup>Cured 1 day at mix temperature at 100 percent relative humidity, then at 72 F (22.2 C) for 27 days at 100 percent relative humidity, then at 72 F (22.2 C) at 50 percent relative humidity until test.

The time of 90 min was chosen for casting to simulate the conditions of a transit-mix operation conforming to ASTM and AASHTO specifications for ready-mix concrete. At the 40 and 65-min time intervals, the concrete was remixed at 5 min, and water as needed was added to maintain a slump of approximately 4 in. (10.2 cm).

Initially, after all the ingredients were in the mixer, the concrete was mixed for 5 min in a 9-ft<sup>3</sup> (0.26-m<sup>3</sup>) rotary drum mixer. After this 5-min period, the temperature, slump, unit weight, and air content were measured. Then, 4 by 8-in. (10.2 by 20.3-cm) cylinders, 4 by 4 by 11<sup>1</sup>/<sub>4</sub>-in. (10.2 by 10.2 by 28.6-cm) bars, and 2 by 2 by 11<sup>1</sup>/<sub>4</sub>-in. (5.1 by 5.1 by 28.6-cm) flexure beams were cast. Mortar was also separated from the concrete for initial and final setting time measurements by Proctor needle penetration.

At 90 min, all tests performed at 5 min were duplicated. It was found that the time of setting as measured by the Proctor needle showed no significant differences for samples taken from the mixer at 5 and at 90 min.

One test difference at 70 F (21.1 C) was  $\pm 9$  min at 6<sup>3</sup>/<sub>4</sub> hours of initial setting and  $\pm 17$  min at 7<sup>3</sup>/<sub>4</sub> hours of final setting.

At each time interval, the weight of concrete deducted from the batch of 7 sacks/yard<sup>3</sup> (390.4 kg/m<sup>3</sup>) was determined, and corrected yard<sup>3</sup> (meter<sup>3</sup>) weights were calculated. The water-cement ratios were then recomputed, and cement content in sacks per yard<sup>3</sup> (kilograms per meter<sup>3</sup>) was calculated.

The cast specimens were cured for 24 hours at the mix temperature to simulate job storage conditions before specimens were taken to the testing storage facility.

The cylinders and beams were then cured up to 28 days at 72 F (22.2 C) and 100 percent relative humidity and then at 72 F (22.2 C) and 50 percent relative humidity until tested. The shrinkage specimens were at 72 F (22.2 C) and 100 percent relative humidity up to 7 days only. Test times chosen for the cylinder breaks were 1, 3, 7, 28, 90, and 365 days.

The shrinkage bars were measured at 1, 3, 7, 14, 21, 28, 35, 100, and 365 days to determine a correlation between short- and long-term shrinkage at the two temperature levels.

Flexural beams were not made from all batches; they were tested in flexure with third-point loading at 3, 7, 28, and 90 days. The 4 by 4 by 11<sup>1</sup>/<sub>4</sub>-in. (10.2 by 10.2 by 28.6-cm) shrinkage bars were tested in flexure, center-point loading at 100 days for all mixes.

Some work was completed at a 2-in. (5.1-cm) slump at the 5-min mix time. In this work 200-lb (90.7-kg) batches mixed in a flat-bottomed Lancaster mixer were used, and 3 by 6-in. (7.6 by 15.2-cm) cylinders were cast and cured in the same manner as the larger batches for 1, 7, and 28-day tests.

Shrinkage bars of 3 by 3 by 11 in. (7.6 by 7.6 by 27.9 cm) and 4 by 4 by 11<sup>1</sup>/<sub>4</sub> in. (10.2 by 10.2 by 28.6 cm) were also cast and measured up to 100 days and then were tested in flexure. Beams of 2 by 2 by 11<sup>1</sup>/<sub>4</sub> in. (5.1 by 5.1 by 28.6 cm) were also cast and tested at 7 and 28 days.

### Properties of White Concrete 1

White concrete 1 was mixed for 90 min and cured at 70 F (21.1 C) at a 4-in. (10.2-cm) slump, through 100 days. The properties of white concrete 1 were as follows:

1. At 70 F (21.1 C), admixture D and the commercial admixtures A and B [4 oz (118.3 ml) per sack] were found to be water-reducing, setting-time retarders.
2. The four admixtures tested (A, B, C, and D) did not entrain air.
3. The compressive strengths of concretes with admixture D, admixture C, and the commercial admixtures A and B were higher than those for the control for both 5 and 90-min mixing times.
4. The 100-day shrinkage bars indicated no additional shrinkage caused by admixture D, admixture C, or the commercial admixtures A and B [4 oz (118.3 ml) per sack].
5. Flexural strength tests indicated that all of the admixtures increased the strengths at both 5 and 90-min mixing times.

### Properties of White Concrete 2

White concrete 2 was mixed for 5 min at 90 F (32.2 C) and cured at 90 F (32.2 C) for 24 hours, through 28 days at 70 F (21.1 C) at a 2-in. (5.1-cm) slump. The properties of white concrete 2 were as follows:

1. Admixture D (0.5 percent by weight of cement), admixture B [6 oz (177.4 ml) per sack], and admixture E (1.5 percent by weight of cement) were successful initial setting-time retarders.
2. Admixture D (0.5 percent by weight of cement) reduced the amount of water required for a 2-in. (5.1-cm) slump by 8.1 percent, but admixture B [6 oz (177.4 ml) per sack] and admixture E (1.5 percent by weight of cement) increased the water demand by 6.1 and 10 percent respectively in comparison to that of the control.
3. Admixture D (0.33 percent by weight of cement) and admixture B [6 oz (177.4 ml) per sack] produced cements with 7.6 and 3.7 percent respectively greater compressive strengths than the control, but cement with admixture E (1.5 percent by weight of cement) had a 47 percent lower strength than the control.
4. Admixture D (0.33 percent by weight of cement), admixture B [6 oz (177.4 ml) per sack], and admixture E (1.5 percent by weight of cement) increased the flexural strength of 2 by 2 by 11<sup>3</sup>/<sub>4</sub>-in. (5.1 by 5.1 by 28.6-cm) beams by 19, 26, and 10 percent respectively.
5. Cement with admixture D (0.33 percent by weight of cement), admixture D (0.5 percent by weight of cement), admixture B [6 oz (177.4 ml) per sack], and admixture E (1.5 percent by weight of cement) had less shrinkage than the control at 100 days.
6. Admixtures B, D, and E did not entrain air.

### Properties of White Concrete 3

White concrete 3 was mixed for 90 min at 90 F (32.2 C) and cured at 90 F (32.2 C) for 24 hours at a 4-in. (10.2-cm) slump, through 100 days at 70 F (21.1 C). The properties of white concrete 3 were as follows:

1. The setting times clearly indicated that admixture D (0.4 percent by weight of cement), admixture D (1.0 percent by weight of cement), admixture C (1.0 percent by weight of cement), admixture A [12 oz (354.9 ml) per sack], admixture E (1.2 percent by weight of cement), and admixture B [9 oz (266.2 ml) per sack] are effective for retarding the setting time of and reducing water in the concrete.
2. Admixture D (1.0 percent by weight of cement) and admixture B [9 oz (266.2 ml) per sack] were excessive dosages causing excessive retardation.
3. Some of the commercial admixtures discolored the white concrete.
4. The compressive strengths at 90 days of cements with admixture D (1.0 percent by weight of cement), admixture C (1.0 percent by weight of cement), and admixture B [9 oz (266.2 ml) per sack] were 32, 15, and 8 percent respectively greater than those of the control at 90-min mixing but were 63, 30, and 40 percent smaller than those of the control at 5 min of mixing. The low strength at 5 min of mixing resulted because the dosage levels were excessive for short mix cycles, but greater strengths were achieved at 90 min mixing through additional mixing time.
5. The compressive strengths at 90 days of cements with admixture D (0.4 percent by weight of cement) and admixture E (1.2 percent by weight of cement) were 39 and 28 percent greater than those of the control at 90-min mixing, but the compressive strengths at 5 min of mixing are 5 percent less for cements with admixture D (0.4 percent by weight of cement) and 7 percent greater for those with admixture E (1.2 percent by weight of cement).
6. Admixture A [12 oz (354.9 ml) per sack] resulted in 8 and 11 percent reductions in compressive strengths at 5 and 90 min of mixing.
7. The 100-day shrinkage bar tests indicated that at 90 min of mixing only admixture A [12 oz (354.9 ml) per sack] had a greater amount of shrinkage than the control.
8. Admixtures A, B, C, D, and E did not entrain air.

### Recommendations for White Cement Concrete

The recommendations for white cement concrete mixed at 90 F (32.2 C) at a 4-in. (10.2-cm) slump are as follows:

1. The use of admixture B as an effective retarder for white cement concrete at elevated temperatures is not recommended because of the resulting discoloration at dosages of 6 to 9 oz (177.4 to 266.2 ml) per sack found necessary for 60 min of initial setting retardation.
2. Admixture A can be used at three times the normal dosage [9 to 12 oz (266.2 to 354.9 ml) per sack] at 90 F (32.2 C) and above.
3. The use of admixture C (1.0 percent by weight of cement) is not recommended because of toxicological properties, although it is an excellent retarder.
4. The use of admixture D ( $0.4 \pm 0.1$  percent by weight of cement) is recommended.
5. The use of dark-colored admixture solutions at two times the normal dosage is not recommended.
6. None of the admixtures tested entrained air.
7. The use of admixture E ( $1.0 \pm 0.1$  percent by weight of cement) is potentially useful.

Many other similar practical questions could be answered in a comprehensive study of the interactions of cement concrete and admixtures. This study would be of tremendous benefit in research and development, technical service work, and promotional activities. It is hoped that such a study might be initiated in the near future.

No work was performed on white structural concrete that contained entrained air. In climates where freezing and thawing are a problem, it would seem desirable to determine the effect of mixing time on air-entraining addition rates, freeze-thaw resistance, and strength, on high-strength, air-entrained white structural concrete. White structural concrete has been used by the Arizona Department of Transportation along I-66 in freeze-thaw areas, and, therefore, some investigation of the white air-entrained concrete, even in the Southwest, would seem appropriate.

### Summary and Conclusions

1. The tests of cement pastes and admixtures indicated that an optimum amount of admixture was necessary to secure maximum retardation.
2. False set characteristics, as defined in ASTM C 451, were not improved by the addition of set-retarding, water-reducing admixtures A, D, and E.
3. The optimum percentage of admixtures required for retardation in the concrete was approximately half of that required in the pastes.
4. Substantial reductions in compressive strengths were obtained in 5 to 90-min mix life intervals at 70 (21.1 C) and 90 F (32.2 C). This is related to the additional water required for maintaining a constant slump.
5. Concretes with admixtures causing excessive retardation generally develop strengths approximately equal to those of concrete without admixtures at 28 days. This occurs even when the earlier strengths were drastically low.
6. Length change was affected by mixing time, admixture type, and admixture dosage level.
7. None of the admixtures tested entrained additional air.
8. Delayed addition of admixtures was not included in this series because this procedure is impractical for ready-mix operations. Field control is difficult, and the additional entrained air would be detrimental to concrete performance, particularly strength.
9. The use of dark-colored admixture solutions is not recommended with white cement unless color slab tests are made that result in satisfying job requirements.
10. Admixture D ( $0.4 \pm 0.1$  percent by weight of cement) is suggested for white cement concrete admixture use at 90 F (32.2 C). This admixture should be dissolved in the mix water first.



11. Admixture A can be used at two to three times the manufacturer's recommended dosage rate at 90 F (32.2 C) to effectively retard the initial setting time of concrete within ASTM C 494-68 specifications.

12. The use of Admixture B (a dark-colored solution) is not suggested because of the discoloration resulting from the multiple dosage level required for initial setting-time retardation.

13. Concrete temperature above 90 F (32.2 C) and a mixing time of 90 min usually result in a loss of strength. It is important that this be considered in the mix design.

14. Although an admixture satisfies the requirements set forth in ASTM C 494-68 at normal temperatures, it does not necessarily satisfy the requirements for mixing times and placing temperatures permitted by ASTM C 94-67 (ready-mixed concrete) or ACI.

15. Mixing time, concrete temperature range, and admixture dosage rate should be included when concrete mixes are designed.

16. ASTM C 494-68 for chemical admixtures for concrete does not provide adequate information for selection of an admixture for hot-weather concreting. This specification requires only 6 min of mixing time at a room temperature that is unrealistic for field use. Field problems are usually not encountered at 70 F (21.1 C); therefore, the implicit assumption that an admixture that retards at 70 F (21.1 C) will also do so at 90 F (32.2 C) is not valid. Our tests indicate that commonly accepted retarders, such as sugar, retard at 70 F (21.1 C), but act as accelerators at 90 F (32.2 C). Mixing times of 90 min and temperatures above the normal 75 F (23.9 C) should be used in evaluating the efficiency of a retarder for high-temperature concreting.

17. White structural concrete generally requires from two to three times the normal addition rate of a retarder, conforming to the requirements of C 494-68, to permit sufficient mixing time without a significant addition of water and subsequent reduction in strength. These greater than normal additions may discolor the concrete and should be selected after field trials indicate that staining will not be a problem.

## PROJECT SCOPE FOR TESTING TYPES 2 AND 3 GRAY CEMENT CONCRETE

This section discusses the use of chemical admixtures as retarders in types 2 and 3 gray cement concrete at 70 F (21.1 C) and 90 F (32.2 C).

All commercial and laboratory admixture selections from the previous discussion were first tested in gray cement pastes at 110 F (43.3 C). Automatic vicat cement setting times of normal consistency pastes (ASTM C 187) were recorded at this temperature with and without admixtures. Concentrations of these admixtures were varied from 3 to 4 times normal recommended dosage to retard the initial set of the pastes by 1 hour (ASTM C 494-68). A delay in setting time in the paste does not correlate directly with a delay in setting time in the concrete. Therefore, adjustments were made in additional levels when the admixtures that proved successful in pastes were used in concretes.

The color of the admixtures used was not a problem in these gray cements, although an overdose of admixture can cause discoloration in a buff-colored cement.

## RESULTS OF TESTS

### Admixtures in Gray Cement Concrete Pastes

Admixtures A, B, D, and E (Table 2) were effective for retarding the setting time of and reducing the water in the paste tests.

These admixtures were used in type 2 gray cement concrete mixes at 70 F (21.1 C) and 90 F (32.2 C) in varying concentrations so that an optimum level at each condition could be found.

Admixtures C and D (Table 2) were tried in type 3 gray cement concrete mixes at

70 F (21.1 C) and 90 F (32.2 C) at one concentration level. Further work with other admixtures and concentration should be conducted in the type 3 cement concrete.

#### Type 2 Gray Cement Concrete at >70 F (21.1 C) and >90 F (32.2 C)

The concrete mix design and mixing procedure in the gray cement project were as follows: a 7-sack/yd<sup>3</sup> (390.4-kg/m<sup>3</sup>) mix; a 4-in. (10.2-cm) slump target maintained over the 90 min of batch life; two mix temperature ranges of 66 to 80 F (18.9 to 26.7 C) and 90 to 104 F (32.2 to 40.0 C); ASTM plastic concrete tests at 5, 50, and 90 min of batch life; and casting of specimens at 5 and 90 min of batch life. The mix sequence involves 5 min of mixing at 0, 40, and 85 min of elapsed batch life time for a total of 15 min of actual mixing. The concrete between mixes remained at rest in the mixing drum. Twenty-five 750-lb (340.2-kg) concrete batches were mixed from 3,060 lb (1388 kg) of cement and 13,000 lb (5897 kg) of aggregate. The following cylinders, shrinkage bars, and flexure beams were cast (1 in. = 2.54 cm):

<u>Item</u>	<u>Number</u>	<u>Measurement (in.)</u>
Cylinders	525	4 × 8
Shrinkage bars	126	4 × 4 × 11 <sup>1</sup> / <sub>4</sub>
Flexure beams	168	2 × 2 × 11 <sup>1</sup> / <sub>4</sub>

Tests were performed on cured specimens at 1, 3, 7, 28, 90, 100, and 180 days.

Concrete mixes at between 70 and 80 F (21.1 and 26.7 C) were performed in laboratory conditions, and materials stored under the same conditions were used. Curing of the cast specimens was performed in a moist room at 70 F (21.1 C) and 100 percent relative humidity and in another room at 70 F (21.1 C) and 50 percent relative humidity.

Concrete mixes at 90 F (32.2 C) were performed in the laboratory, and the materials and the mixer were preconditioned to 100 F (37.8 C). The temperature in the concrete was maintained by the use of hot running water [140 F (60 C)] on the 9-ft<sup>3</sup> (0.26-m<sup>3</sup>) rotary drum when needed.

The ASTM tests performed on the plastic concrete mixes measured slump, temperature, unit weight, air content, and setting time of mortar separated from the concrete.

#### Type 2 Gray Cement Concrete at >70 F (21.1 C) and 180 Days

The findings for type 2 gray cement concrete at >70 F (21.1 C) and 180 days were as follows:

1. Type 2 gray cement concrete responds well to the manufacturer's normal recommended dosage rate of 2 to 3 oz (59.1 to 88.7 ml per sack) at 70 F (21.1 C).
2. Types 2 and 3 gray cement without admixtures have the same concrete setting times at 70 F (21.1 C) as determined by the Proctor penetration resistance setting time test (ASTM C 403-68).
3. None of the admixtures tested entrained air.
4. None of the admixtures tested reduced the water content requirements.
5. All of the admixtures tested retarded the initial and final setting times of the concrete.
6. Admixture B [3 oz (88.7 ml) per sack] and admixture D (0.15 percent by weight of cement) developed concretes with the best compressive (25 and 6 percent greater respectively) and flexural strengths at 70 F (21.1 C).
7. All admixtures tested produced increased shrinkage (from 6 to 35 percent) compared to the control specimens at 100 days. The amount of shrinkage in the admixture B specimens [3 oz (88.7 ml) per sack] exceeds the limits specified in ASTM C 494-68 in both 5 and 90-min mixes.

### Type 2 Gray Cement Concrete at >90 F (32.2 C) and 180 Days

The findings for type 2 gray cement concrete at >90 F (32.2 C) and 180 days were as follows:

1. The type 2 gray cement concrete requires higher admixture additions [3 to 4 oz (88.7 to 118.3 ml) per sack] than the manufacturer's recommended dosage at 90 F (32.2 C).
2. Types 2 and 3 gray cement concretes have the same setting times in concrete at 90 F (32.2 C) without admixtures.
3. None of the admixtures tested entrained air.
4. All of the admixtures tested acted to reduce water in and retard the setting time of concrete.
5. Admixture D (0.30 percent by weight), admixture A [5 oz (147.9 ml) per sack], and admixture B (0.4 percent by weight) have developed concretes with the best compressive (36, 25, and 34 percent respectively) and flexural strengths at 90 F (32.2 C).
6. All of the admixtures tested reduced the shrinkage (from 7 to 48 percent in comparison to the control bars) at both 5 and 90-min mixing times.
7. Admixture A [12 oz (354.9 ml) per sack] was an overdose.

### Type 3 Gray Cement Concrete at >70 F (21.1 C) at 180 Days

Findings for type 3 gray cement concrete at >70 F (21.1 C) at 180 days were as follows:

1. Type 3 gray cement concrete does not require any more than the manufacturer's normal recommended dosages at 70 F (21.1 C) [2 to 4 oz (59.1 to 118.3 ml) per sack].
2. None of the admixtures increased the air content.
3. All of the admixtures used in the concrete increased the drying shrinkage (from 14 to 35 percent) at 100 days in both 5 and 90-min mixing times.
4. Admixture A [4 oz (118.3 ml) per sack] and admixture B [3 oz (88.7 ml) per sack] retarded the setting times and increased the compressive (5 and 34 percent greater respectively) and flexural strengths.
5. Admixture A [4 oz (118.3 ml) per sack] reduced the water demand by 6 percent compared with that for the control.

### Type 3 Gray Cement Concrete at >90 F (32.2 C) and 180 Days

Findings for type 3 gray cement concrete at >90 F (32.2 C) and 180 days were as follows:

1. Type 3 gray cement concrete does not require any more than manufacturer's recommended dosages [2 to 3 oz (59.1 to 88.7 ml) per sack] at 90 F (32.2 C).
2. None of the admixtures used produced more shrinkage than the control batch bars at 100 days in mixing times of 5 and 90 min.
3. Admixture A [6 oz (177.4 ml) per sack] and admixture B [4 oz (118.3 ml) per sack] acted to reduce water in and retard setting of the concrete at 90 F (32.2 C).
4. Admixture B [4 oz (118.3 ml) per sack] developed a 40 percent greater flexural strength than the control.
5. Admixture A [6 oz (177.4 ml) per sack] resulted in an undesirably long setting time.

### Summary and Conclusions

The conclusions about the use of chemical retarding admixtures in types 2 and 3 gray

**Table 5. Use of admixtures at acceptable dosages in gray cement concrete.**

Gray Cement Concrete	Admixture	Dosage Rate	
		At >70 F	At >90 F
Type 2	A	2 to 3 <sup>a</sup>	4 to 5 <sup>a</sup>
	B	2 to 3 <sup>a</sup>	4 to 5 <sup>a</sup>
	D	0.10 to 0.20 <sup>b</sup>	0.30 to 0.40 <sup>b</sup>
	E	0.35 to 0.45 <sup>b</sup>	0.80 to 0.90 <sup>b</sup>
Type 3	A	2 to 3 <sup>a</sup>	2 to 3 <sup>a</sup>
	B	2 to 3 <sup>a</sup>	2 to 3 <sup>a</sup>

Note: 1 F = 1.8 (C) + 32; 1 oz = 29.6 ml.

<sup>a</sup>In ounces (milliliters) per 94 lb (42.6 kg) sack of cement.

<sup>b</sup>In percent by weight of cement.

cement concrete at >70 F (21.1 C) and >90 F (32.2 C) and 180 days are as follows:

1. The use of chemical admixtures A, B, D, and E at the dosage levels proved acceptable by this paper is given in Table 5.
2. All admixtures should be added to the mix water first.
3. Increments of 1 oz (29.6 ml) per sack of cement greater than recommended are very detrimental and should be avoided.
4. Specifications are needed about the use of chemical admixtures in concrete where other than normal type cements, at 5½ sacks or 517 lb/yd<sup>3</sup> (306.7 kg/m<sup>3</sup>), and other than normal temperature conditions exist. ASTM C 494-68 is inadequate in this area and should be revised to contain standards for the above-mentioned conditions.

#### FUTURE STUDIES

A chemical investigation of admixture-concrete systems during mixing and subsequent hardening could provide valuable information for understanding why admixtures under various conditions act as they do. This information could then be correlated with data from physical test results. Many questions such as the following that concern admixture-concrete interactions could then be answered:

1. Why do some set-retarding admixtures produce lower compressive strengths with longer mixing time than others?
2. How do admixtures change with age?
3. Can one determine quantitatively the admixture contained in a 1-year-old specimen of concrete?
4. Why does a particular admixture react differently with the same type of cement from different sources?

#### ACKNOWLEDGMENT

We would like to thank Vernon McIntire and Victor Timmons for their help on various phases of this project. Special thanks are due to Howard McGinnis for his comments; his knowledge of cement and concrete used in the Arizona area aided materially in the results of this paper. We would also like to thank Dale Hensley and the late Hubert McCall for their assistance in mix design and concrete mix control.

# A SETTING PROBLEM INVOLVING WHITE CEMENT AND ADMIXTURE

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Quick setting was experienced when a particular water-reducing admixture was used with certain white cements containing less than 1.6 percent  $\text{SO}_3$ . These cements set normally at normal temperature without the admixture but set rapidly in the presence of the admixture, both at normal and at high concreting temperatures. Other cements from the same mill with higher  $\text{SO}_3$  contents gave normal setting times, both with and without the admixture and irrespective of temperature. Investigation revealed that, in the presence of the admixture, consumption of  $\text{SO}_3$  was accelerated in the case of the problem cements and that insufficient  $\text{SO}_3$  remained in solution in the period immediately following mixing to properly control the hydration reactions of  $\text{C}_3\text{A}$ . Other factors also were involved, such as inherent clinker reactivity and the state of dehydration of the gypsum.

●SEVERAL instances of quick setting of type 1 cements were encountered, and these all involved either use of a water-reducing admixture or high concreting temperatures, or both. At normal temperatures of 70 to 75 F (21.1 to 23.9 C) and in the absence of admixture, the cements set normally. Without exception the quick-setting cements all had rather low  $\text{SO}_3$  contents (about 1.50 to 1.60 percent). However, the  $\text{SO}_3$  deficiency was not so great as it seemed at first glance, since drying shrinkage and 24-hour strength tests had indicated an optimum  $\text{SO}_3$  content of only about 1.8 to 2.0 percent. Other cements from the same mill with higher  $\text{SO}_3$  contents gave normal setting times, both with and without admixture, and even at the high concreting temperatures. Addition to the quick-setting cements of gypsum equivalent to 0.3 or 0.4 percent  $\text{SO}_3$  caused them to set normally.

Although the low  $\text{SO}_3$  content of the cements was clearly a critical factor in their quick-setting tendencies, other cements with equal or only slightly higher  $\text{SO}_3$  contents set normally. An attempt was made to find reasons for this anomaly in chemical differences between the cements, but there was no obvious correlation. The only explanation appeared to be that there were minor differences in the clinkers or in the ground cements that made them slightly more or less reactive on hydration.

This paper describes a specific setting problem experienced with a particular admixture. It is not intended to imply that the type of quick setting described has not been observed before; however, that it is not mentioned in a recent review of the causes of abnormal setting of portland cements (1) suggests that it is not a frequent occurrence. Because of the practical importance of the problem to the field use of white cement, a laboratory study of the factors involved was undertaken. Since the work was originally done to gain information as quickly as possible, the data are not so complete as they would have been had the project been planned from the beginning as a research study.

## MATERIALS AND METHODS OF STUDY

Three cements (A, B, and C) were selected for this investigation, the chemical analyses of which are given in Table 1. One of these, cement A, set rapidly in the field when used at temperatures of about 90 F (32.2 C) with a particular water-reducing admixture and also at normal temperatures in the laboratory. This admixture is reported

to be of the carbohydrate type and is probably based on corn syrup. The second cement, B, set rapidly in the absence of admixture when the temperatures of concreting were between 90 and 102 F (32.2 and 38.9 C). Cement B was not used with admixture in the field. Cement A contained 1.55 percent and cement B contained 1.54 percent  $\text{SO}_3$ . Cement C contained 1.85 percent  $\text{SO}_3$  and behaved satisfactorily with and without admixture. Cements B and C contained approximately 2.5 percent  $\text{Ca}(\text{OH})_2$  by differential thermal analysis (DTA), presumably resulting from hydration of free  $\text{CaO}$ .

The hydration experiments were performed on small paste samples that were hydrated at normal laboratory temperature [approximately 73 F (23 C)] for periods of 5 min, 15 min, 1 hour, and either 3 or 4 hours. The water-cement ratio was 0.50 in all cases. When the admixture was used, it was incorporated in the mixing water at a rate equivalent to 3 oz (8.87 ml) per sack of cement. The admixture was the same as that used with cement A in the field. In some experiments, additional  $\text{SO}_3$  was added to the cement in the form of reagent-quality gypsum.

The unhydrated cements and the pastes hydrated for different periods of time were analyzed by DTA. The hydrated samples were vacuum dried before analysis. The quantity of sample was the same in all DTA experiments, and the relative amounts of hydration products were estimated semiquantitatively from thermal peak intensities. The particles were essentially all small enough to pass the No. 200 sieve, and the rate of heating was 50 F (10 C) per min. In a few instances, X-ray diffraction (XRD) patterns were obtained as confirmation of the DTA results. The DTA data were correlated with setting-time tests.

## EXPERIMENTAL RESULTS

### Cement A

Cement A was hydrated both with and without the admixture. The DTA curves are shown in Figure 1. Calcium sulfate, mostly in the form of gypsum, is indicated on the curve of the unhydrated cement by the double endotherm between 212 and 392 F (100 and 200 C). The curves of the hydrated pastes show that the reaction of  $\text{C}_3\text{A}$  with calcium sulfate to produce ettringite is rapid in the absence of admixture and is accelerated even further in the presence of the admixture. Ettringite is indicated by the deep endotherm between 212 and 392 F (100 and 200 C). Without admixture, a little calcium sulfate remains unreacted after 15 min of hydration but appears to be completely consumed at 3 hours of hydration. In the presence of admixture, the calcium sulfate appears to be completely reacted after 15 min. After 3 hours of hydration with the admixture (bottom curve in Figure 1), a new complex endotherm appears, and the ettringite endotherm is reduced in size. The new endotherm, appearing in the region of 302 to 662 F (150 to 350 C), represents calcium aluminate monosulfate hydrate (or monosulfoaluminate) formed after depletion of the calcium sulfate (2). XRD was used to confirm the presence of monosulfoaluminate in hydrated pastes after occurrence of quick setting. The 8.9 Å line was considered to be characteristic of this compound (3). The monosulfoaluminate was already identifiable in a sample of paste hydrated for 1 hour (not shown in Figure 1). The endotherm at about 932 F (500 C) in the 3-hour samples is due to  $\text{Ca}(\text{OH})_2$ .

It was noted that the formation of monosulfoaluminate corresponded to a marked drying and stiffening of the pastes at about  $\frac{1}{2}$  hour after mixing. This observation correlated with the mortar laboratory tests, in which quick setting was observed about 35 min after mixing when the admixture was used at 73 F (22.8 C). Addition of 0.3 percent  $\text{SO}_3$  as gypsum lengthened the setting time of this cement in the presence of admixture to about 3 hours, even at 90 F (32.2 C).

### Cements B and C

Cements B and C were both hydrated without the admixture, and cement B was also hydrated with the admixture, even though the field problem of quick setting with cement

**Table 1. Chemical composition and fineness of cements A, B, and C.**

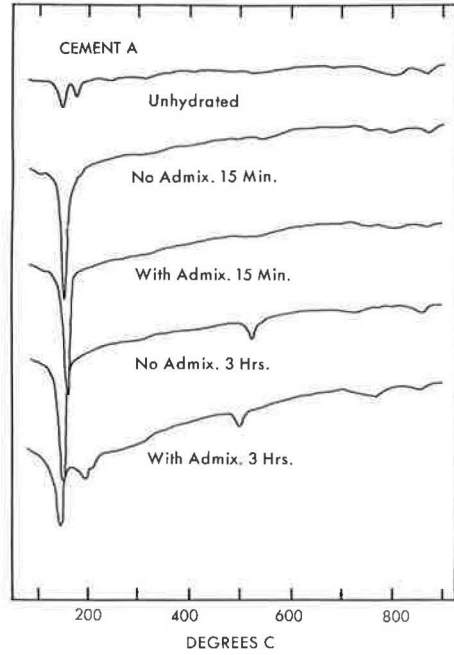
Component	Cement A (percent)	Cement B (percent)	Cement C (percent)
SiO <sub>2</sub>	23.2	22.3	22.7
Al <sub>2</sub> O <sub>3</sub>	5.1	5.5	5.0
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.3	0.3
CaO	67.9	68.5	67.8
MgO	0.8	0.7	0.7
SO <sub>3</sub>	1.55	1.54	1.85
Na <sub>2</sub> O	0.19	0.19	0.15
K <sub>2</sub> O	0.01	0.01	0.00
Loss <sup>a</sup>	1.16	1.28	1.25
Free CaO <sup>b</sup>	0.6	0.4	0.5
C <sub>3</sub> S	61.3	69.2	63.7
C <sub>2</sub> S	20.2	11.8	17.1
C <sub>3</sub> A	13.1	14.0	12.8
C <sub>4</sub> AF	0.9	0.9	0.9
CaSO <sub>4</sub>	2.64	2.62	3.15

Note: Blaine's surface area measurements are 3470 cm<sup>2</sup>/g for cement A; 3720 cm<sup>2</sup>/g for cement B; and 4010 cm<sup>2</sup>/g for cement C.

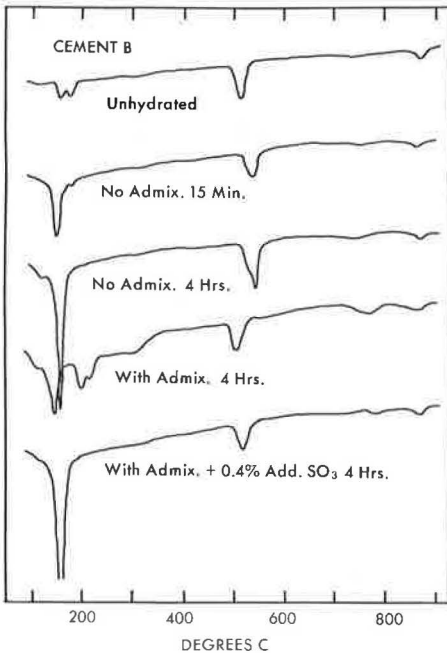
<sup>a</sup>On ignition.

<sup>b</sup>Not determined at time cements were studied; values obtained about 2 years later.

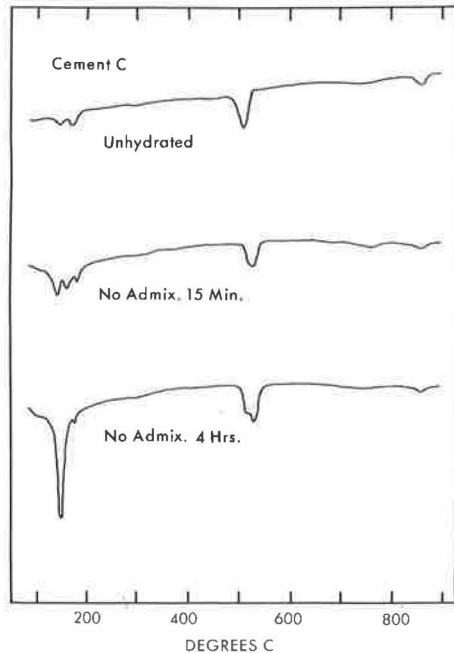
**Figure 1. DTA curves of cement A unhydrated and hydrated for different times with and without water-reducing admixture.**



**Figure 2. DTA curves of cement B unhydrated and hydrated for different times with and without water-reducing admixture.**



**Figure 3. DTA curves of cement C unhydrated and hydrated for different times.**





B had not involved an admixture addition. Both with and without the admixture, cement B behaved much like cement A. The DTA curves are shown in Figure 2. At normal laboratory temperature and in the absence of admixture, the calcium sulfate is essentially completely reacted after 4 hours of hydration, but there was no evidence of monosulfoaluminate formation or of quick setting at this length of time. Since this cement gave quick-setting problems in the field, it is probable that a few degrees of increase in temperature would have triggered the conversion to monosulfoaluminate and given the accompanying quick setting at some time earlier than 4 hours. Unfortunately, no DTA hydration experiments were conducted at temperatures in the range of 90 to 102 F (32.2 to 38.9 C). However, such data would be valuable as supporting evidence for the conclusions of the study. However, since cement B stiffened rapidly in the field at a high concreting temperature without admixture, it seems reasonable to assume that a higher laboratory temperature would also have induced quick setting in the absence of admixture.

When cement B was hydrated in the presence of the admixture, the early reactions were accelerated. Calcium sulfate was depleted and monosulfoaluminate began to form in less than 1 hour (not shown in Figure 2), and quick setting was evident. Figure 2 shows the considerable amount of monosulfoaluminate formed after 4 hours of hydration, compared with the absence of this compound in the paste with no admixture hydrated for the same length of time. The bottom curve of Figure 2 shows that, with the addition of 0.4 percent  $\text{SO}_3$  as gypsum, no monosulfoaluminate was detectable after 4 hours. This confirms the conclusion that additional  $\text{SO}_3$  is needed to properly control the setting of cement B when used with admixture.

Cement C, which contained 1.85 percent  $\text{SO}_3$ , behaved normally in the field and had calcium sulfate remaining unreacted at 4 hours as shown in Figure 3. Cement C contained less ettringite than cement B at 4 hours; this suggests that the  $\text{C}_3\text{A}$ -calcium sulfate reactions were basically slower in this cement. This led to the suspicion that the sensitivity to quick setting of cement B was due to a combination of a deficiency in  $\text{SO}_3$  and a somewhat greater inherent reactivity on hydration. No DTA tests were made with cement C in the presence of the admixture; therefore, no direct comparison with cement B is available under these conditions.

Mortar laboratory tests correlated well with the hydration experiments. Both cements B and C gave setting times at normal temperatures of about 3 hours. At 94 F (34.4 C), cement C gave a setting time of 165 min; cement B set at 81 min. Addition of the admixture to cement C actually prolonged its setting time at 94 F (34.4 C) to greater than 225 min; however, the setting time of cement B was shortened to 23 min under these conditions.

To confirm the suspicion (previously mentioned) that cement B was inherently more reactive than cement C, the two were hydrated with 0.31 percent  $\text{SO}_3$  as gypsum added to cement B so that the total  $\text{SO}_3$  contents would be equal. DTA of the original unhydrated cements had shown that, although cement B had a lower total  $\text{SO}_3$  content, it actually contained more gypsum than cement C. This is seen by comparing the upper curves of Figures 2 and 3. Hydration of the two cements with  $\text{SO}_3$  adjusted to the same level showed quite convincingly that cement B did indeed react more rapidly, as shown in Figure 4. At both 1 and 3 hours not only was more ettringite produced in cement B but also less gypsum was left unreacted, even though the original amount before hydration was considerably more in cement.

Description of other experiments made with cement B follows because they are of considerable technical interest and because they may be of some practical importance. A portion of the cement was heated overnight at 230 F (110 C) to convert the gypsum completely to hemihydrate. The heated cement was hydrated for periods of time up to 3 hours with and without addition of the admixture. The DTA results are shown in Figure 5. Surprisingly, the reactions were found to be much slower than before heating. In fact, the admixture appeared to have less of an accelerating effect on the heated than on the unheated cement. Both with and without admixture, the paste contained considerable unreacted calcium sulfate (gypsum and hemihydrate) after 3 hours of hydration. This was in sharp contrast to the pastes made with unheated cement.

Mortar laboratory results again paralleled the DTA data. At 94 F (34.4 C), the



Figure 4. DTA curves of cement C and cement B with added gypsum to give equal total  $\text{SO}_3$  content, hydrated for different times.

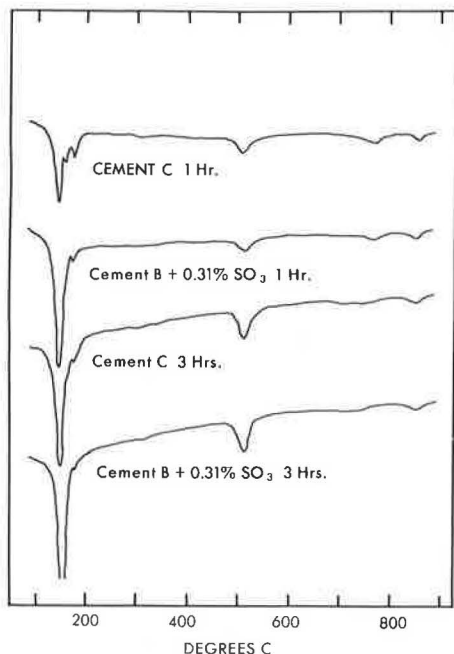
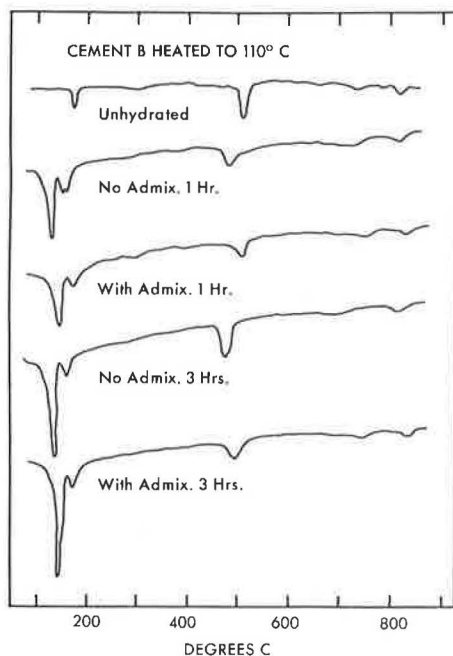


Figure 5. DTA curves of cement B after heating to 230 F (110 C), unhydrated and hydrated for different times with and without water-reducing admixture.



heated sample of cement B gave setting times of 190 min without the admixture and 330 min with the admixture, compared with 81 and 23 min respectively for the unheated sample. The reason for this behavior is not known, but one may theorize that the higher concentration of sulfate in solution resulting from the presence of hemihydrate in the heated cement produced a more impermeable or durable protective coating on the  $\text{C}_3\text{A}$  grains, thereby retarding their reaction. Schwiete and Niel (4) have observed that the ettringite layer on  $\text{C}_3\text{A}$  is stabilized by hemihydrate.

These results suggest the possibility of lengthening the setting time of these sensitive cements by increasing the proportion of hemihydrate through higher grinding temperatures without recourse to an increase in total  $\text{SO}_3$ . It is recognized, however, that this procedure might induce false setting because of gypsum crystallization and thereby cause more problems than it solves. In any case, the practical feasibility of this approach would have to be thoroughly tested.

## DISCUSSION AND CONCLUSIONS

From these experiments it was concluded that the quick-setting problem resulted from insufficient sulfate being available in solution in the period immediately following mixing to properly control the hydration reactions of  $\text{C}_3\text{A}$  when accelerated by temperature or the admixture or a combination of the two. The admixture effect appears to be the same type of acceleration of stage 1 hydration described by Seligmann and Greening (5) when sucrose was used. However, the fact that normal or near-normal setting behavior was observed with other cements having comparable or even lower  $\text{SO}_3$  contents makes it clear that other factors are involved as well. Most important of these is probably the inherent reactivity of the clinker. Later production of white cement from this same mill, containing 1.56 percent  $\text{SO}_3$ , which is in the same range as the quick-setting cements, showed no adverse setting behavior, even with the water-reducing admixture and

and at 95 F (35 C). This proves that factors other than  $\text{SO}_3$  content are involved. The gypsum in this cement had been essentially completely converted to hemihydrate during grinding; therefore, in view of the heating experiment with cement B previously described, it appears that the hydration state of the calcium sulfate may also affect the setting behavior of some cements when used with admixtures.

The most practical and obvious solution to this type of problem is to make sure that there is adequate  $\text{SO}_3$  in the cement for all expected conditions of use. Now the  $\text{SO}_3$  content of type 1 white cement is specified at between 1.8 and 2.2 percent. Further setting problems have not been experienced since this level of  $\text{SO}_3$  has been maintained.

In addition, the problem of insufficient, readily soluble  $\text{SO}_3$  in the presence of admixtures is not restricted to white cement. It can occur and has occurred with gray cements.

#### ACKNOWLEDGMENT

I am grateful to the Ideal Cement Company for permission to publish this paper and to my colleagues in the Research Department for assistance in obtaining the data presented.

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# USE OF ADMIXTURES IN PRODUCTION OF LOW-POROSITY PASTES AND CONCRETES

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This paper reviews the results of studies on the development of a low-porosity, high-strength cement paste and concrete. The paste is made by mixing finely ground cement clinker, containing alkali or alkaline earth lignosulfonates, with 0.20 to 0.30 parts of water containing alkali carbonate. Concretes and mortars made with low-porosity cement paste have improved strength, dimensional stability, and other engineering properties.

•It is commonly accepted that the water-cement ratio (w/c) of portland cement paste at a given temperature determines the porosity of the hardened paste (1, 2, 3, 4). A low w/c leads to low porosity, which, in turn, leads to greater strength and dimensional stability.

Theoretical and experimental work of Pickett (5), Helmuth and Turk (6), and others led to the conclusion that the drying shrinkage of cement paste and concrete diminishes linearly with the porosity of the paste. Thus, the two main engineering properties of concrete, namely strength and dimensional stability, can be improved by using a low w/c that results in low-porosity paste.

The previously mentioned results of experiments led to an interest in cement pastes and concretes having porosities as low as possible. Two different methods for obtaining low-porosity systems are currently under study. One method involves compaction of low w/c mixes as reported recently by Skalny and Bajza (7), Bajza (8), Lawrence (9), and Roy, Gouda, and Bobrowsky (10). The second method (11, 12, 13, 14, 15, 16, 17), discussed in this paper, makes possible a decrease in porosity by using a low w/c and by maintaining workability by the use of a suitable system of chemical additives.

## MATERIALS AND EXPERIMENTAL METHODS

All of the results were obtained on commercially available, grouped types 1 and 2 portland cement clinkers.  $K_2CO_3$  was used to replace gypsum as set regulator, and a Ca-lignosulfonate has been used as a water reducer. Various grinding aids have been used as a means for obtaining Blaine surface areas above 6000  $cm^2/g$ .

During the investigations, the properties of both fresh and hardened cement pastes and concretes have been studied. These include consistency, strengths, volume changes, rates of hydration, density, pore volume and surface area distributions, and absorption and environmental resistance. Details of experimental methods used are given elsewhere (13, 14, 15).

## HYDRATION OF LOW-POROSITY PASTES

### Effect of Experimental Parameters on Degree of Hydration

Degree of hydration  $x$  is defined by the equation

$$x = \frac{W_n}{W_n^0} \quad (1)$$

where  $w_0^o$  is the nonevaporable water at complete hydration, and  $w_n$  is the nonevaporable water at any given age of the D-dried paste per gram of unhydrated cement. Because the clinker minerals present in cement hydrate at different rates (18), the degree of hydration of cement as a whole does have questionable scientific meaning, mainly at early stages of hydration. However, from the practical point of view, the strength and volume changes of cement pastes and concretes are determined by the degree of hydration of the paste. Therefore, the assumption was made that all the unhydrated compounds present in the paste after 1 day of hydration continue to hydrate at equal fractional rates. If we accept the view that the rate-controlling step in this stage of the hydration reaction is the diffusion of particles through the coating of hydrates formed on the unhydrated clinker particles, the use of equation 1 is justified.

The following effects on the degree of hydration of low-porosity pastes have been studied: type of cement and grinding aid, temperature,  $w/c$ , and fineness of cement.

Grinding aids strongly influence the rate of hydration mainly at early stages, as can be seen in Figure 1 [pastes are hydrated at 77 F (25 C) and  $w/c = 0.2$ ]. Of the four sets of type 2 pastes, two hydrate much faster than the two others. After 1 day, there is a sixfold difference between the pastes TMN 2 and REAX-70 2 (1 and 2 characterize the type of clinker used). The degree of hydration of the DEC 1 paste is only about one-third that of the DEC 2 paste after 1 day, but the difference can be attributed to different levels of lignosulfonate (1 versus 0.5 percent).

The fact that the induction or dormant period (as measured by degree of hydration) does not begin at zero time shows that, in addition to the grinding aid and lignosulfonate, the preventing coating (believed to cause the decrease in reaction rate in the dormant period) contains some hydration products. Actually, cement pastes not containing admixtures also exhibit a dormant period. The dormant periods of REAX-70 2 and DEC 2 pastes are very different from those of TMN 2 and AR-100 2 pastes. It seems that the last two form a coating much less pervious to water than the first two. In fact, no dormant period appears in Figure 1 for the REAX 2 and DEC 2 pastes; thus, if there is any dormant period at all, it is shorter than 1 hour.

The effect of temperature on the rate of hydration is shown in Figure 2 [pastes are hydrated at 41, 77, and 122 F (5, 25, and 50 C) from 1 to 180 days;  $w/c = 0.2$ ]. As in other chemical reactions, the rate of hydration increases at early stages of hydration as temperature increases, and the rate decreases as the ultimate degree of hydration is approached. The induction period at 41 F (5 C) lasts for at least 3 days, but it has not been detected at the two higher temperatures.

The effect of  $w/c$  on the degree of hydration is shown in Figure 3 [pastes are hydrated at 77 F (25 C) from 1 to 90 days;  $w/c = 0.2$  and  $0.3$ ]. At all ages, the degrees of hydration of the pastes made with  $w/c = 0.30$  are greater than those of the pastes made with  $w/c = 0.20$ . The higher  $w/c$  produces pastes of higher total porosity; this results in the accommodation of larger quantities of hydration products.

The effect of cement fineness on the degree of hydration was studied on types 1 and 2 clinkers ground to low and high surface areas with 0.5 percent diethylcarbonate (DEC) as a grinding aid. The levels of  $K_2CO_3$  and lignosulfonate, the  $w/c$ , and the temperature were kept constant. The low-surface area type 2 cement had a long dormant period (at the end of 1 day, the degree of hydration was still only 15.8 percent), but the high-surface area cement was hydrated to 44.9 percent. Subsequently the gap continued to become narrower; at 14 days, the values of  $x$  were 68.3 and 70.3 percent; thus, the degree of hydration of the low-surface-area cement almost reached that of the high-surface-area cement.

The influence of the surface of the cement was much greater for the type 1 pastes than for the type 2 pastes. When the same amount (1 percent) of lignosulfonate was used for the high- and low-surface-area type 1 cement, the degree of hydration of the low-surface-area cement even after 14 days was only 23.0 percent, but the value of  $x$  for the high-surface cement was 61.8 percent.

## Mechanism of Hydration Process

The hydration of low-porosity cement pastes may be divided into three stages. After water gels in contact with cement grains, a fast hydration starts that may be called the predormant period. Soon, however, the early hydration products plus the grinding aids and the calcium lignosulfonate form an almost impervious coating on the grains, and the hydration becomes very slow. This is the dormant or induction period that starts at about 10 to 15 percent hydration and ends at about 15 to 20 percent hydration. The beginning and the duration of the induction period strongly depend on the temperature and the amount of lignosulfonate used.

During the induction stage, there is a slow reaction. Because the hydration products have larger volumes than unhydrated cement, pressure caused by newly formed hydration products may build up under the coating. This results in eventual breakup of the coating. After this happens, water again has direct access to the unhydrated grains, and the reaction speeds up. Hydration products now accumulate in the pore system, and, after the degree of hydration reaches about 30 percent, diffusion through the hydration products becomes the rate-controlling step, and the rate of hydration gradually slows down again. This is the third stage in the hydration process, and it continues until the ultimate degree of hydration is reached.

It is uncertain whether the diffusion of water through the hydration products to the unhydrated grains or whether the diffusion of the hydrated ions from the surfaces of the unhydrated grains, through the hydration products, and to water-filled pores (in which they can precipitate and form new hydration products) is the slowest and therefore rate-determining step. For convenience it was assumed that the slow step is the diffusion of water to the unhydrated grains.

The formation of the hydration products is accompanied by the formation of very small pores, called gel pores. As the hydration progresses, these pores become narrower, and the path through which molecules or ions must diffuse becomes longer. Thus, diffusion becomes slower as the amount of hydration products increases. Because the clinker minerals hydrate at different rates (as mentioned previously), only the third stage of hydration was found amenable to discussion of the kinetics in quantitative terms.

Analysis of the process has shown that, in addition to the amount of unhydrated cement in the paste and hydration products formed and the original w/c, the rate of hydration is a function of the volume of the hydration products at equal degrees of hydration. This volume, in turn, depends on the composition of cement present in the paste. The results indicate that the retardation of the rate of hydration is becoming increasingly greater as the pore space becomes more and more filled by newly formed hydration products. These products cause even greater retardation of the diffusion of water to the unhydrated grains.

For example, DEC 1 pastes, hydrated at the same temperature and with the same w/c, hydrated more slowly than DEC 2 pastes. On the basis of the compositions of the two clinkers, one would expect only a slight difference, if any, in the hydration rates at the beginning of the third stage.

It seems, therefore, that the double amount of lignosulfonate in the type 1 cement has a considerable effect not only on the early stages of hydration (e.g., Figure 1) but even in the beginning of the third stage.

The difference between the ultimate degree of hydration of these two pastes (75.4 percent for DEC 2 versus 69 percent for DEC 1) may also be due partly to the same cause. The double amount of lignosulfonate in the DEC 1 pastes may make the hydration products less pervious to water; thus, a negligible hydration rate may be reached when the amount of hydration products in the pore system of the paste is smaller than that in the DEC 2 paste. As discussed earlier, however, the volume of the hydration products, at equal values of  $x$ , in the type 1 pastes was 5 percent greater than that of the type 2 pastes, and this may explain the differences found in the rate of hydration.

The apparent energy of activation can be evaluated without reference to any mechanism if the rate of hydration is known at, at least, two different temperature levels and if the rate of the reverse reaction is negligible compared with the rate of the forward

reaction. This is certainly true for the hydration of portland cement. If a single step in a complex process is the rate-controlling step, the rate of reaction can be expressed as the product of the function of the temperature only and the function of the composition variables only. The apparent energies of activation (an indication of relative energy barriers) were evaluated for DEC 1, DEC 2, and REAX-70 2 pastes, with  $w/c = 0.20$ , by using the equation

$$\frac{d \ln \left[ - \frac{d(100 - x)}{dt} \right]}{d(1/T)} = \frac{d \ln k(T)}{d(1/T)} \quad (2)$$

DEC 1 pastes gave excellent straight lines. Figure 4 shows this as an Arrhenius plot of  $\log R$  versus  $1/T$ , where  $R$  is the rate and  $T$  is the absolute temperature. The points were obtained from three DEC 1 pastes, each with a 40 percent degree of hydration at 41, 77, and 122 F (5, 25, and 50 C). The slope multiplied by 2.303 gave an apparent energy of activation of 4,700 cal (19.7 MJ), rounded to the nearest 100 cal (418 kJ), for 40 percent hydration. The apparent energies of activation for 50 and 60 percent hydration were 6,300 and 7,700 cal (26.4 and 32.2 MJ) respectively. The increases in apparent energies of activation with progressing hydration indicate that the energy barrier to diffusion becomes greater as the hydration products keep on accumulating in the pore system. One possible reason for this is the formation of more constructed entrances of the ink-bottle pores, i.e., pores with wide bodies and narrow entrances.

The 122 F (50 C) curve for REAX-70 2 was out of line with the others; consequently, only the 41 and 77 F (5 and 25 C) curves could be used for the calculation of the energies of activation. The values for 40, 50, and 60 percent hydration were 9,000, 10,600, and 11,200 cal (37.7, 44.4, and 46.9 MJ) respectively. The trend with progressing hydration was the same as that for DEC 1, but the values were much higher.

The DEC 2 pastes did not give good straight lines. Nevertheless, it is worth noting that the apparent energies of activation for DEC 2 at 40 and 50 percent hydration were 10,800 and 9,000 cal (45.2 and 37.7 MJ) respectively. These are almost exactly the reverse of the values given above for REAX-70 2. Thus, in spite of the questionable results, it can be concluded that the apparent energies of activation for REAX-70 2 and DEC 2 were about equal and were higher than the values obtained for DEC 1. Apparently, for some reason, the energy barrier is higher for the type 2 pastes than for the type 1 pastes.

### Action of Admixtures

The effect of  $K_2CO_3$  on the setting time and strength development of cement mortars was studied by Niël (20). He concluded that  $K_2CO_3$  affects the early hydration process through an interaction with the  $C_3A$  and gypsum in the cement. In that the materials system used in this study did not contain gypsum, the results obtained by Niël are only partly applicable to the present work. However, in agreement with our results, Niël found that  $K_2CO_3$ , up to a certain level, improves workability, prolongs setting times, and increases early strength.

The interaction of  $K_2CO_3$  with  $C_3S$  was studied by several authors (15, 21, 22). It was shown that, in the absence of retarding admixtures (such as lignosulfonates),  $K_2CO_3$  accelerates the hydration of  $C_3S$ . It causes changes in the compositions of liquid phase and in the composition and microstructure of hydrates formed. Presence of  $K_2CO_3$  causes complicated heat effects in the first hour of hydration; the mechanism of these effects is not known as yet.

Based on theoretical considerations and limited amount of experiments, Brunauer et al. (13) suggested a probable mechanism for the effect of the additives and admixtures on the hydration of low-porosity cements. The effect of  $K_2CO_3$  in the low-porosity



pastes is similar in part to the effect of gypsum in normal cement pastes. In place of the sulfoaluminate, the carbonate ions form a carboaluminate, which is partly responsible for the retardation of the fast set. However, the 0.5 percent  $K_2CO_3$  used in the present work is not sufficient to convert the  $C_3A$  into carboaluminate even in the type 2 cement, which contains only 1.4 percent  $C_3A$ . Besides the retarding action of  $Ca(OH)_2$  and of the carbonate ion, it is the coating formed by the grinding aid and calcium lignosulfonate that probably makes an important contribution to the prevention of flash setting.

$K_2CO_3$  has two other effects besides the formation of carboaluminate. Alkalies increase the rate of hydration of cement. The potassium part of  $K_2CO_3$  forms KOH. This decreases the solubility of  $Ca(OH)_2$ . Thus, the carbonate ion acts as a retarder, but the potassium part of the compound acts as an accelerator.

The third effect of  $K_2CO_3$  is connected with the calcium lignosulfonate additive. The lignosulfonate ion is adsorbed on the cement grains. The unhydrated grain surfaces are predominately composed of oxide ions; it is possible, therefore, that calcium and lignosulfonate ions are jointly adsorbed or are adsorbed as molecules. Nevertheless, this is not necessarily true. Kane, La Mer, and Linfor (22) have shown that large negative ions may be adsorbed even on negatively charged surfaces because the attractive van der Waal's forces may overcome the electrostatic repulsion.

The mechanism of the joint action of  $K_2CO_3$  and lignosulfonate is probably the following. Without the presence of  $K_2CO_3$ , the calcium lignosulfonate would quickly precipitate out of the solution because there are enough calcium ions in the aqueous phase of hydrating cement to exceed its solubility product. However, the  $K_2CO_3$  produces  $OH^-$  ions, which diminish the concentration of the  $Ca^{++}$  ions in the solution; therefore, the lignosulfonate is not precipitated. This gives the lignosulfonate ions a chance to be adsorbed on the grains of the cement.

## PROPERTIES OF LOW-POROSITY CEMENT PASTES

### Workability and Setting Time

Because of the low w/c and the absence of gypsum in the low-porosity cement, special emphasis was given to the question of setting time and consistency. An arbitrary empirical scale was adopted for the consistency, and a paste flowing into a mold with no other help than gravity was considered to be of ideal consistency. As expected, the setting times and the consistency of the pastes depend on several factors, such as surface area of cement, type and amount of additives, temperature of curing, and type of cement. From the investigations, several conclusions were made:

1. The same quantities of different grinding aids, under otherwise constant conditions, have different effects on the consistency and setting time,
2. The grinding aid determines the consistency and setting times in conjunction with the other additives,
3. Increasing the  $K_2CO_3$  and lignosulfonate content above certain value does not necessarily improve the properties of paste, and
4. For different clinkers, different amounts of grinding aid,  $K_2CO_3$ , and lignosulfonate give the optimal consistency.

It is believed that, for different applications of low-porosity concrete, cements giving desirable workabilities and setting times can be produced.

### Porosity and Pore Structure

In the study of total surface areas, total pore volumes, and the pore volume and surface area distributions of low-porosity pastes, nitrogen and water vapor were used as adsorbates. One clinker type, two different grinding aids, two w/c, and three

temperatures were the variables.

It was found that the nitrogen molecules were unable to penetrate not only into the micropores (widths  $< 20 \text{ \AA}$ ) but even into many wider pores in spite of the fact that the diameter of a nitrogen molecule is only  $3.5 \text{ \AA}$ . This is explained by the presence of ink-bottle pores. As the hydration progresses, a part of the wide pores is converted into micropores. After 1 day, about one-half of the surface of the pastes is located in the micropores; the fraction increases to about three-fourths after 28 days. The grinding aid has an important effect on the pore volume and surface distribution. With REAX-70 2 as grinding aid, a larger fraction of the pore volume of the pastes is in micropores and a smaller fraction is in wide pores than with DEC as grinding aid.

Some differences in the strength of low-porosity pastes can be explained by the differences in the pore-volume distribution. This factor was found to be complementary to the degree of hydration and total porosity.

### Compressive Strength

The strength of hardened portland cement paste is usually correlated with degree of hydration and total porosity. As hydration progresses, the total porosity decreases because the hydration products occupy a greater volume than the unhydrated cement. Consequently, a part of the hydration products deposit in the pores. Thus, the two effects work in the same direction. The compressive strength results show good correlations with degree of hydration and with total porosity. Figure 5 shows the early strength development of DEC 1 and TMN 1 pastes, hydrated at 77 F (25 C) from 1 to 72 hours, with  $w/c = 0.2$ . The dormant period of the DEC 1 pastes is about 1 day, after which the strength increases sharply. The dormant period for strength development is not the same as for the degree of hydration because strength development is not a function of the degree of hydration only.

The dormant period of the TMN 1 pastes is only about 15 hours; thus, the difference of the 1-day strengths between DEC 1 and TMN 1 is very great. Obviously TMN, together with the lignosulfonate and the hydration products, forms a coating that is more pervious to water than that formed by DEC.

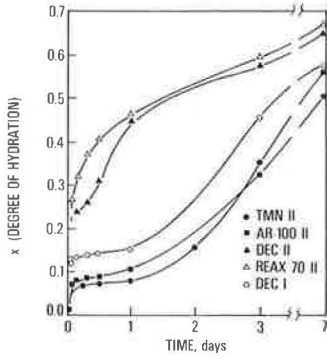
The early strength development of the type 2 pastes is shown in Figure 6 [pastes are hydrated at 77 F (25 C) from 1 to 72 hours;  $w/c = 0.2$ ]. Compressive strength and degree of hydration at 1 day are very low for TMN 2 and AR-100 2, and they are high for REAX-70 2 and DEC 2. However, a new factor appears here. On the basis of degree of hydration and porosity, the REAX-70 2 pastes should have slightly higher compressive strengths than the DEC 1 and 2 pastes, but, both at 1 day and 3 days, they are about 4,000 psi (27.6 MPa) lower than those of the DEC 1 and 2 pastes. Thus, there must be at least one other factor, besides degree of hydration and porosity, that has an influence on strength. It was found to be the pore volume distribution.

Grinding aids probably have some effect on the final strength, but, if so, the effect is not very great. The final strengths of the pastes made from types 1 and 2 cement and ground with the same grinding aids were found to be nearly equal.

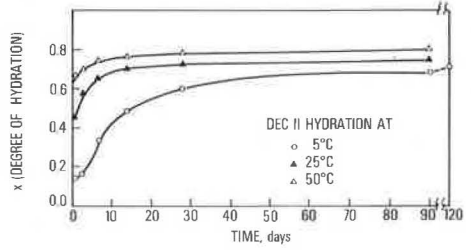
The temperature dependence of the compressive strength was investigated for the DEC 1, DEC 2, and REAX-70 2 pastes. The strength gain is enhanced by increasing the temperature. The dormant periods at 41 F (5 C) are much longer than at 77 F (25 C). At every age, the strength is higher at higher temperatures. For example, the final strength of the DEC 1 paste at 122 F (50 C) measured after 90 days of hydration is 40,000 psi (275.8 MPa). At the same age, the 77 F (25 C) paste has a compressive strength of 34,600 psi (238.6 MPa). For the 41 and 77 F (5 and 25 C) pastes, strengths were measured at 180 days; they are 27,000 and 36,400 psi (186.2 and 238.6 MPa) respectively. It is not likely that the strengths of the 122 F (50 C) pastes would have increased significantly after 90 days, nor is it likely that the strengths at 77 F (25 C) would have increased significantly after 180 days. The strengths at 41 F (5 C) would probably have increased after 180 days, but it is very unlikely that they would have reached an ultimate strength as high as those for the 77 F (25 C) pastes. Thus, the ultimate strength appears to increase significantly as temperature increases.



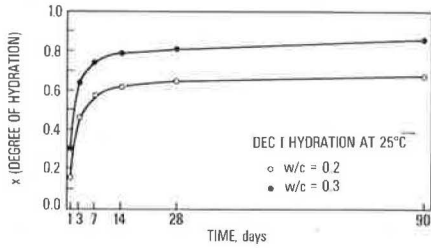
**Figure 1. Degree of hydration versus time of four sets of type 2 and one set of type 1 pastes from 1 hour to 7 days.**



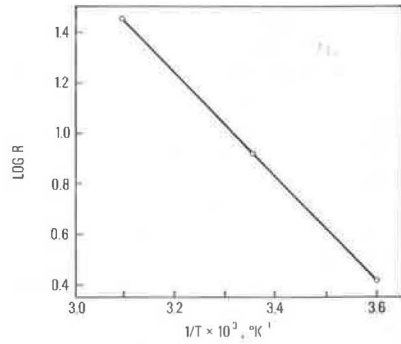
**Figure 2. Degree of hydration versus time of DEC 2 pastes.**



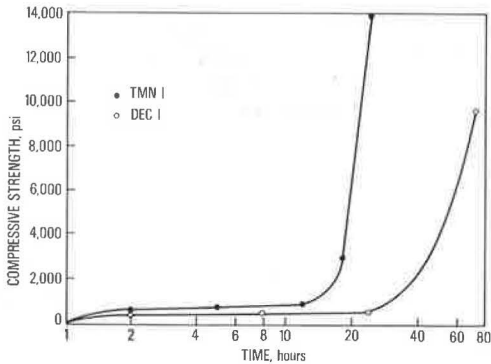
**Figure 3. Degree of hydration versus time of DEC 1 pastes.**



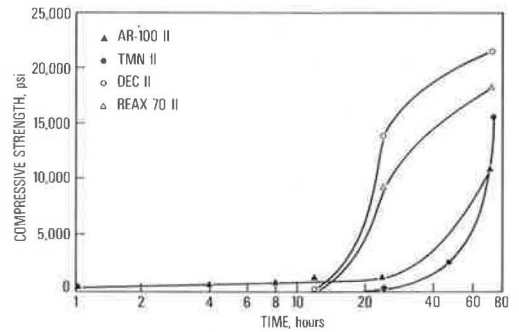
**Figure 4. Arrhenius plot of log R versus 1/T.**



**Figure 5. Compressive strength versus time of DEC 1 and TMN 1 pastes.**



**Figure 6. Compressive strength versus time of four sets of type 2 pastes.**



Similar results were obtained for the other pastes.

The dormant period of the DEC 1 pastes made with  $w/c = 0.3$  is about the same as that of the pastes made with  $w/c = 0.2$ ; it is about 1 day. At 3 days, the paste with the higher  $w/c$  appears to have somewhat higher strength, though this may be within the experimental error. From then on, the pastes with the lower  $w/c$  increase in strength much faster than the others. The strengths of the pastes with  $w/c = 0.3$  level off after 28 days; the 29, 90, and 180-day strengths are all approximately 25,000 psi (172.4 MPa). Thus, as expected, the final strength is much lower than that of the paste with  $w/c = 0.2$ . The pastes with the higher  $w/c$  have a higher degree of hydration, but this is greatly overcompensated by the much higher porosity of these pastes. The porosities at 90 days of the pastes with  $w/c = 0.2$  and  $0.3$  are 17.2 and 27.7 percent of the paste volume respectively.

The DEC 2 pastes gave somewhat different results. The dormant period of the pastes with  $w/c = 0.2$  is very short; therefore, at the age of 1 day the paste already has a strength of 14,000 psi (96.5 MPa). The dormant period of the paste with  $w/c = 0.3$  is much longer; therefore, at 1 day the strength is almost nil. Because of this, the strengths of the pastes with  $w/c = 0.3$  are lower at all ages. The final strength of the paste with  $w/c = 0.3$ , measured at 90 days, is 29,000 psi (199.9 MPa). At the same age, the paste with  $w/c = 0.2$  has a strength of 35,200 psi (242.7 MPa). The difference is again due to the difference in porosity.

The effect of the surface area of the cement on compressive strength was investigated for the DEC 1 and DEC 2 pastes at 77 F (25 C), from 1 day to 28 days in which  $w/c = 0.2$ . The dormant period of the DEC 1 pastes of the high-surface cement (7600  $\text{cm}^2/\text{g}$ ) is 1 day; that of the pastes of the low-surface cement (4300  $\text{cm}^2/\text{g}$ ) is 3 days. It is clear that the coating on the low-surface cement grains is much thicker.

The DEC 2 pastes of the high-surface cement (8400  $\text{cm}^2/\text{g}$ ) have a very short dormant period; those of the low-surface cement (4000  $\text{cm}^2/\text{g}$ ) have a dormant period of 2 days. The 28-day strength of the paste of the high-surface cement is 27,000 psi (186.2 MPa); that of the low-surface cement is only 3,000 psi (20.7 MPa) lower. However, the strength values of the pastes of the low-surface cement appear to flatten out and may not be much higher at later ages; however, there is a greater further increase in the strengths of the pastes of the high-surface cement.

As mentioned previously, there must be at least one other factor besides degree of hydration and total porosity that has a significant influence on compressive strength. A possible explanation of the strength differences may be found in the pore volume distribution. Further studies are needed to substantiate this claim.

### Dimensional Changes

Two different dimensional changes were studied in this project: the expansion of the fresh cement paste and the drying shrinkage of hardened cement paste. The expansion was calculated, but the drying shrinkage was obtained experimentally.

The expansions of the pastes were calculated from the equation

$$\text{Exp} = 100(v_p - v_{p \text{ theor}})/v_{p \text{ theor}} \quad (3)$$

where  $v_p$  is the actual volume of the paste produced by the hydration of 1 g of cement, and  $v_{p \text{ theor}}$  is the volume of the paste without expansion. Two opposing factors influence this expansion. The hydration products have greater volume than the unhydrated cement, and, because the pore space in this paste is limited by the low  $w/c$ , the accumulation of the hydration products builds up an internal pressure that tends to enlarge the paste, thus increasing the pore volume available for further hydration. This internal pressure is resisted by the increasing strength of the paste. After the paste reaches certain strength, it also acquires a stable volume. The above hypothesis explains the fact that the expansion of a paste depends on the initial  $w/c$ . The greater

this ratio is, the greater the available internal pore space and the smaller internal pressure will be. Consequently, greatest expansion values are expected, and were found, in low-porosity pastes studied.

The work on drying shrinkage showed

1. Type 2 pastes exhibited considerably less shrinkage after 1 day of curing than the type 1 pastes, but after 28 days of curing the differences were slight;
2. Shrinkage differences due to different grinding aids were slight;
3. After 28 days of curing, pastes of clinkers ground to specific surfaces of about 6500 cm<sup>2</sup>/g showed less shrinkage than those of clinkers ground to specific surfaces of about 7500 cm<sup>2</sup>/g or greater; and
4. The low-porosity pastes showed one-third to one-half as large length changes as pastes made from the same cement with w/c = 0.4 and one-fourth to one-third as large as those made with w/c = 0.6. Therefore, volume changes can be greatly reduced by using low-porosity cement pastes.

## PROPERTIES OF LOW-POROSITY CONCRETES

It has been shown previously that the engineering properties of low-porosity cement pastes are influenced by variables such as cement composition and surface area, w/c, type and amount of additives, and temperature of curing. Properties of low-porosity concretes are also influenced by variables such as the type, composition, and gradation of sand and aggregate. The concrete studies were related mainly to workability and strength development problems.

### Workability

It was soon realized that a combination of admixtures that gives excellent properties to a fresh and hardened cement paste is not necessarily the best combination for use in concrete. The concentrations of Ca-lignosulfonate and K<sub>2</sub>CO<sub>3</sub> had to be increased from 0.5 to 0.65 and from 0.5 to 1.00 percent respectively to obtain workable mixes. These are typical values; the optimum concentrations depend on the grinding aid used. Even at the mentioned levels of admixtures, the setting time was shorter than that of normal concretes having the same slump.

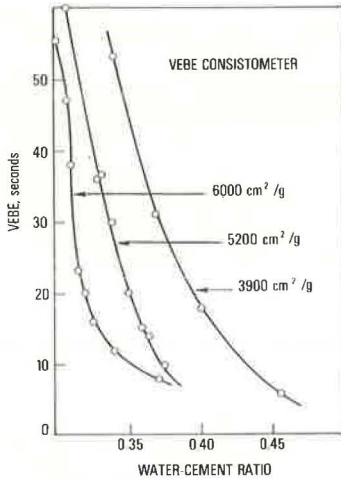
Figure 7 shows the effect of the w/c on workability, as measured by the Vebe consistometer for three Blaine cement surface areas. The 6000-cm<sup>2</sup>/g cement at 32 sec of vibration, which is the upper limit of extremely dry concrete according to standards, yielded a concrete with approximately 1½-in. (3.8-cm) slump. Vibration times for concretes with w/c < 0.3 were excessively long, sometimes as long as 3 min. The workability problem has not been conquered because comparatively long vibrating times are required to compact the concrete.

### Strengths

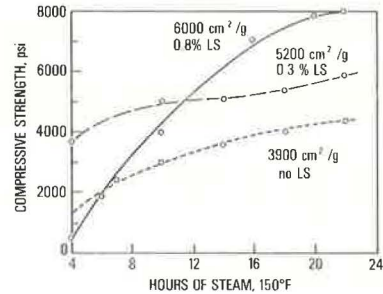
In spite of some problems with the workability of low-porosity concretes, specimens with a w/c as low as 0.26 were cast. Contrary to the early strength development in cement pastes, that of moist-cured concrete was strongly retarded by the admixtures present. Steam curing had to be used to obtain very high early strengths. The difference between paste strengths and concrete strengths may be explained by a weaker bond, caused by the admixtures used, between the aggregate and cement paste at early stages of hydration.

Concretes made of cements ground to three Blaine surface areas were steam cured for various lengths of time. Some results are shown in Figure 8. All 6 by 12-in. (15.2 by 30.5-cm) specimens had preset times of 1 hour and a 40 F (4.4 C)/hour temperature rise to 150 F (65.6 C), at which they were soaked for various times. When

**Figure 7. Workability versus water-cement ratio for concretes made with cements having different Blaine surface areas.**



**Figure 8. Compressive strengths of concretes made with cements of different surface areas.**



**Table 1. Strengths of concretes made with Blaine and control cement samples.**

Sample	Steam Temperature (F)	Curing Time (hours)	Modulus of Rupture <sup>a</sup> (psi)			Compressive Strength <sup>b</sup> (psi)		
			1-Day	7-Day	28-Day	1-Day	7-Day	28-Day
Blaine	130	4	759	933	1,148	6,213	10,800	13,033
	130	20	1,082	1,060	1,466	10,384	12,600	14,190
	150	15	1,075	1,180	1,543	12,675	14,813	14,300
	150	20	1,008	1,208	1,306	10,808	11,780	14,525
	170	4	1,010	1,020	1,163	9,482	11,838	14,734
	170	10	953	1,090	1,350	11,766	12,875	13,000
Control	130	4	661		980	3,725		6,175
	130	20	848		1,022	5,904		7,500
	150	15	724		1,036	4,450		6,713
	170	4	744		882	3,875		6,875
	170	20	760		946	5,520		7,720

Note: Cement: aggregate = 1:5 and sand:rock = 2:3. 1 F = 1.8 (C) + 32. 1 psi = 6.9 kPa.  
<sup>a</sup>For 2 by 2 by 12-in. (5.1 by 5.1 by 30.5-cm) beams.      <sup>b</sup>For 2 by 2-in. (5.1 by 5.1-cm) cubes.

they were removed, they were allowed to cool for 1 hour and then tested. All batches were made with a 1:5 cement-aggregate ratio, and different levels of the Ca-lignosulfonate admixture were used, depending on the cement fineness. The 3900-cm<sup>2</sup>/g system had a typical rise. The 5200-cm<sup>2</sup>/g system was slightly retarded but then rapidly gained strength. The 6000-cm<sup>2</sup>/g system was retarded for almost 4 hours, but the strength rise was very sharp to an eventual 8,000-psi (55.2-MPa) strength after 22 hours of steaming.

A comparison of some typical concretes prepared with both a normal type 2 cement and a 6000-cm<sup>2</sup>/g Blaine special cement made from the same type 2 clinker is given in Table 1. All 6000-cm<sup>2</sup>/g Blaine cement samples were prepared by using w/c = 0.26; 0.5 percent Ca-lignosulfonate and 0.9 percent K<sub>2</sub>CO<sub>3</sub> by weight of cement were added. The 3000-cm<sup>2</sup>/g control samples made with w/c = 0.41 had a 1-in. (2.5-cm) slump. In all cases, saturated surface dry aggregate was used. All samples had preset time of 1 hour. On an average, 100 percent higher compressive strength and 30 percent higher moduli of rupture were obtained for samples made from the 6000-cm<sup>2</sup>/g cement.

## Other Properties

Shrinkage tests included both steam-cured and moist-cured samples. Steam curing was performed at 150 F (65.6 C) for 15 hours and at 130 F (54.4 C) and 170 F (76.7 C) for 4 hours. Without exception, all samples had lower shrinkage than the limit given by Structural Engineers Association of California [0.032 percent for 4 by 4 by 12-in. (10.2 by 10.2 by 30.5-cm) specimens; 0.415 percent for 3 by 3 by 12-in. (7.6 by 7.6 by 30.5-cm) specimens], and a majority of the samples had lower shrinkage than the control samples made from type 2 cement. Because of the limited amount of tests and samples, no quantitative conclusions similar to those given by Brunauer, Skalny, and Yudenfreund (12) can be given at this time.

The beams for freeze-thaw resistance were made by using the mix design and mixing conditions that gave the highest 28-day compressive strengths. Two different steam-curing temperatures and periods were used. Low-w/c concrete performed much better than the controls, as would be expected because of its higher density. At 100 cycles, all beams appeared to be unaffected. At 135 cycles some beams had begun to develop small cracks along the upper surface, but no scaling was yet visible. The affected specimens were those that had the longer steam-curing periods (15 hours), both at 130 F (54.4 C) and 170 F (76.7 C). No air-entraining agents were used.

## SUMMARY

The results show that it is possible to prepare workable cement paste and concrete mixes at lower than usual w/c and that these ratios at the same time will give higher early and ultimate strength and better dimensional stability. However, the technical problems connected with larger scale production of low-w/c concretes are far from being solved. The mechanisms of the interaction of the different admixtures used with the clinker minerals, both individually and in the presence of others, should be investigated more thoroughly. The presence of sand and aggregate in concrete mixes adds to the long list of variables.

The combination of admixtures used in this study is not optimal, and admixture systems giving better workability and strength should be available in the future; however, these were not available when this study was initiated.

## ACKNOWLEDGMENT

We would like to thank the New York State Department of Transportation and the U.S. Department of Transportation, for their support of the research on low-porosity cement pastes at Clarkson College of Technology. We would also like to acknowledge the invaluable input of Stephen Brunauer, principle investigator of the project, and the help of other colleagues on whose work this review is based. The constructive criticism of the reviewers is appreciated.

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