Third Pacific Area Meeting Papers

Symposium on

Effect of Water-Reducing Admixtures and Set-Retarding Admixtures on Properties of Concrete

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SYMPOSIUM ON EFFECT OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES ON PROPERTIES OF CONCRETE

Presented at the
Third Pacific Area National Meeting
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FOREWORD

The use of water-reducing admixtures and set retarders in concrete has grown continuously since their introduction over 25 years ago, with a present estimated usage in the production of 25 million cubic yards of concrete annually in the United States alone. Further indication of current interest is evidenced by the fact that ASTM Committee C-9 on Concrete and Concrete Aggregates and certain public agencies are actively drafting standard methods of test and specifications to govern the purchase and performance requirements of these admixtures for concrete.

The future of better concrete lies in an increased understanding of concreting materials and the best manner of combining them to produce the maximum in strength and durability. It is with this in mind that Committee C-1 on Cement and Committee C-9 have jointly sponsored this Symposium, held during the Third Pacific Area National Meeting of the Society from October 11–16, 1959, in San Francisco, Calif.

The Symposium consisted of ten papers and a summary. It is of interest to note that four of the papers represent the joint contribution of four principal producers of admixtures. The remaining papers were prepared by representatives of consumer interests, research organizations, and the cement industry.

The Symposium was held during two sessions on Wednesday, October 14. Professors R. E. Davis and Milos Polivka, both of the University of California, presided over the two sessions respectively.

The Joint Symposium Committee, representing Committees C-1 and C-9, included the following members:

R. E. Davis, University of California (*Chairman*)
W. C. Hanna, California Portland Cement Co. (*Vice-Chairman*)
Milos Polivka, University of California (*Secretary*)
R. L. Blaine, National Bureau of Standards
Joseph E. Gray, National Crushed Stone Assn.
E. C. Higginson, U. S. Bureau of Reclamation
Thomas B. Kennedy, Corps of Engineers
William Lerch, Portland Cement Assn.
W. J. McCoy, Lehigh Portland Cement Co.
Richard C. Mielenz, Master Builders Co.

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SYMPOSIUM ON EFFECT OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES ON PROPERTIES OF CONCRETE

INTRODUCTION

By Bruce Foster[1]

Admixtures for portland cement concrete are those ingredients which are added to the primary constituents (portland cement, aggregates, and water) to (1) improve or modify the properties of the concrete, (2) compensate for some deficiency in a primary constituent, or (3) effect a reduction in cost. Some materials which we class as admixtures, such as pozzolan and blood, were concrete ingredients used by the Romans.

Because the addition of another ingredient is very likely to require additional control and technical skill on the part of the concrete producer and inspection agency, and extra facilities for handling and proportioning, and because admixtures in general were originally frowned upon by the cement and concrete industries, these materials were for many years slow in gaining general acceptance. However, the recognition of the role of entrained air in imparting frost resistance to concrete has led to almost universal acceptance of the value of air-entraining admixtures and to departure from the previously widely-held concept that all admixtures were of doubtful value.

Appreciation of the advantages in the use of another group of admixtures, the pozzolans, was evidenced by the "Symposium on Use of Pozzolanic Materials in Mortars and Concrete"[2] which formed an important part of the program of the First Pacific Area National Meeting of the ASTM held in San Francisco in 1949.

Further evidence of the new stature of admixtures is found in the activities of Subcommittee III-h on Methods of Testing and Specifications for Admixtures of ASTM Committee C-9 on Concrete and Concrete Aggregates which prepared specifications and test procedures for air-entraining agents in 1950, for fly ash in 1954, for natural pozzolans in 1957, and which is now preparing specifications for accelerators, for set retarders, and for water-reducing admixtures.

The last two mentioned, water-reducing and set-retarding admixtures, are the subject of this symposium. As its name implies, a water-reducing admixture, when added to a concrete, permits a reduction in mixing water with no loss in slump, or, if the water content is maintained constant, produces an increase in slump. The name is not wholly descriptive, however, because as will be brought out during the symposium, the benfit in strength at constant slump are normally greater than would be expected from the resulting reduction in water-cement ratio.

A set-retarding admixture reduces the

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[1] National Bureau of Standards, Washington, D. C.

[2] Am. Soc. Testing Mats. (1950). (Published as separate publication *ASTM STP No. 99.*)

early rate of hardening and so permits the concrete to be handled and vibrated for an additional period after mixing.

The principal agents now in use fall in one of two classes: (1) lignosulfonic acids and their salts and (2) hydroxylated carboxylic acids and their salts. Both classes of materials, when added to concrete, reduce the water requirement and also retard the set. Modifications and derivatives of these materials may retain the water-reducing property of the admixture without modifying the hardening rate, or may even accelerate the set.

The Symposium Committee representing Committees C-1 on Cement and C-9 on Concrete and Concrete Aggregates, planned to bring together information on admixtures as follows: (1) the mechanisms by which these materials modify concrete properties; (2) the effects of the admixtures on the properties of plastic and hardened concrete and the variation of these effects depending upon the other materials involved, the type of concrete, and the existing temperature; (3) the types of construction and the conditions under which their use is particularly advantageous; (4) the problems in control and application brought about by their use; (5) the problems of preparing adequate purchase specifications; and, (6) research under way to produce even better and more reliable admixtures and thereby better and more economical concretes.

To accomplish this, contributions were sought from a variety of sources including universities and government agencies, as well as the producers of portland cement, ready-mixed concrete, and admixtures. A great amount of laboratory and field data are presented as well as descriptions of field experience with the use of the various products in a wide range of applications. Of necessity, there is some overlapping in the treatment of the subject matter, but this will be found to have more advantages than disadvantages.

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ACTIONS OF CALCIUM SULFATE AND ADMIXTURES IN PORTLAND CEMENT PASTES

By W. C. Hansen[1]

Synopsis

This paper presents a mechanism to explain the ability of $Ca(OH)_2$ and $CaSO_4$ to prevent flash set in portland cement pastes and the ability of $CaSO_4$ and other salts to accelerate the rates at which calcium silicates develop strengths. The mechanism is developed on the basis of solid state reactions in which ions from the liquid phase of a cement paste are chemisorbed by ions in the surfaces of the crystals of the cement minerals and then diffuse into the crystals to produce the reaction products responsible for the setting and hardening of the cement paste. The abilities of organic compounds to retard the rates of these reactions, cause dispersion of the particles, reduce water requirements, and act as grinding aids are explained in terms of adsorbtion of molecules and negative ions.

The purpose of this paper is to suggest a mechanism whereby admixtures affect certain properties of pastes of portland cement and water. Very early in the development of the cement industry (**1**),[2] it was found necessary to use calcium sulfate with most clinkers to produce cements with satisfactory setting characteristics.

A given admixture may show different behaviors with different clinkers, but it is likely to show a consistent behavior if the clinkers are ground with calcium sulfate as is done in making portland cement. This paper is, therefore, concerned with the mechanism whereby calcium sulfate influences the reactions of the cement minerals with water and the mechanism whereby admixtures modify these reactions and alter the physical properties of the cement. It makes no attempt to deal with reactions that might occur with the portland cement minerals in the absence of calcium sulfate.

Rankin and Wright (**2**) showed that, if a portland-cement clinker consisted only of CaO, Al_2O_3, and SiO_2, it would, at equilibrium, consist of the three compounds: $3CaO\cdot SiO_2$, $2CaO\cdot SiO_2$, and $3CaO\cdot Al_2O_3$. Since that time, many investigators have added information on the roles of the minor oxides (Fe_2O_3, MgO, Na_2O, and K_2O) in the constitution of portland-cement clinkers. The various phases of the constitution of these clinkers were reviewed in 1952 by Jeffery, Nurse, Ordway, Malquori, Cirilli, Newkirk, Insley, and by a number of discussors of their papers (**3**).

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[1] Director, Research Laboratories, Universal Atlas Cement Division of United States Steel Corp., Buffington, Ind.

[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

Those reviews show that the principal compound of such clinkers, which is $3CaO \cdot SiO_2$ in the CaO-Al_2O_3-SiO_2 system, probably contains some MgO and Al_2O_3 and may have the composition $54CaO \cdot 16SiO_2 \cdot MgO \cdot Al_2O_3$. They show that the $2CaO \cdot SiO_2$ phase of the CaO-Al_2O_3-SiO_2 system may be a solid solution of $2CaO \cdot SiO_2$-$23CaO \cdot K_2O \cdot 12SiO_2$ in portland-cement clinkers. Also, that the Al_2O_3 may exist as $3CaO \cdot Al_2O_3$, $8CaO \cdot Na_2O \cdot Al_2O_3$ and as a solid solution of $2CaO \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$. The alkalies K_2O and Na_2O combine with SO_3 in the clinkers to form alkali sulfates, and those in excess of the SO_3 form the alkali-bearing phases listed above.

EARLY STUDIES WITH CALCIUM SULFATE

Bates and Klein (4) and Bates (5) studied several of the pure compounds of the CaO-Al_2O_3-SiO_2 system and found that:

1. A paste of powdered $3CaO \cdot Al_2O_3$ and water steamed and hardened very quickly;
2. The rate of this reaction could be retarded by blending the powdered $3CaO \cdot Al_2O_3$ with calcium sulfate and that small amounts of calcium hydroxide added to this blend increased the retarding power of the calcium sulfate;
3. $3CaO \cdot SiO_2$ augmented the retarding power of calcium sulfate, probably because of the $Ca(OH)_2$ released by the hydrolysis of this silicate;
4. $3CaO \cdot SiO_2$ reacted fairly rapidly with water and that the rate of this reaction was accelerated by calcium sulfate; and
5. $3CaO \cdot SiO_2$ and the other compounds in portland-cement clinkers, when mixed with water, did not require any retarders for satisfactory placing in molds.

Phillips (6), working with Bates and Klein, studied the reactions of $3CaO \cdot Al_2O_3$ and water from the standpoint of colloidal chemistry. He pointed out, as earlier investigators had, that $3CaO \cdot Al_2O_3$ and the calcium silicates hydrolyzed in water with the splitting off of $Ca(OH)_2$ and the formation of less basic aluminates and silicates. It appears from his paper that he had reached the conclusion that $3CaO \cdot Al_2O_3$ in a paste with water did not dissolve but reacted with water to split off $Ca(OH)_2$ and form a dispersion of solid calcium aluminate. He states:

> "In the normal pastes, we should suppose that the very fine material would be hydrated and dispersed to a sol which would later coagulate to form a gel with elimination of water, while the coarse material would very slowly hydrate and distend to form a gel . . . The control of hydration is affected to a considerable extent by the adsorption of electrolytic ions . . . In examining the aluminate we find a good example of adsorption, for the treatment with water changes the composition of the outer surface only, a hydrated film being formed while the interior is unchanged. Any ion activity will therefore be confined to the surface . . . It has been previously stated that lime water effects a greater dispersion of the aluminate than does pure water. This is due to the fact that the positive calcium-ions of the lime hydrate are adsorbed by the hydrated aluminate. When the concentration of the adsorbed ions becomes sufficiently great, or when a sufficient number of ions have been adsorbed, their charges repulse each other and the aluminate is dispersed. In order to get the repelling action we must suppose that the positive calcium ions are adsorbed more than the negative hydroxyl ions. The results show that this occurs or, in other words, there is a preferential adsorption of one kind of ion."

Roller (7), from his own work and that of others, concluded that calcium sulfate retarded the setting of portland cement by a combination of two reactions. First, it reacted with alkali hydroxides released from the cement to form $Ca(OH)_2$ as illustrated in Reaction 1, where M is either or both K and Na. Then, the $Ca(OH)_2$ reacted with $3CaO \cdot Al_2O_3$ as illustrated in Reaction 2.

$$CaSO_4 + 2MOH = M_2SO_4 + Ca(OH)_2 \ldots (1)$$

$$3CaO \cdot Al_2O_3 + Ca(OH)_2 + 12H_2O = 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O \ldots\ldots (2)$$

It is well known (8) that $3CaO \cdot Al_2O_3$ reacts with water saturated with $Ca(OH)_2$ as shown in Reaction 3 and with $CaSO_4$ in a solution saturated with $Ca(OH)_2$ as shown in Reactions 4 and 5:

$$3CaO \cdot Al_2O_3 + 6H_2O = 3CaO \cdot Al_2O_3 \cdot 6H_2O \ldots (3)$$

$$3CaO \cdot Al_2O_3 + CaSO_4 + 13H_2O = 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 13H_2O \ldots\ldots (4)$$

$$3CaO \cdot Al_2O_3 + 3CaSO_4 + 32H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \ldots\ldots (5)$$

Since the publication by Roller, it has been established (9) that $3CaO \cdot Al_2O_3 \cdot Ca(OH) \cdot 12H_2O$ and $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 13H_2O$ form a complete series of solid solutions and that $3CaO \cdot Al_2O_3 . 3Ca(OH)_2 \cdot 3OH_2O$ and $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ also form a complete series of solid solutions. These series might be represented as follows:

$$3CaO \cdot Al_2O_3 + XCaSO_4 + YCa(OH)_2 + ZH_2O = 3CaO \cdot Al_2O_3 \cdot XCaSO_4 \cdot YCa(OH)_2 \cdot ZH_2O \ldots\ldots (6)$$

where X may vary between 0 and 1 and Y may vary between 0 and 1 for the first series, and where X may vary between 0 and 3 and Y may vary between 0 and 3 for the second series.

Roller believed that Reactions 3, 4, and 5 would cause flash setting and that this could be prevented by forming a certain amount of $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ as illustrated in Reaction 2 on the surfaces of the grains of $3CaO \cdot Al_2O_3$. Also, that Reactions 2 to 6, inclusive, could take place without either the $3CaO \cdot Al_2O_3$ or the reaction products going into solution. In other words, these could be considered to be solid state reactions in which one of the reactants reacts as a solid with other reactants which are in solution to form directly solid reaction products. This conclusion was based on the observation that extracts from cement pastes contain only very minor amounts of Al_2O_3 and SiO_2.

It is indicated in Reaction 1 that the alkalies entered the liquid phase of cement pastes as hydroxides. It is now known (10) that most of the alkalies that enter the liquid phase during the first few minutes do so as alkali sulfates. However, since $3CaO \cdot Al_2O_3$ can react very rapidly with $CaSO_4$, the small amount of SO_3 that enters as an alkali sulfate is converted to $CaSO_4$ by reaction with $Ca(OH)_2$ released from other cement minerals and is removed from the solution very quickly. This leaves the alkalies in the solution, in the absence of added salts, as the hydroxides and Roller's Reaction 1 is essentially correct when it is recognized that the hydroxide entered the solution principally as $Ca(OH)_2$.

Roller believed that work of others had shown that calcium sulfate did not retard the rate of reaction of $3CaO \cdot Al_2O_3$ with water. However, Bates (5), working with pure $3CaO \cdot Al_2O_3$, states:

> "Five per cent of plaster of Paris retarded the steaming sufficiently to permit the making of test pieces. Five per cent of plaster in the presence of two per cent of hydrated lime produced a much more marked retardation of the initial set but was accompanied as before by an evolution of steam. Increasing amounts of plaster produced increased retardation."

In analyzing the results of tests made on pastes in which all reactants, except water, are initially solids, it must be recognized that compounds such as $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$, and plaster of Paris are unstable in water whereas $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$ are stable. Hence, even if the ions of the last two are capable of retarding the rate of reaction of $3CaO \cdot Al_2O_3$ with water, the $3CaO \cdot Al_2O_3$ in a paste made from the three solids may have undergone considerable reaction before the other two had dissolved sufficiently to exert a retarding effect. However, when plaster of Paris is used, it may dissolve fast enough to be fairly effective as a retarder. It seems that the experiments by Bates show that both calcium sulfate and calcium hydroxide can retard to some extent the rate at which $3CaO \cdot Al_2O_3$ reacts with water and that calcium hydroxide may be more effective than calcium sulfate.

Forsen (11), from a review of the literature and from extensive studies of his own, makes the following statements:

> "When portland cement reacts with water, the components enter into solution in the same stoichiometric proportions as the water-free components have, forming solutions which are supersaturated with respect to hydrates as solids."

This behavior of the cement minerals probably was first postulated by Le Chatelier (12).

This conclusion by Forsen was based on experiments in which 0.2 g of a compound was treated with a liter of water. He states, however, that Flint and Wells (34) "examined the behavior of $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ in water (20 g per liter) and found that, even after short periods of shaking, the proportion of lime to silicic acid was higher in the solution than in the water-free components."

It seems very unlikely that any of the calcium silicates and aluminates of cement clinkers dissolve in pastes as Forsen states.

> "Most technical cements containing alkali are quick setting without gypsum. Alkali aluminates and silicates enter instantaneously into solution and coagulation between silicate and aluminate occurs. The quick set of such cement cannot be prevented by the addition of lime, because the solubility of the lime is low in the instantaneously formed alkali hydroxide solution and because the lime is dissolved much slower than the alkali aluminate and the alkali silicate. The addition of readily soluble gypsum or other calcium salts neutralizes the alkali hydroxide because calcium hydroxide is less soluble than alkali hydroxide. A saturated or supersaturation of calcium hydroxide in a calcium and alkali salt solution is formed and the aluminates are immediately precipitated. A protecting film is formed around the cement grains, which retards the dissolution of the components including the alkali compounds."

It is now well known that, generally, a relatively large part of the alkalies in cement occur as either K_2SO_4 or Na_2SO_4 or as a solid solution of the two (Newkirk (3)) and that it is these alkali salts that are dissolved almost immediately when the cement is mixed with water (13). Within a minute after such clinkers are mixed with water, the liquid phase contains relatively high concentrations of alkalies, lime, and sulfate but only traces of alumina and silica.

Schlapper (14), in discussing the retarding effect of calcium sulfate states:

> "According to Forsen, this is supposed to prevent the precipitation of silicic acid by the aluminates, which in turn is supposed to retard the setting process. We were able to confirm by our experiments that silicic acid and alumina precipitate each other flocculariy, but, on the other hand, we also established in accordance with the investigations on equilibrium mentioned above that the quantities of silicic acid in solution are very slight; the question, therefore, arises whether the quick setting of a mixture of $3CaO \cdot SiO_2$ and aluminate is caused chiefly by this deflocculation."

Forsen, in reply to a discussion of his paper by Roller, states: "I have also verified—analytically and synthetically—the formation of a protective film of tetracalcium aluminate when anhydrous calcium aluminates react with limewater. This fact was first established—microscopically—by Assarson."

Strelkov (15), in reviewing the work carried out by Baikov during the years 1923 to 1932, states: "Baikov demonstrated that the colloidal stage is common to all cementing materials. As an intermediate stage, it brings about the recrystallization of the initially formed hydrates due to the chemical reactions of cement particles with water without their preliminary dissolution."

In this theory, Strelkov believes that both plaster of Paris and portland cement react with water without going into solution to form products with high solubilities around the anhydrous grains. These new products then dissolve and form supersaturated solutions from which the stable reaction products precipitate. He points out that probably hydroxyl ions rather than water molecules participate in the diffusion process. He is proposing a mechanism involving solid state reactions followed by rapid solution of the reaction products.

When studying the reactions undergone by $3CaO \cdot Al_2O_3$, it must be remembered that this compound can react with water to form hydrated compounds and with calcium sulfate, calcium hydroxide, and other calcium salts to form double salts. Portland cements contain only a few per cent of $3CaO \cdot Al_2O_3$, generally well under 15 per cent. Pastes of many powdered cement clinkers will steam and harden almost immediately upon mixing of the powder and water. This is generally referred to as flash set. The addition of small amounts of calcium sulfate to these clinkers usually gives products which, when mixed with water, produce pastes that heat up very slowly and harden gradually. This has led to the practice of calling calcium sulfate a retarder. However, it appears from the work of Bates that the retarding properties of this salt might not be great if $3CaO \cdot SiO_2$ did not furnish $Ca(OH)_2$ to assist the calcium sulfate. On the other hand, it appears necessary to conclude that sulfate and hydroxide function as a team in preventing flash set.

Several investigators found that the early strengths of many cements were increased with increasing amounts of calcium sulfate. This indicated that this salt played a role as an accelerator as well as a retarder.

Lerch (16) in 1946 published the results of a very thorough study of the influence of calcium sulfate on various properties of portland-cement mortars. It seems very evident from that study that calcium sulfate accelerates the rate at which either or both $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ develop strength during the early life of the cement paste. It is, of course, possible that the calcium sulfate also influences the rates at which other phases contribute to strength. However, in this paper, the discussion of the accelerating effect with respect to the development of strength will be confined to the two calcium silicates.

Many studies have been made to determine the effects of salts, other than calcium sulfate, and other compounds upon the rates of setting and hardening of cement pastes.[3] In most of these, no effort was made to determine whether or not an observed retardation or an observed acceleration applied to the reactions of $3CaO \cdot Al_2O_3$ or to those of the silicates. One other confusing element in the literature on setting is that some

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[3] In this paper, no attempt will be made to indicate whether neat pastes, mortars, or concretes are involved, since the reactions under consideration pertain to cement-water systems.

investigators worked with cements that contained sufficient dehydrated gypsum to cause what is classed as false set (1). For these reasons, one should examine carefully any report of work on accelerators and retarders to be certain that the author's definitions of accelerators and retarders are clearly understood.

It seems, from this review of the literature,[4] that the investigators who attempted to explain the reactions of the cement minerals with water very quickly reached a point where they had to enlarge their explanation to include the formation of precipitates on the surfaces of the crystals. Phillips, Baikov, and Roller particularly appear to have recognized that the solution theory was inadequate. Much more is known today about surfaces and reactions at surfaces so that it may be possible now to overcome the difficulties of these early investigators in formulating a satisfactory theory. Therefore, this paper is an attempt to explain by means of solid state reactions the mechanism by which calcium sulfate and calcium hydroxide control flash set and by which calcium sulfate accelerates the strength-producing reactions of the calcium silicates. The behavior of other inorganic and organic compounds are studied in the light of this mechanism. For simplicity, the paper will refer to retardation of flash set and retardation and acceleration of the rates of silicate reactions.

SOLID STATE REACTIONS

The production of portland-cement clinker probably is entirely by solid state reactions. For example:

1. $CaCO_3$ is decomposed into CaO and CO_2 and clay is dehydrated and decomposed into SiO_2 and Al_2O_3 in the solid states,
2. CaO combines with SiO_2, Al_2O_3, and Fe_2O_3 in the solid state to form the solid cement minerals, and
3. After some liquid is formed by melting, CaO from the liquid probably combines with solid $2CaO \cdot SiO_2$ to form solid $3CaO \cdot SiO_2$.

Most of the industries that use catalysts are based on solid state reactions. For example, Weyl (17) states: "We are now standing at the threshold of a new phase in chemistry, the chemistry of the solid state. Recent progress in the atomic structure of solids justifies the hope that, soon, we shall be able to understand the participation of solids in chemical reactions, including heterogeneous catalysis."

Some studies of solid state reactions that seem particularly important to the student of portland cement are set forth below:

Jeffery (18) discusses a number of solid state reactions and makes the following statements regarding the reaction of $3CaO \cdot SiO_2$ with water:

> "But even in this initial period when an excess of water is present, it is not certain that the hydrate is formed by precipitation. Hansen has produced evidence indicating that even in this case the reaction with $3CaO \cdot SiO_2$ is really a direct transformation of the anhydrous solid and not a precipitation from solution. During the hardening process, extending up to a year or more, it is difficult to see how it can be anything else."

McConnell (19), from a study of the transformation of natural bredigite ($\alpha 2CaO \cdot SiO_2$) and natural larnite ($\beta 2CaO \cdot SiO_2$) to a gelatinous hydrated phase similar to tobermorite ($3CaO \cdot 2SiO_2 \cdot 3H_2O$), found that much of the gel occurs as a homogeneous flint-like sheath, up to 5 cm thick, around nodules

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[4] For a comprehensive review, see H. H. Steinour, "The Setting of Portland Cement—A Review of Theory, Performance, and Control," *Bulletin 98*, Research and Development Laboratories, Portland Cement Assn.

of unaltered larnite and he concluded, from a detailed study of the gel, that the progress of hydration is a solid state reaction which is effected by diffusion.

TABLE I.—ANALYSIS OF CEMENT PASTE ABSTRACTS AFTER MIXING OF CEMENT AND WATER, g per liter.

	7 min after mixing		2 hr after mixing	
	Without Gypsum	With Gypsum	Without Gypsum	With Gypsum
SiO_2	0.000	0.002	0.000	0.002
R_2O_3	0.002	0.003	0.004	0.004
CaO	1.73	2.22	1.47	2.30
SO_3	0.02	0.96	0.03	1.05
K_2O	0.07	0.06	0.59	0.06
Na_2O	0.02	0.02	0.09	0.02

A number of investigators have made quantitative analyses of extracts from cement pastes at early periods after the cement and water are mixed which show the presence of only very minor amounts of SiO_2 and Al_2O_3 in these extracts. For example, Kalousek, Jumper, and Tregoning (13) obtained the data in Table I from the extract at 7 min and 2 hr from pastes of a clinker ground with and without gypsum.

Similar data are obtained when the extraction periods are reduced to less than 7 min. These extraction studies give no indication that the concentrations of SiO_2 and Al_2O_3 build up to relatively high values as is common for supersaturated solutions and then decrease as precipitation occurs.

Hansen (3) endeavored to show that the following reaction was a solid state reaction:

$$3CaO \cdot Al_2O_3 + CaCl_2 + 10H_2O$$
$$= 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O \quad \text{........(7)}$$

A cement clinker was reburned to reduce the SO_3 content to a low value. The clinker, after reburning, had the following composition in per cent by weight:

CaO	65.2	MgO	2.6
Al_2O_3	6.5	SO_3	0.06
Fe_2O_3	3.0	K_2O	0.03
SiO_2	2.5	Na_2O	0.09
MnO	0.51		

This was ground to a fine powder and pastes were made of 200 g of clinker plus 150 ml of a $CaCl_2$ solution. These were shaken at room temperature for 1 min and filtered immediately on a suction filter, which gave a time of contact between the solid and liquid of a few seconds more than 1 min. The filtrates were titrated for $(OH)_2$ content and analyzed for SO_3, Cl_2, CaO, K_2O and Na_2O with the results given in Table II.

TABLE II.—COMPOSITION OF FILTRATES FROM PASTES OF 200 g CEMENT PLUS 150 ml OF $CaCl_2$ SOLUTION.

$CaCl_2$ moles per liter	Composition of Filtrate, moles per liter						Cl_2 Combined, moles per liter	CaO Released, moles per liter
	SO_3	$(OH)_2$	Cl_2	CaO	K_2O	Na_2O		
0.0075	None	0.0254	0.0017	0.0232	0.0013	0.0011	0.0058	0.0215
0.0150	None	0.0257	0.0039	0.0272	0.0013	0.0011	0.0112	0.0234
0.0300	None	0.0267	0.0143	0.0387	0.0013	0.0011	0.0157	0.0240
0.0600	None	0.0255	0.0442	0.0672	0.0013	0.0011	0.0158	0.0230
0.1200	None	0.0250	0.1014	0.1249	0.0013	0.0011	0.0186	0.0235

The values in the next to the last column are the differences between the Cl_2 content of the mixing water and that of the filtrate. This, it is believed, is the amount of Cl_2 that has combined as illustrated in Reaction 7.

The values in the last column are the amounts of CaO released by the cement, probably largely from the $3CaO \cdot SiO_2$.

These are obtained by subtracting the values for Cl_2 in the filtrate because the CaO required by this Cl_2 was added in the calcium chloride.

In accordance with Reaction 7, one mole (270 g) of $3CaO \cdot Al_2O_3$ combines with one mole of $CaCl_2$. In the solution initially containing 0.06 moles of $CaCl_2$, 0.0158 moles had combined. This indicates that 270 × 0.0158 or 4.3 g $3CaO \cdot Al_2O_3$ per liter reacted with $CaCl_2$ in a period of slightly more than 1 min.

TABLE III.—GRAMS Cl_2 COMBINED WITH 100 g OF CLINKER FOR TIME INDICATED.

Sample	1 min	5 min	15 min	30 min
As Received.....	0.22	0.28	0.34	0.36
Aerated 24 hr....	0.08	0.14	0.22	0.24
Aerated 48 hr....	0.03	0.11	0.22	0.26

On the assumption that all of the CaO released to the solution was released as follows:

$$2(3CaO \cdot SiO_2) + 3H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad \ldots (8)$$

two moles (456 g) of $3CaO \cdot SiO_2$ release three moles of CaO, or two thirds of a mole (152 g) release one mole of CaO. This indicates that 152 × 0.0230 = 3.5 g of $3CaO \cdot SiO_2$ per liter hydrolyzed in slightly more than 1 min. This is equivalent to 0.9 g SiO_2 per liter that would have been dissolved and precipitated from the solution in this period of time if the solution theory was correct.

The 4.3 g of $3CaO \cdot Al_2O_3$ that combined with the $CaCl_2$ is equivalent to 1.6 g Al_2O_3 per liter. It seems impossible for these quantities of SiO_2 and Al_2O_3 to go through the solution phase in a period of 1 min when only traces of these oxides can be found in the liquid phase. It seems necessary, therefore, to conclude that the major portions of the calcium aluminates and silicates in portland cement do not react with water and calcium sulfate by going into solution.

Further evidence of a solid state reaction was obtained by Hansen (20) in a study of aerated and nonaerated cement. In this study, a clinker was ground to a powder without added calcium sulfate. This powdered clinker as ground and after exposure in a thin layer to laboratory air for 24 and 48 hr was made into slurries with a solution of calcium chloride, 200 g powder to 150 ml of solution containing the equivalent of 3.0 per cent Cl_2 by weight. The slurries were filtered at 1, 5, 15, and 30 min intervals and analyzed for Cl_2 with the results shown in Table III.

The explanation for the decreased rate of reaction with $CaCl_2$ after aeration appears to be that the surfaces of the grains of $3CaO \cdot Al_2O_3$ reacted with H_2O and CO_2 from the air during aeration. If the reaction with calcium chloride was a solid state reaction in which this salt is adsorbed from the solution onto the surface of the crystals as will be explained later, it is readily understood how the previous adsorption of H_2O and CO_2 could interfere with this reaction. It is not easy to believe that this adsorption of H_2O and CO_2 would so markedly reduce the rate at which the $3CaO \cdot Al_2O_3$ crystals would dissolve.

Brown (21) examined thin sections of hardened cement pastes microscopically and found that grains of CaO and of MgO had hydrated to the hydroxides without evidence of having gone through a solution phase. This hydration *in situ* is used to explain the ability of these oxides to produce expansion in concrete.

Roller (22) and others have found the flash-setting properties of cements could be destroyed by treating the cement with either steam or moist air.

Razouk and Mikhail (23) suggest a mechanism for the hydration of MgO by water vapor which probably is similar to reactions of cement minerals in cement pastes. They state: "Experiments on the rate of hydration of magnesium oxide at various temperatures and on the effect of temperature on the sorption isotherms of water vapor suggest that the initial stage in the uptake of water vapor by the oxide is essentially a rapid Van der Waals physical adsorption, together with slower chemisorption, and this is followed by a diffusion process to the inside of the solid. The present investigation indicates that the last stage in the hydration process is the recrystallization of the magnesium oxide water complex, formed by the interaction of water molecules with magnesium oxide crystallites (probably through O^{-} ions) to yield the stable magnesium oxide lattice."

In suggesting that the reactions in a cement paste are primarily solid state reactions, it is, of course, realized that some or all of the minerals will dissolve to some limited extent. This has been demonstrated by the analyses of extracts from cement pastes which always contain very minor amounts of SiO_2 and Al_2O_3.

PROPERTIES OF SURFACES

For most physical properties of a solid, it is sufficient to assume that the properties of every element of a volume within a given particle has the same properties as any other. However, this assumption of homogeneity breaks down near the surface of the particle.

According to Weyl (17), V. M. Goldschmidt was the first to attempt a correlation between crystal structures and physicochemical properties of matter. He explained crystal structure in terms of the three fundamental properties of ions: namely, their charges, their size, and their polarization properties.

The modern concept of crystals is that they are made up of ions. For example, in a crystal of NaCl, a sodium ion is bonded to six chlorine ions by equal forces. Attractions between ions of unlike charges and repulsions between ions of like charges are important for an understanding of crystal structures.

The present concept of the atom is that it consists of a positive nucleus and a number of planetary electrons. The atomic number assigned to an atom is

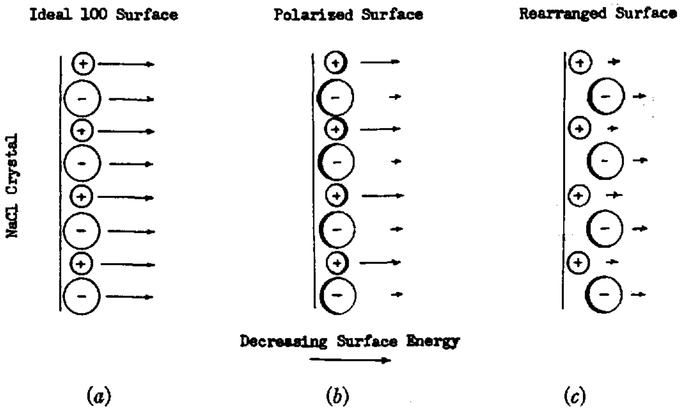

FIG. 1.— Electronic Deformation and Ionic Rearrangement in a NaCl Surface. After Weyl (17). Sodium chloride is to the left of the vertical line representing the crystal face. Small spheres represent sodium ions, large spheres represent chloride ions.

the number of its planetary electrons which equals the number of positive charges in the nucleus. The atomic weight is approximately the weight of the nucleus. When an atom is converted to an ion, it loses or gains one or more electrons. The ions in the interior of a crystal are mutually attracted and repelled by each other. However, those on the surface of a crystal are unbalanced toward the atmosphere. Weyl illustrates this in Fig. 1(*a*). He pictures this surface as consisting of rigid spheres with excess electrical charges. He states:

> "However, the electron distribution probability of the surface ions cannot remain spherical because the ions of high polarizability, the Cl^- ions, must develop a higher than average electron density towards the interior of the crystal because their electron clouds are attracted by the Na^+ ions. As a result, they exhibit lower electron density toward space. In a similar fashion, the electron distribution density of the cations undergoes a change. Each surface Na^+ ion is exposed to the attraction of a Cl^- ion of the lower layer but has no corresponding anion on the opposite side which balances this attraction. As a result of this one-sided polarization, the electron clouds of the Na^+ ions are repelled towards the vacuum, a deformation which decreases their positive potentials."

Weyl represents this polarized surface in Fig. 1(*b*). The heavier lines indicate the spots of higher electronic density of the outer electron shell. The length of the arrow indicates the residual potential field emanating from a surface ion into space.

The atomic number of sodium is 11 and that of chlorine is 17. The larger Cl^- ion is polarized to a greater extent than is the smaller Na^+ ion and, accordingly, its surface forces are weakened to a greater extent than those of the Na^+ ion by polarization.

Figure 1(*c*) represents a rearranged surface in which the Na^+ ions tend to recede slightly so that they are more completely surrounded by Cl^- ions. Weyl refers to this as a screening of the Na^+ ions by Cl^- ions. This screening gives a surface of lower surface energy than that in Fig. 1 (*b*). This surface has also become predominately negative whereas that in Fig. 1 (*b*) was predominately positive.

Polarization and screening as illustrated in Fig. 1 for NaCl must be important in the reactions of cement in the water. In dealing with a material made up of powdered crystals such as portland cement, the freshly produced surface might tend to exhibit the characteristics of Fig. 1(*a*) but probably would very quickly assume the characteristics of either (*b*) or (*c*).

Much has been written (24) about defects in crystals which play a prominent part in solid state reactions. These may play an important role in the reactions in cement pastes and possibly the studies that are being made in a number of laboratories on the structures of the cement minerals will eventually throw light on this role. Also, the particles of cement, except for the very finest, are agglomerates of many fine crystals. The following quotation from Weyl appears pertinent in this connection: "Can a polycrystalline aggregate of an oxide ever be considered to be a precise stoichiometric ratio, or are all grain boundaries and internal surfaces the seat of 'available electrons' and do they represent a potential source of O^- ions? Recent experimental work led us to suspect that even apparently stable substances can undergo an exchange of electrons with adsorbed O_2 molecules which leads to the formation of atomic oxygen. Grain boundaries, interfaces, and surfaces are the seats of these reactions."

SURFACES OF CALCIUM ALUMINATE AND SILICATE CRYSTALS

In accordance with the above discussion, the surface of a calcium aluminate crystal would consist of Ca^{++}, Al^{+++} and $O^{=}$ ions and that of a calcium silicate crystal would consist of Ca^{++}, Si^{++++} and $O^{=}$ ions. However, the smaller and less numerous Al^{+++} and Si^{++++} ions, atomic numbers 13 and 14 respectively, would likely be screened by the larger and more numerous Ca^{++} ions and by the more numerous $O^{=}$ ions. Hence, the ions in the surfaces of $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$, and $2CaO \cdot SiO_2$ are probably principally Ca^{++} and $O^{=}$ ions and will be so considered in the discussions which follow.

If these surfaces were either polarized or rearranged to the extent that they were either predominately negative or positive, the particles would repel each other. Steinour (25) and others have shown that particles of cement in water tend to attract each other and form flocs. Hence, it appears that the surfaces of the powdered crystals of the cement minerals carry approximately equal amounts of positive and negative charges.

When either of these surfaces is exposed to water, the positive ions Ca^{++} should attract the OH^- ions of the water and the $O^{=}$ ions should attract the H_3O^+ ions of the water. As Razouk and Mikhail suggest for MgO, the first step may be a physical adsorption followed by chemisorption and then by a diffusion of OH^- and H_3O^+ ions into the crystal.

Physical adsorption, as suggested by Razouk and Mikhail, must be a dynamic process in which a Ca^{++} ion may temporarily unite with a negative ion and then release it to the solution and unite with another negative ion. If these adsorbed ions are able to migrate into the crystal and cause a rearrangement of the crystal, the process becomes chemisorption which means that the ions have reacted chemically with the solid surface. This chemical reaction, as in the case cited by Razouk and Mikhail, has taken place without the solid going into solution in water.

Weyl refers to the dynamics of a surface as follows:

> "Using models or sketches of atomic arrays in order to bring out the importance of geometrical arrangements, lattice, distances, etc. for chemisorption, carries along additional information which can be misleading. All pictures are necessarily static but we do know that a surface is not only the seat of constant motion and rearrangements, but sometimes of very lively chemical reactions. The work of E. R. S. Winter, as well as that of G. A. Mills and S. G. Handin, with O^{18}, shows clearly that there is a continuous exchange of oxygen ions of the surface layer of an oxide and the oxygen molecules of the atmosphere."

The rate at which the diffusion into the crystal takes place should depend on the crystal structure of the compound. Weyl suggests that crystal structure can explain the difference between the reactivity toward water of β and $\gamma 2CaO \cdot SiO_2$ and Jeffery suggests that the difference between the reactivities toward water of $\beta 2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ may be explained by differences in crystal structure. Foreign atoms, such as MgO and Al_2O_3 in the $3CaO \cdot SiO_2$ crystal, may markedly affect the reactivity of the crystal in a solid state reaction.

One of the common arrangements of SiO_2 in crystals is the SiO_4-tetrahedron and the formula for an orthosilicate such as $2CaO \cdot SiO_2$ is usually written as Ca_2SiO_4.

Jeffery (3) says regarding the pseudostructure of $3CaO \cdot SiO_2$: "The structure is built from discrete SiO_4-tetrahedra together with separate oxygen and calcium ions—the main features of the structure of $3CaO \cdot SiO_2$ are the irregular coordination of the calcium ions and the 'holes' adjacent to these ions. Since irregular coordination gives rise to distortion of the electrostatic field between ions, $3CaO \cdot SiO_2$ necessarily has a high lattice energy."

Midgley (26) makes the following statements regarding the structure of $\beta 2CaO\cdot SiO_2$:

> "The structure is built up of isolated SiO_4-tetrahedra and calcium ions. Although the coordination of calcium ions is irregular, there are no open spaces as in $3CaO\cdot SiO_2$ which would allow ready attack by hydroxyl ions. This would account for the fact that, although both compounds have valuable cementing properties, $3CaO\cdot SiO_2$ is very rapidly hydrated and $2CaO\cdot SiO_2$ only slowly."

The many investigations (18) on the CaO-SiO_2-H_2O system have not as yet clearly defined the compositions of the hydrated calcium silicates that exist in the normal hardened pastes of mortars and concretes. Some (27) believe that the equilibrium compound is what may be classed as tobermorite, $3CaO\cdot 2SiO_2\cdot 3H_2O$. There is some evidence (27) that afwillite, $3CaO\cdot 2SiO_2\cdot 3H_2O$, might be formed in these pastes and there is considerable evidence (18) that the product might be $2CaO\cdot SiO_2\cdot H_2O$.

Heller (28) studied the crystal structure of $2CaO\cdot SiO_2\,\alpha$ hydrate which is formed at elevated temperatures. This work indicated the silicon formed $(SiO_3(OH)^{---}$ tetrahedra in this compound and Megaw (29) concluded that the silicon occurred in the same manner in afwillite. Heller concluded that the formula for the $2CaO\cdot SiO_2\,\alpha$ hydrate was $Ca_2(SiO_3OH)\cdot OH$ and Megaw concluded that the formula for afwillite was $Ca_3(SiO_3OH)_2\cdot 2H_2O$.

The $Ca_2(SiO_3OH)OH$ could be formed as follows:

$$Ca^{++} + OH^- = CaOH^+$$

$$SiO_3O^{----} + H_3O^+ = SiO_3OH\cdot H_2O^{---}$$

That is, a Ca^{++} ion in the surface of the crystal could chemisorb an OH^- ion which could then diffuse into the crystal.

An O^- ion in the surface could chemisorb an H_3O^+ ion and form $SiO_3OH\cdot H_2O^{---}$ from which the H_3O^+ ion could diffuse into the crystal. Both of these chemisorption processes could be repeated over and over without the $2CaO\cdot SiO_2$ going into solution but with a gradual rearrangement of its crystal structure.

The reactions to form $Ca_3(SiO_3OH)_2\cdot 2H_2O$ could be as follows:

$$Ca^{++} + 2OH^- = Ca(OH)_2$$

$$2(SiO_3O)^{----} + 2H_3O^+ = 2(SiO_3OH\cdot H_2O)^{---}$$

In this reaction, one Ca^{++} ion in the surface of the crystal chemisorbs two OH^- ions and splits off as $Ca(OH)_2$. Two O^- ions chemisorb $2H_3O^+$ ions to form $2(SiO_3OH\cdot H_2O)^{---}$ ions. The chemisorbed H_3O^+ ions could diffuse into the crystal and change the structure of the crystal.

These reactions need not be limited to chemisorption of ions. However, it seems that, in solutions where ions are present, ions would be chemisorbed in preference to molecules of water. However, when crystals of such unstable compounds as $3CaO\cdot Al_2O_3$ and $3CaO\cdot SiO_2$ are exposed to water vapor, they must react rather rapidly with water as is indicated by considerable experimental evidence. Typical reactions might be as follows:

$$Ca^{++} + H_2O = Ca(OH)_2$$

$$SiO_3\cdot O^{----} + H_2O = SiO_3\cdot OH^{---} + OH^-$$

$$Ca^{++} + OH^- = CaOH^+$$

One reaction suggested for $3CaO\cdot SiO_2$ in cement pastes is:

$$2(3CaO\cdot SiO_2) + 6H_2O = 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2 \quad\ldots\ldots(8)$$

If this reaction occurred only by the anhydrous silicate dissolving congruently and reprecipitating as the two reaction products, one would expect the hydrated silicate to have a uniform composition. Also, one would expect, if the paste reached a stage in which liquid water no longer existed, that the reaction would stop and leave unreacted crystals of $3CaO \cdot SiO_2$. These crystals could continue their reaction later whenever liquid water could contact them.

In the suggested solid state reaction, it is visualized that the reaction could continue in the absence of free water, which seems to be clearly established, and that the composition of the hydrated calcium silicate reaction product might vary widely from what was originally the outside of a crystal of $3CaO \cdot SiO_2$ to the center of that crystal. The degree to which this product assumes a well defined crystalline structure would be expected to vary. It can also be visualized that $Ca(OH)_2$ that splits out of the silicate could exist physically within the hydrated silicate in a finely divided amorphous state. Similar reactions would be expected for the other compounds, such as $3CaO \cdot Al_2O_3$ and $2CaO \cdot SiO_2$.

In attempting to give a picture of the mechanism of setting and hardening of a cement paste, it is necessary to use equations to illustrate reactions. Reactions such as 5 and 8 are written to indicate what might happen to crystals of $3CaO \cdot Al_2O_3$ and $3CaO \cdot SiO_2$ in a normal concrete. In such concrete, sufficient OH^-, H_3O^+ and SO_4^{--} ions to destroy the crystal structures of the anhydrous crystals might migrate into the crystals in relatively short periods of time but it might require much longer periods of time for a sufficient number of molecules of water to diffuse into those partially reacted crystals and cause the complete rearrangement of the structures to those of compounds such as ettringite and tobermorite as indicated by Reactions 5 and 8. That is, one may visualize a hardened cement paste to be a system which is tending toward a certain equilibrium but which may never reach that equilibrium in normal concrete.

It is not possible at this time to present these reactions as more than possible explanations of the solid state reactions that might be responsible for the setting and hardening of cement pastes. However, it does seem, from what is known about reactions at surfaces and from the evidence that indicates that the cement minerals do not dissolve at rates required by the rates at which cement pastes set, that it is necessary to conclude that the setting and hardening are caused by the chemisorption and migration of OH^- and H_3O^+ ions from water into the crystals of the cement minerals. If this is true, then the problem of controlling the rates of these reactions becomes one of controlling the concentrations of OH^- and H_3O^+ ions available to the surfaces of the cement particles and by controlling the amount of surface available to those ions. The latter has, of course, been found to be effective by changing the fineness of the cement.

RETARDATION OF FLASH SET WITH SALTS AND CALCIUM HYDROXIDE

When $3CaO \cdot Al_2O_3$ is treated with a relatively large amount of water, the crystalline phases formed are $2CaO \cdot Al_2O_3 \cdot 8H_2O$ and either or both $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ when the amount of CaO in solution exceeds the ratio of 3 CaO to 1 Al_2O_3. This indicates that the first reaction of $3CaO \cdot Al_2O_3$ with water is

$$3CaO \cdot Al_2O_3 + 9H_2O = 2CaO \cdot Al_2O_3 \cdot 8H_2O + Ca(OH)_2 \quad \ldots\ldots (9)$$

In a cement paste with a limited amount of water, this reaction probably takes place as follows:

$$Ca^{++} + 2(OH)^- = Ca(OH)_2 \quad \ldots\ldots (10)$$

$$O^- + H_3O^+ = H_2O + OH^- \quad \ldots\ldots (11)$$

That is, a Ca^{++} ion in the surface of the crystal chemisorbs two OH^- ions and splits off as $Ca(OH)_2$ and an O^- ion chemisorbs an H_3O^+ ion to form H_2O and an OH^- ion. The $H_2O + OH^-$ then diffuse into the crystal and the chemisorption processes are repeated.

As the concentration of $Ca(OH)_2$ builds up in the liquid phase of the paste, the $2CaO \cdot Al_2O_3 \cdot 8H_2O$ formed on the surface of the crystal of $3CaO \cdot Al_2O_3$ can chemisorb Ca^{++} and OH^- ions to form either $3CaO \cdot Al_2O_3 \cdot 6H_2O$, $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$, or $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot 30H_2O$. The extent to which these compounds can be formed is dependent on $Ca(OH)_2$ released in Reaction 9 unless $Ca(OH)_2$ is furnished from other sources, such as the hydrolysis of $3CaO \cdot SiO_2$.

Phillips observed that, if a paste of $3CaO \cdot Al_2O_3$ and water that had heated up and stiffened, was reworked, it would heat up and stiffen at a slower rate. This indicates that the $Ca(OH)_2$ released in accordance with Reaction 9 during the first period is capable of retarding the rate of further reaction. This also indicates that the formation of $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ on the surfaces of the crystals of $3CaO \cdot Al_2O_3$, as postulated by Roller, cannot be the mechanism by which flash setting is prevented.

The difference between the original and the reworked paste is that the liquid phase of the latter contained dissolved $Ca(OH)_2$ which the former did not. This $Ca(OH)_2$ represses the ionization of water and the concentration of the H_3O^+ ions is much lower in the liquid phase of the reworked paste than in that of the original paste.

If the reaction of Reaction 9 is a solid state reaction, its rate depends upon the rate at which O^- ions can chemisorb H_3O^+ ions. Since the liberation of $Ca(OH)_2$ by $3CaO \cdot Al_2O_3$ can retard the rate of the reaction, it seems evident that the concentration of H_3O^+ ions is the governing factor and that the reaction of Reaction 9 is the reaction responsible for flash set. One might then ask whether or not the addition of $CaSO_4$ to the mixing water can retard the rate of this reaction.

The addition of calcium sulfate to water has very little effect upon the ionization of water. Hence, from this standpoint, it should neither retard nor accelerate the rate of this reaction. However, the SO_4^{--} ion is fairly large and the adsorption of it by the Ca^{++} ions in the surface of the crystal would interfere with the adsorption of OH^- ions. The adsorption of Ca^{++} ions from the solution by O^- ions could also interfere with the adsorption of H_3O^+ ions. There appears to be no way at present of determining the influence of these factors upon the rate of this reaction, but one might expect that this would not be very great unless the SO_4^{--} ions were very effective in screening the O^{--} ions. Since Bates found very little retardation by $CaSO_4$, it appears that the SO_4^{--} ion is not very effective in preventing chemisorption of H_3O^+ ions by the O^- ions. However, when solid calcium sulfate is mixed with solid $3CaO \cdot Al_2O_3$, the salt cannot be effective until it gets into solution and, by the time an appreciable amount has dissolved, a considerable reaction between the $3CaO \cdot Al_2O_3$ and H_2O may have taken place. Hence, the results obtained by Bates with pastes with only minor admixtures of either $CaSO_4$ or $Ca(OH)_2$ or blends of the two may not give a true picture of the retarding powers of these materials.

When a cement is flash setting, the paste heats up and stiffens very markedly within one or two minutes after the cement and water are mixed. It is generally believed that gypsum will prevent flash set in most cements. This belief is based on results with cements in which gypsum was ground with the clinker but it neglects the fact that, in many of the cements, some or all of the gypsum probably was converted to either hemihydrate or soluble anhydrite either during grinding or storage. There are some clinkers that will produce flash setting cements when ground with gypsum but will produce normal setting cements when ground with a blend of gypsum and hemihydrate.

As pointed out earlier, most of the alkalies enter the mixing water as sulfates and not as hydroxides as believed by Roller. Most clinkers combine with SO_3 at a fairly rapid rate. As stated previously, Hansen showed that one clinker combined with 0.22 g Cl_2 per 100 g of cement in 1 min, which was calculated to be equivalent to 0.74 per cent SO_3 by weight of cement. Roller made his extractions 15 min after the paste was made and his analyses showed very little SO_3 in those extracts. He, therefore, assumed that the alkalies had dissolved as hydroxides whereas they very likely dissolved as sulfates because his clinkers contained from 0.23 to 1.02 per cent SO_3.

Most of the hydroxide required for Roller's Reaction 1 comes as $Ca(OH)_2$ from the hydrolysis of the cement minerals, such as $3CaO \cdot Al_2O_3$ and $3CaO \cdot SiO_2$. It is true that the calcium sulfate would tend to permit a larger amount of $Ca(OH)_2$ to remain in solution than would be possible if the solution was primarily a solution of alkali hydroxides instead of alkali sulfates. However, if the $Ca(OH)_2$ is dissolved from the $3CaO \cdot SiO_2$ for example, it would be available to react with $3CaO \cdot Al_2O_3$ before it precipitated out as solid $Ca(OH)_2$. The point that Roller and others appear to overlook is that the reaction or reactions that cause flash set are proceeding rapidly within seconds after the water comes in contact with the cement.

It does not appear possible for $3CaO \cdot Al_2O_3$ to furnish the $Ca(OH)_2$ required to form a coating on itself of $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$. Hence, it appears, if such a coating is required to prevent flash set, that the $Ca(OH)_2$ has to come from the hydrolysis of $3CaO \cdot SiO_2$. In that case, one would have to explain why $CaSO_4$ accelerated the rate of hydrolysis of $3CaO \cdot SiO_2$. This subject will be discussed later. However, it does not seem likely that the retarding power of $CaSO_4$ lies solely in its ability to accelerate the rate of hydrolysis of $3CaO \cdot SiO_2$ or of any of the other cement minerals.

It seems necessary, therefore, to return to the conclusion held by many investigators to the effect that some combination of SO_3 with $3CaO \cdot Al_2O_3$ prevents flash set. It is well known that SO_3 can combine very rapidly with $3CaO \cdot Al_2O_3$ without causing flash set. This indicates that Roller was wrong when he postulated that the formation of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ caused flash set. However, as pointed out above, there are cases in which a cement that combines rapidly with SO_3 shows flash set when the liquid phase of the paste is not saturated with respect to gypsum but which shows no flash set when the liquid phase is supersaturated with respect to gypsum. This indicates that some other reaction of $3CaO \cdot Al_2O_3$ than the formation of one or the other sulfoaluminate is responsible for flash set and supports the conclusion that Reaction 9 is that reaction.

If this is true, then what property of $CaSO_4$ is involved? Since increasing the quantity of $CaSO_4$ in solution will prevent flash set, it seems that the dissolved $CaSO_4$ must interfere with this reaction. If the rate of the reaction producing flash set depends upon the rates at which the Ca^{++} and O^{-} ions in the surfaces of the crystals chemisorb OH^{-} and H_3O^{+} ions, then calcium sulfate can interfere with this reaction by the Ca^{++} and SO_4^{--} ions of the calcium sulfate being physically adsorbed on the surface Ca^{++} and

O^- and blocking these sites from OH^- and H_3O^+ ions. Calcium sulfate hemihydrate and soluble anhydrite are two compounds that, when present to the extent of a few per cent in a cement paste of normal water content, can produce relatively high concentrations of $CaSO_4$ in the liquid phase in a few seconds because they are unstable in water.

So far as one can determine, the first use of calcium sulfate for preventing flash set was the addition of plaster of Paris to the mixing water. This was followed by grinding the clinker with plaster of Paris and later by grinding with gypsum. However, in the latter, the gypsum probably was converted to plaster of Paris either during grinding or storage. If the first investigators had added powdered gypsum to the mixing water, they very likely would not have been satisfied with the performance of their concrete because their cements probably contained relatively large amounts of $3CaO \cdot Al_2O_3$ and the addition of gypsum probably would not have prevented flash set.

Flash setting can be eliminated from a clinker by permitting the clinker to absorb moisture. Hansen showed that this treatment greatly reduces the rate at which the clinker reacts with calcium chloride and sulfate. This indicates that reactive sites on the surfaces of the clinker have been blocked by chemisorption of moisture from the air. It seems that it would be impossible to form $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ by the chemisorption of water by $3CaO \cdot Al_2O_3$ and, of course, no sulfoaluminate can be formed on the surface. Hence, something besides the formation of these double salts has destroyed the false setting properties of the clinker.

From the standpoint of flash set, portland-cement clinkers vary widely. Some show no signs of flash set when tested without an admixture, some have mild flash setting tendencies that are easily controlled by small additions of gypsum, and others have strong flash setting tendencies that can only be controlled by the addition of either hemihydrate or soluble anhydrite. It is conceivable that salts other than $CaSO_4$ might be effective in preventing flash set with some clinkers and not with others.

From the standpoint of the solid state reactions proposed above, one might predict that any salt with one large ion might be effective to some degree, provided it did not react in some other way with the cement minerals. Soluble magnesium salts, for example, would react with $Ca(OH)_2$ and precipitate insoluble $Mg(OH)_2$ and yield a calcium salt. Alkali phosphates would react with $Ca(OH)_2$ to produce insoluble calcium phosphates and alkali hydroxides. Salts of these types, Forsen classified as destroyers.

All evidence points to the conclusion that the reaction of $3CaO \cdot Al_2O_3$ with water starts at an extremely high rate the moment that water comes in contact with the crystals. Hence, any material that is going to exert a retarding effect upon this reaction must be able to dissolve at an extremely rapid rate and form ions that are adsorbed by the O^- ions sufficiently to block most of the O^- ions against the adsorption of H_3O^+ ions. Plaster of Paris and soluble anhydrite are two compounds that can dissolve at such rates and $3CaO \cdot SiO_2$ is a compound from which $Ca(OH)_2$ can hydrolyze at a rapid rate. It appears that this combination of an unstable calcium sulfate and $3CaO \cdot SiO_2$ is required to prevent flash set in cements containing relatively large amounts of $3CaO \cdot Al_2O_3$. From this, it seems evident that it would be unsafe to generalize regarding the retarding powers of salts.

ACCELERATION OF THE CALCIUM SILICATE REACTIONS

As pointed out earlier, it is known that salts, such as $CaSO_4$ and $CaCl_2$, accelerate the rates at which cements develop strengths. This, it seems, must be due to effects that these salts have upon the rates at which $3CaO \cdot SiO_2$ and possibly $2CaO \cdot SiO_2$ react with water. Forbrich (30) showed that calcium chloride increased the rate at which a paste of $3CaO \cdot SiO_2$ released heat.

As discussed under properties of surfaces, these silicates may react to form minerals, such as $2CaO \cdot SiO_2 \cdot 2H_2O$; afwillite, $3CaO \cdot 2SiO_2 \cdot 3H_2O$; and tobermorite, $3CaO \cdot 2SiO_2 \cdot 3H_2O$. These reactions are explainable as follows:

$$Ca^{++} + 2OH^- = Ca(OH)_2 \text{......} (10)$$

$$Ca^{++} + OH^- = CaOH^- \text{.......} (11)$$

$$(SiO_3 \cdot O)^{----} + H_3O^+$$
$$= (SiO_3OH \cdot H_2O)^{---} \text{...........} (12)$$

In Reaction 10, a Ca^{++} ion has combined with two OH^- ions to split out a molecule of $Ca(OH)_2$. In Reaction 11, a Ca^{++} ion chemisorbs an OH^- ion which can then diffuse in the crystal to other Ca^{++} ions. In Reaction 12, an O^- ion in the surface of a silicate chemisorbs a H_3O^+ ion to form an $(SiO_3OH \cdot H_2O)^{---}$ ion. The adsorbed H_3O^+ ion can then diffuse to other O^- ions.

Presumably, Reactions 10 and 11 could not progress to an appreciable extent unless Reaction 12 occurred simultaneously or vice versa. Hence, these reactions are controlled by the concentrations of OH^- and H_3O^+ ions in the liquid phase of the cement paste. Since $3CaO \cdot Al_2O_3$ and $3CaO \cdot SiO_2$ split off $Ca(OH)_2$, the liquid phase of the cement paste almost immediately contains an abundance of OH^- ions. These ions, although required for Reactions 10 and 11, act as retarders for Reaction 12 by depressing the ionization of water. Therefore, to increase the rates of Reactions 10, 11, and 12, it is necessary to offset the depressing effect of the OH^- ions in the ionization of water.

Roller removed extracts from pastes of clinkers with and without added calcium sulfate 15 min after the pastes were made. The OH^- equivalents expressed as milliequivalents per ml were 0.2320, 0.2638 and 0.3860 for three clinkers and 0.0730, 0.1030, and 0.1150, respectively, for the clinkers with added calcium sulfate. These data demonstrate that salts will have the effect of increasing the concentrations of H_3O^+ ions and, accordingly, should have the effect of accelerating the rates at which the silicates develop strengths.

Other calcium salts should have this ability shown by calcium sulfate to precipitate calcium hydroxide from solutions of alkali hydroxides and, accordingly, increase the concentration of H_3O^+ ions in the solution. All such salts should act as accelerators unless their anions could block the surfaces of the crystals against the chemisorption of H_3O^+ ions. This will be discussed in more detail in the next section.

One might expect that SO_4^{--} ions should screen much more effectively than the Cl^- ions and that $CaCl_2$ would be a better accelerator than $CaSO_4$. This seems to be the case. However, since $CaCl_2$ is much more soluble than $CaSO_4$, it might tend to depress the solubility of $Ca(OH)_2$ more than the latter does and be a more effective accelerator because of that.

ORGANIC MODIFIERS

According to Kennedy (31), the application of dispersing agents in the cement industry developed from research in a program of developing dispersing agents for pigments in aqueous suspensions. This led to the discovery that certain polymers of condensed naphthalene sulfonic acid, when used in amounts of approximately 0.1 per cent by weight of cement, would almost completely disperse the flocs of cement particles observed in cement pastes when viewed on a slide under a microscope. These studies were followed by studying derivatives of lignin and finding that salts of lignosulfonic acids were effective dispersing agents. Other experiments demonstrated that a dispersing agent, when added to the mills used in grinding cement, acted as a "grinding aid" by increasing the fineness of cement at constant rate of grinding or by increasing the rate of grinding at constant fineness. They also showed that the amount of water required by a given concrete of a given slump could be reduced when a dispersing agent was added to the concrete. This led to referring to these products as "water reducers." These products retarded the rate at which concrete developed strength and, accordingly, became known as "retarders." From this, it is seen that certain agents which can counteract the natural flocculating properties of the powdered cement minerals may be used as a grinding aid, as water-reducing agents and as retarders. The following is an attempt to explain the mechanisms whereby water-reducing admixtures and set-retarding admixtures function.

It should be pointed out that these materials, except when used as grinding aids, were always used with cements, clinker, plus calcium sulfate. Hence, classifying them as retarders did not imply that they were useful in preventing flash set. Limited experience has shown that the small amounts normally used for dispersion and a moderate retardation of the rate of developing strength will not prevent flash set with some clinkers in the absence of calcium sulfate. Forbrich (30) found that a dispersing agent added to a paste of $3CaO \cdot Al_2O_3$ plus 12 per cent gypsum delayed the rate of evolution of heat. He found the same effect when the dispersing agent was added to a paste of $3CaO \cdot SiO_2$ that contained no calcium sulfate. He found that calcium chloride had very little effect on the paste of $3CaO \cdot Al_2O_3$ plus calcium sulfate but increased the rate at which heat was liberated from the paste of $3CaO \cdot SiO_2$. Steinour (3) has shown that many organic compounds retard the rate at which pastes of $2CaO \cdot SiO_2$ develop strength.

Ernsberger and France (32) studied the electrophoretic migration under a microscope of particles of cement suspended in water and in a solution of calcium lignosulfonate. Cement particles suspended in distilled water showed no tendency to migrate toward either electrode but they tended to flocculate. In the solution of calcium lignosulfonate, the cement particles tended to be dispersed and to migrate to the anode. This indicated that they had acquired negative charges by adsorbing negative ions from the solution. The existence of such anions was demonstrated by applying a potential to a solution of calcium lignosulfonate in an electrophoresis cell which caused the brown lignosulfonate complex to move toward the anode and a precipitate of calcium hydroxide to form at the cathode.

Ernsberger and France determined the adsorptions by portland cement of the calcium salts of three lignosulfonic acids of different molecular weights. At concentrations of 0.02 g per liter, the adsorptions in mg per g of cement were approximately 13.0, 4.2, and 1.8, respectively, for the acids having average molecular weights of 9500, 2140, and 250 to 920.

These demonstrations led to the conclusion that the adsorption of the large anion was responsible for dispersion, water reduction, and retardation. However, no effort was made to explain the mechanism by which the anion operated.

The oil well cement industry has used organic materials, not for the purpose of preventing flash set but of prolonging the period during which a cement slurry remains sufficiently fluid for transporting by pumps at elevated temperatures. Hansen (3) pointed out that the organic materials used for this purpose generally contained one or more CHOH groups and Steinour (3) suggested that the active group was the OH group. He pointed out that compounds with OH groups attached to benzene rings, as well as some inorganic acids containing OH groups, were effective retarders. This led him to the conclusion that these compounds were adsorbed by means of hydrogen bonding on the surfaces of the crystals of the cement minerals.

The principal organic materials used as water-reducing and retarding agents at normal temperatures are either the acids or the salts and derivatives of lignosulfonic and hydroxylated carboxylic acids. Chemists are not in complete agreement regarding the structures of lignin compounds but cement technologists probably are safe in visualizing lignosulfonic acids as being composed of several of the following units:

$$HOCH_3OC_6H_3CH_2CHOCHHSO_3\,.$$

This unit contains an OH group attached to a benzene ring and an HSO_3 group. The latter is a relatively strong acid and ionizes to yield H_3O^+ ions and, accordingly, can combine with cations to give the MSO_3 group, where M represents a cation. For simplicity, a lignosulfonic acid salt might then be written $(HORSO_3M)_x$ which then yields $(HORSO_3^-)_x + XM^+$ ions. For simplicity, we may consider X to be 2.

The negative ions of these salts could react as follows by ionic bonding with the Ca^{++} ions in the surfaces of the cement minerals:

$$Ca^{++} + (O_3SROH^-)_2 = Ca(O_3SROH)_2\,.$$

In hydrogen bonding, an O reacts as follows with an OH group:

$$O + HO = OHO.$$

Hence, these ions could react as follows by hydrogen bonding with O^- ions in the surfaces of the cement minerals:

$$O^- + (HORSO_3^-)_2 = O(HORSO_3^-)_2\,.$$

The unionized molecules could also react as follows by hydrogen bonding with the O^- ions:

$$O^- + (HORSO_3M)_2 = O(HORSO_3M)_2\,.$$

There are a number of hydroxylated carboxylic acids. Tetrahydroxy adipic acid, for example, has the following formula:

$$(HO)_4C_4H_4(COOH)_2\,.$$

The negative ions of salts of this acid could react as follows by ionic bonding with Ca^{++} ions in the surfaces of the cement minerals:

$$Ca^{++} + (OOC)_2H_4C_4(OH)_4^{--} = Ca(OOC)_2H_4C_4(OH)_4\,.$$

They could react as follows by hydrogen bonding with O^- ions:

$$O^- + (HO)_4C_4H_4(COO^{--})_2 = O(HO)_4C_4H_4(COO)_2\,.$$

The unionized molecules could react as follows by hydrogen bonding with O^- ions:

$$O^- + (HO)_4C_4H_4(COOM)_2 = O(HO)_4C_4H_4(COOM)_2\,.$$

These hydroxylated carboxylated acids may undergo what is known as chelation by hydrogen bond formation (33) whereby an OH group in one molecule may react as follows with an OH group in another molecule:

$$ROH + OHR = ROHOHR.$$

A number of molecules may be combined in this way to give very large molecules.

Weyl has shown how the ions in the surfaces of crystals may be rearranged to lower the surface energy. It is not possible with our present knowledge to predict the arrangements of adsorbed ions and molecules on the crystals of the cement minerals. However, it is known that some of these are arranged to give particles that repel each other. Also, it is known that certain adsorbed ions and molecules retard the rate at which cement pastes stiffen. If the rate of the reaction shown in Reaction 12 controls the rate at which the cement reacts with water, then the adsorbed ions and molecules must retard the rate at which H_3O^+ ions can be adsorbed by O^- ions in the surfaces of the cement minerals.

A large ion such as $(HORSO_3^-)_x$ adsorbed on Ca^{++} ions might screen the O^- ions and in that way retard the rate at which they can adsorb H_3O^+ ions. The adsorption by O^- ions through hydrogen bonding of ions such as $(HORSO_3^-)_x$ or $(HO)_4C_4H_4(COO^-)_2$ or of molecules such as $(HORSO_3M)_x$ and $(HO)_4C_4H_4(COOM)_2$ would block the O^- ions from H_3O^+ ions. These adsorbed ions and molecules might go through some rearrangement by the action of polarizing forces or they themselves might adsorb other ions or molecules through hydrogen bonding.

It is not within the scope of this paper to attempt to differentiate either between classes of compounds or between members of a given class in their ability to influence dispersion, water reduction, and retardation in cement pastes. However, it seems reasonable to believe from what may be expected regarding the adsorption of different types of ions and molecules that the characteristics of the surfaces produced by the adsorptions of different classes of compounds on the cement minerals will differ and that these differences will be reflected in properties of the cement pastes.

The retarding effect of these organic retarders appears to diminish with time. Flint and Wells (34) showed that $3CaO \cdot Al_2O_3$ could form the compounds $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 30$ to $32H_2O$ and $3CaO \cdot Al_2O_3 \cdot CaSiO_3 \cdot 12H_2O$ and that $3CaO \cdot Al_2O_3$ could form the compound $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot 30H_2O$ as well as the compound $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$. They classified the compounds in which one mole of $3CaO \cdot Al_2O_3$ combines with 3 moles of another salt as type I compounds, and the others as type II compounds, and listed formulas for ten of the type I and for nine of the type II compounds, taken from work of other investigators. It seems, from the work reviewed by Steinour (9), that most of the type I compounds will form complete series of solid solutions with each other and that most of the type II compounds will form complete series of solid solutions with each other.

It appears from these studies on these type I and II compounds that $3CaO \cdot Al_2O_3$ will form double salts with all calcium salts. Hence, calcium salts of both organic and inorganic acids should be removed from the liquid phase of a cement paste by forming a double salt with $3CaO \cdot Al_2O_3$.

Lerch, Ashton, and Bogue (8) showed that the sulfoaluminate formed in preference to the chloroaluminate in a mixed solution of calcium sulfate and chloride. It seems that the least soluble double salt should be formed first. Hence, if the compound formed with the calcium salt of an organic acid was less soluble than the sulfoaluminate, it should form in preference to the latter. If this occurred, the organic salt might be removed rather rapidly from the liquid phase of the cement paste and, accordingly, exert its retarding power for a relatively short period of time. It would seem, therefore, that the length of time during which such a retarder would function would depend upon the $3CaO \cdot Al_2O_3$ content of the cement. Tuthill and Cordon (35) found that 0.5 per cent of a retarder prolonged the setting time of one cement from 6 to 11 hr and of another from 6 to 14 hr. Lukyanova, Segalova, and Rehbinder (36) found that the adsorption of sulfite liquor by cement was a function of the $3CaO \cdot Al_2O_3$ content of the cement and was an irreversible process.

In some cases, it is desirable to use a dispersing agent to reduce the amount of water required for a given concrete without retarding greatly the rate of attaining early strength. In such cases, a mixture, for example, of an organic retarding agent and calcium chloride may be used as the admixture. The large negative ions and molecules of the dispersing agent are adsorbed and retard the rates of the reactions. However, as its concentration is reduced by reaction with the $3CaO \cdot Al_2O_3$, the added $CaCl_2$ can function to increase the rates at which the silicates develop strength. This increase might equal or exceed the retardation produced during the life of the dispersing agent.

SUMMARY

A review of the literature leads to the conclusion that many investigators of the setting and hardening of portland cement pastes recognized that the cement minerals reacted with water without dissolving in the liquid phase of the cement-water paste.

This paper considers the reactions in such pastes in terms of $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$, and $2CaO \cdot SiO_2$. It suggests a mechanism for these reactions based on the chemisorption of OH^- and H_3O^+ ions from water by Ca^{++} and $O^=$ ions in the surfaces of the crystals in which the chemisorbed ions diffuse into the solid crystals and transform them into solid reaction products. In this mechanism, $3CaO \cdot Al_2O_3$ causes flash set by the following reaction:

$$3CaO \cdot Al_2O_3 + 9H_2O$$
$$= 2CaO \cdot Al_2O_3 \cdot 8H_2O + Ca(OH)_2.$$

Calcium salts accelerate the rate at which pastes of the calcium silicates develop strength by decreasing the concentration of $Ca(OH)_2$ in the liquid phase of the cement paste by the following reaction which causes $Ca(OH)_2$ to be precipitated:

$$2MOH + CaR = M_2R + Ca(OH)_2$$

where M is either or both Na and K, and R is an anion.

By decreasing the amount of $Ca(OH)_2$ in solution, the concentration of H_3O^+ ions is increased and thereby the rate at which these ions can be chemisorbed by $O^=$ ions.

The dispersing, water-reducing, and retarding properties of organic materials are explained on the basis of adsorption of the organic anions and molecules. A large anion adsorbed by the Ca^{++} ions in the surfaces of the crystals will tend to block the $O^=$ ions in those surfaces and, accordingly, retard the rates at which they can chemisorb H_3O^+ ions. The charges in the adsorbed anion may be rearranged in the surface to produce surfaces which are predominantly negatively charged and, accordingly, repel each other. Similarly, the $O^=$ ions may adsorb by hydrogen-bonding anions and molecules that contain OH groups. These will block the $O^=$ from H_3O^+ ions and may undergo rearrangement to produce surfaces that are predominantly negatively charged.

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DISCUSSION

MR. HAROLD H. STEINOUR[1] (*presented in written form*).—As the author's paper shows, the past experimental work leaves much uncertainty regarding the chemical and physical events that take place in portland cement paste before it hardens. There are, of course, good reasons for this. Portland cement is a very complex material, and the paste is a thick suspension ill adapted to the study of what goes on inside. Thus the evidence that we now have is in large degree indirect or incomplete.

To present a detailed picture on the basis of present knowledge involves, therefore, considerable speculation. Before we can eliminate the speculative elements we shall have to do much more research. I know from discussion with the author that he is fully as convinced as I am of the great inadequacy of present information.

As is natural in so speculative an area, the author shows that different investigators arrived at different interpretations. He accepts a part, rejects a part, and builds his own conception of things. The foundation of his edifice is the assumption of "solid state reactions."

This is a bold move. Although, as he shows, some others have also assumed direct, or *in situ* reaction, none has gone into the detail that he has or been so articulate about diffusion into crystals as a major feature of the reaction mechanisms.

In thus presenting something new in so controversial a field, I am sure that the author did not expect, nor wish, to avoid critical comment. Following his own pattern, I am inclined to accept a part and question a part of what he has offered.

Retardation by Gypsum:

What I can accept wholeheartedly is the prominant role assigned to adsorption. I

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[1] Assistant to Director of Research, Portland Cement Assn., Research and Development Laboratories, Skokie, Ill.

think of this as formation of surface layers or coatings (held by either physical or chemical adsorption and not limited to monolayers), which coatings act to hinder further reaction of the underlying solid. However, I think of these coatings as forming by precipitation onto the reacting solids. My views are expressed in a paper published in 1958 (**1**).[2] Though my ideas of mechanism differ from those of the author, I agree with his conclusion that in retardation by gypsum or other form of calcium sulfate "some combination of SO_3 with $3CaO \cdot Al_2O_3$ prevents flash set." This product is called a calcium sulfoaluminate. Experiments have shown that a large proportion of the gypsum retarder reacts within the first moments of contact with water, forming apparently such a product (**2**,**3**). This sulfoaluminate apparently coats the surfaces of the tricalcium aluminate, thus preventing ready access to the solution, for the reaction with sulfate drops abruptly to a very low rate. The paste remains plastic, showing that flash set has been avoided.

The coating is not wholly protective, for the tricalcium aluminate continues to react slowly, but the reaction simply forms more sulfoaluminate which can continually repair the coating as long as any calcium sulfate remains. However, experiment shows that the sulfate is eventually consumed. There then occurs in some cements the "delayed rapid reaction" that Lerch (reference (**16**) of the paper) demonstrated by means of the heat liberation. This is apparently a rapid reaction of the tricalcium aluminate that can occur when no more sulfoaluminate can form and calcium aluminate hydrate starts forming instead. Formation of this new product apparently breaks up the coating, thus allowing the reaction to accelerate. A point of special interest is that in cements in which this delayed rapid reaction develops use of ample gypsum causes it to occur after final set. Under such circumstances it is evident that hydration of the aluminate is not what caused the set. Indeed the very fact that so rapid a reaction of aluminate can occur in already set cement suggests that the reaction cementing the mass together has been occurring at other than the aluminate surfaces. In a case like this, the set evidently occurs as a result of the hydration of tricalcium silicate, for experiments with pastes of this compound show that they set in about the same time as normal cement pastes.

Of course, when too little gypsum is used, the control exercised over the reaction of the tricalcium aluminate may cease at a relatively early stage, with relatively early onset of the "delayed rapid reaction." If the cement has not already set, this reaction of the aluminate can evidently produce set much as in unretarded cement. The nature of the reaction causing set is thus dependent on the amount of gypsum used. However, cements that contain what Lerch defined as the optimum gypsum content should apparently all set because of hydration of the tricalcium silicate—the aluminate reaction being sufficiently controlled.

Slowness of Solid State Reactions:

Returning now to the author's theory of solid state reactions, I regret that a part of it is very difficult for me to accept. He assumes that ions can diffuse with great rapidity into the clinker compounds at ordinary temperature. Moreover, rough calculations indicate that diffusion through many molecular layers would be necessary to account by this mechanism for the amount of reaction that he obtained in 1 min. This rapid diffusion into the solids is so basic an element of his theory that I regret to dispute it, but to me it seems very unlikely.

Our laboratory library has several

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[2] The boldface numbers in parentheses refer to the list of references appended to this discussion.

books and journal papers that review solid state reactions. Examination of these has confirmed my previous impression that such reactions have nearly always been studied at elevated temperatures for the reason that they do not generally occur with sufficient or even measurable rapidity at room temperature. The reference here is to solid reactions that require diffusion into the solid, as distinguished from reactions such as dehydrations that simply remove a part of the crystal lattice and can open up channels for further removal. I exempt, also, reactions such as those of zeolites, where the crystal lattices are so open-structured that ions can move through the channels as they might along an exterior surface. Though the atoms in the cement compounds may not all be in the closest packing, the crystals certainly contain no such channels as in the zeolites. The densities of the cement compounds are relatively high, and diffusion of such ions as H_3O^+ and OH^- into the crystals would apparently have to occur by displacements such as occur in those solid state reactions that proceed very slowly or not at all at room temperature. The author's discussion is in terms of diffusion into these original solids, but I find that the diffusion that is generally discussed in solid state reaction theory is that through the layer of reaction product that builds up. Indeed, it is hard for me to see how there could be much diffusion into the cement compounds since the products are of greater volume, and there would apparently be a breaking up at the surface. If diffusion into the original solids does not have to occur and if the products (other than $Ca(OH)_2$) are gels and thus relatively permeable, then I can see more possibility of some kind of direct, or *in situ* reaction, but the author has assumed diffusion into the original solids. Hence my discussion relates to diffusion of this kind.

Since solid state reactions are studied in the absence of a liquid phase, the pertinent literature relates mainly to reactions between solids. My examination disclosed one so-called reaction or "starting" temperature as low as 160 C. Other reactions were indicated to proceed between 200 and 300 C and others between 300 and 400 C. These seemed to be regarded as the lower ranges of temperatures for solid state reactions involving interaction of inorganic salts and oxides.

Tammann, an early experimenter in this field, reported an approximate relationship between reaction temperature and melting point of the solid. Welsh (4) reporting in 1955 defined the "Tammann temperature" as "very approximately the minimum temperature at which the solid may be expected to enter into a solid state reaction of appreciable rate." He said, "Such characteristic temperatures are only a general guide to solid reactivity, but as such they are useful." For reaction involving lattice diffusion he gives the Tammann temperature as one half the melting point on the absolute scale. For appreciable "surface mobility of lattice units," the corresponding fraction is three tenths of melting point. Since the major compounds in cement clinker have melting or decomposition points ranging from about 1400 C to above 2000 C, the reaction temperature on either basis would be far above room temperature.

Hedvall, another extensive investigator in this field, found that for a number of reactions involving calcium oxide the reaction temperatures were all somewhat above 500 C (4).

Viewed against this background, solid state reactions involving diffusion into the crystal do not appear to me to provide a sufficiently plausible explanation of the rapid formation of reaction product when portland cement first comes into contact with water.

Volume Considerations:

Support for this viewpoint can also be drawn from the fact that the hydration products occupy much greater volume than the anhydrous solids. Even if the calcium hydroxide that is split off is thought of as dissolving and going elsewhere, there is still a large volume increase. This is true even for tricalcium silicate, owing to the pore volume that Powers (5) has found to be an essential part of the hydration product, or cement gel. Thus, if solid state reaction is the correct mechanism throughout, the original particle must obviously expand greatly and can only do so by pressing out against its surroundings. A similar action evidently does occur in the case of delayed hydration of calcium and magnesium oxides, as the author has noted. These, however, are disruptive and disintegrative reactions whereas the normal hydration of portland cement is not.

Hydration by dissolution and precipitation, which is the usual mechanism of low-temperature reactions in the presence of a liquid phase, does not involve this problem. Of course, as reaction proceeds and the cement particles become enveloped with reaction product, reaction by solution and precipitation must become more involved. Presumably, surface forces are then felt at all times. Solution may then take on a somewhat different meaning while still involving the loosening of ions from their positions in the crystal, with passage into a more fluid film before being reoriented and deposited as part of a hydrate molecule. Some hydrate could be deposited in the space made available by the dissolution, and some would evidently have to form by transport of ions out through narrow channels until spaces affording sufficient room for deposition of product were reached. Powers (6) has given considerable thought to matters of this kind. Here, we are concerned with the early reactions before this problem becomes acute.

However, before leaving the subject, it is of interest to refer to the observations of McConnell (reference (19) of the author's paper). McConnell found naturally occurring nodules of dicalcium silicate surrounded by pseudomorphic sheaths of considerable thickness. In this case, leaching of the original crystals was a prominent feature of the mechanism for there were left only 6 silicon and 5 calcium atoms in unit volume that originally contained 8 silicon and 16 calcium atoms. Thus, ample space was cleared for the hydrate water.

Lack of Direct Data:

The author rejects the solution and precipitation mechanism because he thinks it could not operate fast enough to give as much product as was formed during the first minute. It might perhaps be argued that the experiments on which he bases this conclusion involved reaction with calcium chloride instead of the usual reaction with gypsum; however, I do not raise this point because I believe, as he does, that the usual reaction rate is comparable.

As I understand it, the autho is not arguing, as a general truth, that reactions of solution and precipitation cannot occur so fast as the reaction that did occur. This would be a very difficult position to maintain, for it is common knowledge that solution and precipitation can progress with great rapidity. What he finds impossible to believe is that the reactions of compounds containing silica and alumina could occur so fast "when only traces of these oxides can be found in the liquid phase."

Study of this qualification indicates that the assumed impossibility of the reaction reduces to assumed impossibility of the very high rate of transfer or diffusion of ions through the solution which would be necessary if the concentrations during reaction stay so low. Calculations could no doubt be made that would establish the possibilities or impossibilities more definitely, but I am much more inclined to dispute the premise than the logic that is based on it. That is, I do not believe that the concentrations did remain, during the initial minute of reaction, at such trace amounts.

The only numerical data that the paper presents on this point are for extracts taken at 7 min and 2 hr. But 7 min is too late a time to furnish a reliable indication of the situation during the first minute, which is the period for which the amount of reaction was determined. The author recognized this, for he stated that similar data are obtained for shorter reaction periods. I do not doubt this, but I do doubt that data that support his position have been obtained within the initial 1-min period, which is what is required.

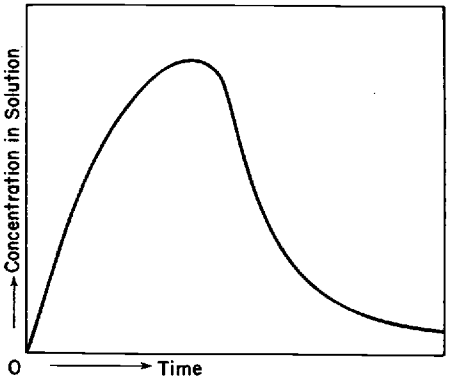

FIG. 2.—Hydration by Solution and Precipitation.

In an earlier report (reference (3) of the paper, pp. 318–321) the author used the 1-min data of his Table I as indicating low silica and alumina concentrations because rather good electrostatic balances of positive and negative ions are obtained without counting these ions. This indication, though more subject to error than a direct determination, warrants attention, but it too does not take us within the first minute. In other words, it does not show how high the concentrations may have risen during the period of solution and precipitation with which we are concerned.

Data for More Dilute Suspensions Support the Solution Theory:

I am not aware of any extraction data having been obtained short of 1 min, but extracts taken at longer time intervals from more dilute suspensions give indications of what happens earlier in dense paste such as cement paste. Whatever the concentration of particles in the initial suspension, the concentration in solution builds up toward a peak by striving toward the solubility-concentration of the initial solid, and then as precipitation occurs it drops toward the lower solubility-concentration of the product. This course is indicated by the accompanying Fig. 2. Decreasing the concentration of solid in the suspension naturally lengthens the time that would be required to reach saturation if precipitation did not occur. Obviously, too, it lengthens the time required to reach the same height of peak when precipitation does develop. Owing to this stretched-out time scale (which may favor precipitation at less supersaturation) the peak may not go so high, but it is probable that the decline from the peak will also be stretched out because of increase of distance between precipitation points. That is, precipitation probably occurs largely on the original particles and thus occurs less rapidly when these are farther apart. On the whole, therefore, it appears that for the more dilute suspensions there would be a rather general stretching of the time scale of Fig. 2. Thus, it is indicated that

TABLE IV.—SOLUTIONS DERIVED FROM A PORTLAND CEMENT, 20 G PER LITER (FLINT AND WELLS).

Time of Contact	CaO, g per liter	SO_3, g per liter	Al_2O_3, g per liter	SiO_2, g per liter
1 min	0.5168	0.3423	0.0064	0.0234
3 min	0.5236	0.3414	0.0050	0.0208
5 min	0.5586	0.3509	0.0052	0.0198
10 min	0.5634	0.3358	0.0022	0.0216
30 min	0.5744	0.3214	0.0020	0.0202
1 hr	0.6284	0.3317	0.0028	0.0154
2 hr	0.7624	0.3095	0.0008	0.0102
8 hr	1.6125	0.1538	0.0025	0.0020

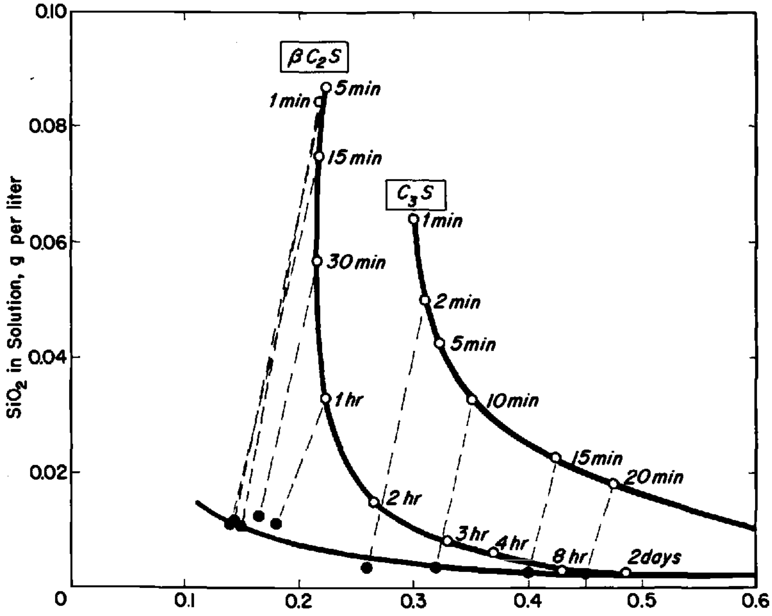

FIG. 3.—Solution Derived from β C_2S and C_3S (20 g per liter) (7).

high concentrations representing supersaturation relative to the products will be found at later times when the dilution of the initial suspension is increased. Making tests at a fixed period on suspensions of progressively increased dilution would then be comparable in effect to moving backward on the time scale of Fig. 2. In any case, if concentrations are permanently low after 1 min in dense paste but are found to be relatively high after this same period in less dense suspensions, we may be confident that at earlier moments relatively high concentrations were also developed in the dense paste.

In the author's experiments with calcium chloride, he used 200 g of clinker to 150 ml of solution, or 1333 g of clinker per liter. In the work of Kalousek, Jumper, and Tregoning (reference (13) of the paper), for which the author reports the 7-min and 2-hr data, a water-cement ratio of 0.35 was used, or 2860 g of clinker or cement per liter. It is therefore of interest to examine data of Flint and Wells (7) which were obtained by shaking only 20 g of cement with 1 liter of water. These data are shown in the accompanying Table IV. At 1 min the concentrations of Al_2O_3 and SiO_2 may still appear small, but they are much larger than the 3 mg and less shown by the 7-min data of Kalousek and his associates. It is apparent also that the values diminish with time, thus suggesting that at 1 min the values were already on the wane. It is to be noted, however, that the CaO values are increasing with time. This is owing to hydrolysis with production of calcium hydroxide which is more soluble than the other products. Thus, although the other hydrates are already precipitating, the calcium hydroxide concentration has not yet reached saturation. The increase in calcium hydroxide concentration depresses the solubilities of the silicate and aluminate hydrates and causes their concentrations to drop more rapidly than would otherwise be the case. In the 7-min Kalousek data, the CaO values were high, which was sufficient reason for the low values of SiO_2 and Al_2O_3. Before these high CaO values were attained, the SiO_2 and Al_2O_3 values would have been higher because of the higher solubilities, even had there been no supersaturation.

Valuable information is also provided by Fig. 3 which shows data obtained by Flint and Wells (7) upon shaking tricalcium silicate and beta-dicalcium silicate with water, using the same proportions as for cement, namely, 20 g per liter. Here the SiO_2 concentration is plotted against the CaO concentration, and the points are labeled to show the times at which the extracts were taken. Dashed tie lines connect the curves representing the analyses of the extracts with a lower curve that shows the equilibrium concentrations attained after precipitation occurred in the extracts.

In the case of the slowly reacting dicalcium silicate, the relative positions of the 1-min and 5-min points indicates that the SiO_2 concentration probably did not go much higher than was found at these times, namely, about 85 mg per liter. But in the case of the tricalcium silicate it is evident that the SiO_2 concentration may have gone considerably higher than the 64 mg per liter found at 3 min. It is the rapid increase of the calcium hydroxide concentration that has forced this value down below that found for the dicalcium silicate at 1 min. The 64 mg per liter is, however, a very high value as compared with the value of less than 1 mg per liter shown by Kalousek's 7-min data reported by the author.

Forsen (reference (11) of the paper, pp. 298–363) reported work in which only 0.2 g of tricalcium silicate was shaken with 1 liter of water. Even this very weak suspension gave a 1-min extract containing 18.4 mg SiO_2 per liter. This is 34.8 per cent of the total SiO_2 in the sample. Although this percentage is surprisingly large, comparison with data for other periods indicates that if filtration was adequate it is perhaps a fairly reliable result. Under the prevailing conditions, the precipitation was small, for the total amount of tricalcium silicate that reacted was calculated as only 5.4 per cent more, that is, 40.2 per cent. Here then is evidence that exceedingly rapid solution of tricalcium silicate may occur when blocking by the product is reduced to a minimum.

Forsen also reported that 0.2 g of tricalcium aluminate shaken with a liter of water for 1 min gave an Al_2O_3 concentration of 23.7 mg per liter, which is 31.2 per cent of the total Al_2O_3. It is a very high concentration as compared with that in the 7-min extract reported by the author.

These various data lead me to believe that the early reactions occurring in cement paste at ordinary temperature do not depart from the usual rule but occur mainly by solution and precipitation. It is natural that in a cement paste these initial reactions should largely cease within a very short time since 1 min is a reasonably adequate mixing period for concrete, and a proper mixing period must be long enough for establishment of the conditions of retardation. With cessation of the reaction, the concentrations of silica and alumina quickly approach the very low values that correspond to the solubilities of the products. The data indicate that at earlier moments the concentrations are much higher. They may indeed be considerably higher than any of the values reported, since there is no reason to believe that these represent the peak amounts attainable in the paste.

The reaction of tricalcium silicate is peculiar in that the initial rapid reaction is so quickly reduced to a low rate that it does not cause setting and yet later on the reaction again accelerates, is not quickly damped, and does cause setting. This course is followed even in pure tricalcium silicate paste, and the changes in reaction rate are shown by data on heat liberation (reference (30) of the paper, pp. 161–184). This self-regulating effect of tricalcium silicate has received no satisfactory explanation. One may assume that the initial reaction is cut short by the blanketing effect of hydration product, but the reason why the effect should later be overcome is not clear. Some possibilities suggest themselves, but only further research can provide a decisive answer.

Importance of Hydroxyl Groups:

I am glad now to turn from these considerations to an area in which the author and I are in rather complete agreement. The author greatly advanced our understanding of the action of the majority of organic retarders when, in 1952 (reference (3) of the paper, pp. 598–627), he reported that most retarders used in oil-well cements fall in three main classes and that all three classes consist of compounds that contain the atom group HCOH. As he reports in the present paper, I presented additional data which indicated that the active factor is simply the OH group, for OH groups attached to the benzene ring appear to be effective in this way also (reference (3) of the paper, pp. 627–631). In tests of chemical additions to pastes of beta-dicalcium silicate I had found an apparent relationship between degree of retardation and number of un-ionized or undissociated OH groups. It appeared also that OH groups in some inorganic compounds are similarly effective if they do not dissociate or ionize off. The most plausible mechanism appeared to be that of adsorption through formation of a hydrogen bond. From the author's study of cement retarders, it seems clear that what was found for dicalcium silicate can be extended to cements. Indeed, in cements with good contents of gypsum in which setting is due to hydration of the tricalcium silicate, it is logical to assume that in order to obtain further retardation it is the reaction of the silicate that must be slowed up. An agent that is adsorbed on dicalcium silicate would presumably be adsorbed on tricalcium silicate also. There is also good reason to believe that adsorption through hydrogen bonding occurs on tricalcium aluminate. A common form of hydrogen bonding is attachment to oxygen atoms, and all of the major clinker compounds are combinations of oxides. As the author has pointed out, the lignosulfonates contain OH groups. Russian investigators have made extensive studies with the lignosulfonates and report extensive adsorption on tricalcium aluminate (8).

The molecules of chemicals that contain OH groups tend to form hydrogen bonds with one another. Thus compounds with more than one OH group may perhaps form particularly stable adsorbed layers owing to the ability to form cross linkages. Perhaps this is one reason for the apparent relationship between number of OH groups and efficiency of retardation. As the author pointed out in his 1952 paper, the fact that a compound contains an OH group does not insure that it will be a retarder, for there may be opposing influences. However, a compound containing several OH groups appears generally to be a strong retarder. Ordinary sugar (sucrose) is reputed to be a very destructive retarder. It sometimes gives a very quick set owing apparently to the amount of reaction that can sometimes occur before the retardation is established, but fairly small amounts can seriously affect early strength development. This compound, $C_{12}H_{22}O_{11}$, contains eight OH groups.

MR. W. C. HANSEN (*author*).—I am pleased that the case for the solution-precipitation hypothesis has been presented. I cannot, of course, present data to refute Mr. Steinour's arguments because the same data are available to both of us. In other words, as both agree, there is need for experimental work in this field.

This position by Mr. Steinour is somewhat surprising because he and T. C. Powers (9) published a paper in which they seemed to accept the previously published hypothesis that grains of opal encased in a hardened cement paste could chemisorb alkali and hydroxyl ions from the liquid phase of the hardened paste and form solid alkali silicates. It seems to me that the mechanism suggested for the reactions between cement minerals and ions from the liquid phase of cement pastes is similar to that postulated for the reaction of opal and alkalies.

After my paper was written, I obtained a translation of a paper by Funk (10) who reacted β $2CaO \cdot SiO_2$ with water vapor at 100 C and obtained a product that had an X-ray diffraction pattern similar to that of the tobermorite-like product obtained when β $2CaO \cdot SiO_2$ is hydrated in water. He states:

> "Le Chatelier's hypothesis is generally accepted as correct, namely, that $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ go into solution during hydrolysis and that calcium silicate hydrate is precipitated out of solution due to its low solubility. Formation of the tobermorite-like calcium silicate hydrate phase through action of water vapor on β $2CaO \cdot SiO_2$ at 100 C demonstrates that some other mechanism may be at work during the reaction of H_2O with β $2CaO \cdot SiO_2$."

Chemists long ago recognized that reactions occurred at the surfaces of solids. In some cases, they were certain that these were chemical reactions and used the word chemisorption for such reactions. When they were in doubt about them being chemical reactions, they used the term adsorption. However, they did limit these reactions, at least by definition, to reactions of a solid with ions and molecules from a liquid or a gaseous phase. That is, the definition of adsorption did not include any reaction of one solid with another as adsorption. The solution-precipitation theory appears to include a reaction between two solids under the heading of adsorption. That is, it seems to visualize, for example, the precipitation of a hydrated calcium silicate on the surface of a crystal of $3CaO \cdot SiO_2$ as adsorption. I cannot visualize this type of a process as one that should be classed as either adsorption or chemisorption. It seems that a precipitation could occur in which the surface of the $3CaO \cdot SiO_2$ would be covered with the hydrated silicate without any interaction between the two solids. The precipitate could interfere with the further reaction of the $3CaO \cdot SiO_2$ and water by a more or less blanketing effect.

A number of investigators have suggested that the hydrated calcium silicates formed by the reactions of $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ contained adsorbed $Ca(OH)_2$. It was never clear whether this was visualized as a case of one solid adsorbing another solid or whether calcium and hydroxyl ions were adsorbed from solution by the solid hydrated calcium silicate. Recently, Brunauer, Kantro, and Copeland (11), from their studies and from studies of the work of others, concluded that the adsorption of $Ca(OH)_2$ on the surface of tobermorite must not be appreciable. The results of their studies also indicate that some $Ca(OH)_2$ would exist in hardened cement pastes as amorphous or poorly crystallized $Ca(OH)_2$. This, together with the evidence that the other reaction products are also either amorphous or poorly crystallized, does not support the solution-precipitation process.

One can also visualize the case in which a hydrated silicate could crystallize on the surface of a crystal of $3CaO \cdot SiO_2$ by using the $3CaO \cdot SiO_2$ as a nucleus on which to crystallize. This, it seems, should not be called adsorption. However, if it did occur, there is the problem of the mechanism whereby the $3CaO \cdot SiO_2$ that acted as the nucleus reacts with water for its final hydration.

Mr. Steinour argues against what I have classed as solid state reactions occurring at atmospheric temperatures. However, he seems to have accepted the idea that opal and sodium hydroxide can react at such temperatures without the opal going into solution. He likewise accepts the reaction of MgO with water vapor at these temperatures. I see no reason for doubting the possibility that minerals, such as $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$, can undergo a similar type of reaction with water at atmospheric temperatures.

Mr. Steinour cannot visualize these solid state reactions occurring without causing expansions. Our picture of the structure of hardened cement paste is not based on direct evidence. It is built up primarily from sorption data. These data may give a fairly accurate measure of porosity of the paste. However, it does not seem that they can possibly reveal whether or not a crystal of $3CaO \cdot SiO_2$ has reacted with water to give a cluster of identical particles of a hydrated silicate in which the porosity of the cluster is uniform throughout. It seems that the same sorption results might be obtained if the porosity of that cluster varied widely from the center to outside and also if the amount of water combined in the individual particles varied widely. The picture as revealed by these data is an average picture and, as such, cannot, in my opinion, be used to furnish data for calculating the volume change of any given particle of cement as it reacts in a cement paste. It is necessary to build these pictures to help in research but they should not be accepted as established facts.

Mr. Steinour uses data in his Table IV and Fig. 3, taken from work by Flint and Wells, to support the solution theory. In our laboratory we have made many extraction tests on pastes with water-cement ratios of about 0.50 to 0.75. The compositions of these extracts show that generally the liquid phase of a cement paste is slightly supersaturated with calcium hydroxide at the 1-min period. Therefore, it seems that the liquid phase of the cement pastes in normal mortars and concretes must be saturated with respect to calcium hydroxide almost immediately when cement and water come in contact with each other. If this is true, then attempts to study extracts at periods of less than 1 min might not yield information different from that obtained from extracts taken approximately 1 min after mixing.

The data from Flint and Wells used by Mr. Steinour were obtained from solutions that were not saturated with calcium hydroxide for periods of several hours. These data show that the concentrations of SiO_2 and Al_2O_3 are each about 0.002 g per liter when the solutions are saturated with calcium hydroxide. These values compare with those reported by

Kalousek, Jumper, and Tregoning for 7-min and 2-hr periods.

The data by Flint and Wells are more meaningful when expressed in moles per liter instead of g per liter. The 1-min data in Table IV then become 0.0092, 0.0046, 0.00006, and 0.0004 for CaO, SO_3, Al_2O_3, and SiO_2 respectively. Subtracting the 0.0046 for SO_3 from the 0.0092 for CaO to give $CaSO_4$, there remains 0.0046 CaO to combine with 0.00006 Al_2O_3 and 0.0004 SiO_2. The ratio of CaO to Al_2O_3 is 80 to 1 and for CaO to SiO_2 is about 12 to 1.

The data from Fig. 3 for $3CaO \cdot SiO_2$ at 1 min show a ratio of moles of CaO to SiO_2 of about 5 to 1. The ratio for $2CaO \cdot SiO_2$ at the same period is about 4 to 1. The data of Table IV and of Fig. 3 show one of the following:

1. The compounds $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, and $3CaO \cdot Al_2O_3$ do not dissolve congruently, or
2. If the compounds dissolve congruently the reaction products precipitate from the solution within the first minute after mixing.

If the compounds do not dissolve congruently, then solid reaction products are formed without the anhydrous crystals going completely into solution. This is what I have called a solid state reaction. It seems to me that most of the evidence when thoroughly analyzed favors some mechanism other than a solution-precipitation process; for example Chapelle (12) states "But Le Chateliers theory as given is still insufficient to explain why hydrated cement pastes reach such great mechanical strengths."

Mr. Steinour qualifies this theory by saying:

> "Of course, as reaction proceeds and the cement particles become enveloped with reaction product, reaction by solution and precipitation must become more involved. Presumably, surface forces are then felt at all times. Solution may then take on a somewhat different meaning while still involving the loosening of ions from their positions in the crystal, with passage into a more fluid film before being reoriented and deposited as part of a hydrate molecule."

MESSRS. R. C. MIELENZ AND R. B. PEPPLER[3] (*by letter*).—The author's contribution constitutes a body of very interesting postulations of solid state reactions in cement hydration, which extends but is grounded in modern thinking. It is difficult to determine what is generally accepted by cement technologists as the most probable mechanism or mechanisms of cement hydration, but it seems likely that it will be agreed generally that mechanisms similar to those postulated by the author govern all but the early hydration reactions. It is the author's contention that solution mechanisms play only a negligibly small role even in these very early reactions, that is, in the first few minutes of cement-water contact. This and certain other theories of the author are open to some criticism.

The author observes the relatively small concentrations of silicate and of aluminate ions in solution in the filtrates of cement pastes taken a few minutes after mixing the cement and water and further observes the evidence which indicates that hydration of the cement has proceeded to a relatively great extent in this short time interval. From these two observations, the author concludes that the mechanism of hydration in this time interval must be solid state reactions rather than solution reactions. Such a conclusion is not supported adequately by available data.

The kinetics of solid state reactions such as the author postulates are governed by rates of diffusion of ions into crystals, among other things. Although

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[3] Director of Research and Assistant Director of Research, respectively, The Master Builders Co., Cleveland, Ohio.

data on the particular diffusion rates under consideration are not available, it seems more reasonable to suppose that the postulated solid state mechanisms would be slower, not faster than solution mechanisms.

The absolute magnitude of the concentrations of the aluminate and of the silicate ions in solution at a given time are not important in this context. The solubility of calcium aluminate hydrates and of calcium silicate hydrates, respectively, in saturated calcic solutions is very slight and a concentration of silicate or aluminate ions which is small in absolute magnitude may yet represent supersaturated solutions of the corresponding hydrates.

The author points to the fact that prehydrated and carbonated C_3A reacts more slowly than unaltered C_3A, as indicating that hydration of C_3A is by solid state reactions rather than by solution mechanisms. On the contrary, it seems to be reasonable that surface layers of highly insoluble calcium aluminate hydrates and calcite should slow down further hydration of the underlying C_3A crystals, if such occurred by solution mechanisms.

Perhaps the most controversial statement of the author is to the effect that C_3A will form sulfoaluminate analogues with all calcium salts, including salts of high-molecular-weight polymers. This is difficult to imagine since it is well known that ettringite is composed of close-packed layers of O and OH, with embedded Ca, S, and Al (13). Formation of compounds isostructural with the sulfoaluminates and containing such large anions as lignosulfonate would violate the fundamental principles of substitution into crystal lattices. Molecular weights of lignosulfonates range from 2000 to about 100,000 (14). This may be contrasted with a molecular weight of 186 for calcium propionate. Therefore, the extrapolation of the fact that sulfoaluminate analogues based upon calcium propionate have been reported, to the presumption that similar calcium lignosulfonate analogues will form, is unwarranted.

It would appear also that retardation of C_3A hydration as effected by materials like lignosulfonates might better be explained in terms of adsorption of lignosulfonate anions upon C_3A grains or of precipitation of insoluble highly calcic lignosulfonate around the grains of C_3A.

Although formation of reaction products of C_3A and lignosulfonates, isostructural with sulfoaluminates, probably is impossible, one should not conclude that no chemical reaction occurs between C_3A and lignosulfonates.

MR. HANSEN.—Messrs. Mielenz and Peppler suggest that the solid state mechanism would be slower than a solution mechanism. I did not suggest the solid state mechanism because it seemed to be required by the rates at which reaction products are formed. This mechanism was suggested because there seems to be no evidence that shows that the calcium silicates and aluminates dissolve congruently and then react with water to form hydrated products and because this mechanism seems to explain the behaviors of portland cement pastes much better than does the solution mechanism.

I did explain the retarding effect of lignosulfonates on the basis of the adsorption of either the lignosulfonate anions or the lignosulfonate molecules. However, I suggested that this adsorption became chemisorption with respect to $3CaO \cdot Al_2O_3$ and, in that way, the lignosulfonate was rendered inactive as a retarding agent. Mielenz and Peppler seem to feel that it would be sufficient to say that the lignosulfonate anions were adsorbed by the $3CaO \cdot Al_2O_3$.

I visualize that the lignosulfonate retards the rate at which $3CaO \cdot SiO_2$ reacts with water as well as the rate at which $3CaO \cdot Al_2O_3$ reacts with water. Also, I visualize adsorption as a reversible process in which the adsorbed material moves back and forth from the adsorbing surface and the solution. According to my concept of these mechanisms, $3CaO \cdot Al_2O_3$ can, by chemisorbing the lignosulfonate, but not by adsorption, remove this material so it no longer retards the rates at which the $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ react with water. Since the lignosulfonate is not chemisorbed by $3CaO \cdot SiO_2$, the amount originally adsorbed becomes less and less as it is chemisorbed from the liquid phase by the $3CaO \cdot Al_2O_3$.

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STRUCTURAL AND LEAN MASS CONCRETE AS AFFECTED BY WATER-REDUCING, SET-RETARDING AGENTS

By George B. Wallace[1] and Elwood L. Ore[1]

Synopsis

Several commercial water-reducing, set-retarding agents of the lignin and hydroxylated carboxylic acid classes are explored as to their effect on mix design and on the many properties of fresh and hardened concrete. Their benefits and limitations are explained so that the agents may be intelligently and confidently utilized. Methodology consisted of comparing various concretes containing water-reducing retarding agents with similar concretes without agent. Results of several hundred laboratory and field tests conducted over the past 5 years show that optimum dosages of many agents on the market today will increase the compressive, tensile, and shearing strength of mass and structural concrete and improve its resistance to freezing and thawing and sulfate-induced expansive forces. The principal contribution of water-reducing retarding agents toward improved workability is through their ability to extend the length of time in which concrete can be consolidated by vibration and thus reduce the risk of obtaining cold joints. They do not, however, improve the ease of handling concrete as gaged by the slump test, and in a few cases will increase the rate of slump loss. Volume change due to wetting and drying, and permeability of mass concrete are not affected by water-reducing retarding agents in amounts sufficient to warrant changes in design and construction considerations. However, reduced temperature rise and savings in cooling mass concrete may be achieved as a result of lower cement requirement attendant to their use.

New ideas and improved techniques have characterized the concrete industry during the spectacular growth of heavy construction in America at midcentury. This symposium study is a part of this activity focused on establishing a body of knowledge necessary for rational selection and use of water-reducing retarding agents. The Bureau of Reclamation experiences in the past few years have aided in establishing criteria as to when and how to use water-reducing retarding admixtures to achieve economical improvements in the quality of concrete. These experiences indicate that many agents on the market today will produce satisfactory results. The effects of such admixtures on the many properties of concrete must be known if intelligent selection procedures are to be followed. Understanding their benefits and accepting their limitations will reduce the number of unsatisfactory experiences with these agents and accelerate the growth of confidence needed for their full utilization.

Both laboratory and field tests are described herein to show the influences of various water-reducing retarding agents (*WR* agents) on mix design, workability,

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[1] Engineers, Concrete Laboratory, United States Bureau of Reclamation, Denver, Colo.

TABLE I.— CHEMICAL AND PHYSICAL PROPERTIES OF CEMENTS.

	Type I			Type II								
Laboratory Number......	M-2598	M-2592	M-1219	M-2610	M-2595	M-2400	M-3100	M-2005	M-1779	M-1700	M-3329	M-3389
Specific gravity.......	3.13	3.15	3.16	3.20	3.20	3.17	3.17	3.17	3.18	3.19	3.13	3.17
Time of set, hr:min												
Initial............	4:40	3:10	4:00	3:50	4:05	4:50	4:15	3:40	4:00	4:30	3:30	3:55
Final.............	8:20	5:15	6:50	7:30	7:15	7:10	6:45	6:25	7:10	6:45	6:00	6:30
False set............	no	no	no	yes	no	no	no	yes	yes	no	no	yes
Blaine fineness, sq cm per g............	3116	3363	3240	3484	3484	3426	3360	3376	3520	3314	3407	3541
325 sieve, per cent passing............	88.0	89.5	92.4	96.5	94.6	94.1	90.9	94.0	96.1	93.4	94.2	94.6
Air, per cent.........	9.2	9.8	8.4	13.2	9.5	9.1	9.5	10.7	11.0	12.0	9.3	8.1
Chemicals, per cent												
SiO_2..............	21.34	20.42	21.56	22.54	21.60	22.70	22.72	24.83	23.24	22.27	23.2	21.74
Al_2O_3............	5.49	6.63	6.20	4.80	5.11	4.81	4.70	3.13	5.45	5.44	4.6	5.18
Fe_2O_3............	2.55	3.50	2.29	4.54	4.85	3.56	3.28	2.67	3.75	3.80	2.3	3.96
CaO..............	63.20	64.44	65.19	62.37	62.86	62.81	62.86	65.41	64.15	63.46	63.8	62.90
MgO.............	2.16	1.12	1.46	1.25	1.50	2.24	2.69	1.32	0.81	1.08	2.45	2.67
SO_3..............	2.21	2.24	1.84	1.78	1.81	1.84	1.86	1.61	1.75	1.72	1.9	2.32
Na O.............	0.15	0.15	0.08	0.13	0.27	0.22	0.23	0.14	0.14	0.07	0.05	0.10
K_2O..............	0.51	0.27	0.64	0.62	0.61	0.47	0.41	0.14	0.46	0.48	0.55	0.56
Ignition loss, per cent............	2.06	0.98	0.93	1.74	1.06	1.25	1.28	1.12	1.10	1.32	1.4	0.85
Insoluble residue, per cent............	0.13	0.21	0.13	0.22	0.14	0.17	0.11	0.08	0.18	0.12	0.07	0.35
Compounds, per cent												
C_3S...............	48.2	51.1	51.3	38.7	45.3	40.5	41.60	48.1	37.5	42.1	42.0	43.69
C_2S...............	24.9	20.0	23.2	35.5	27.9	34.6	33.84	35.0	38.4	32.1	35.0	29.45
C_4AF.............	10.7	10.6	7.0	13.8	14.7	10.8	9.97	8.1	11.4	11.6	7.0	12.04
C_3A...............	10.2	11.6	12.6	5.0	5.3	6.7	6.91	3.8	8.1	8.0	8.0	7.04
$CaSO_4$............	3.7	3.8	3.1	3.0	3.1	3.1	3.16	2.7	...	...	3.2	3.94

TABLE II.—CHEMICAL AND PHYSICAL PROPERTIES OF POZZOLANS.

Laboratory Number....................	M-2017	M-1236	M-3233	M-3053	M-3364	M-3337	M-2942B	M-3439A	M-3439B
Physical properties:									
Grinding time, hr:min...........	...	...	...	0:30	...	0:55	0:45	0:17	0:35
No. 325 sieve. per cent passing...	88.0	91.2	94.1	94.3	94.7	96.4	96.8	99.0	99.4
Air permeability surface, sq cm per g........................	18 140	2930	3496	5772	...	9484	9403	8417	9450
Specific gravity.................	2.44	2.52	2.53	2.39	2.54	2.36	2.38	2.35	2.35
Water requirement, per cent......	110	91.2	94.0	100.5	101.0	101.3	107.2	100.5	100.5
Shrinkage at 28 days, per cent....	0.108	0.065	−0.014	0.004	−0.005	0.024	0.018	0.017	0.019
Reduction of reactive expansion at 14 days, per cent..........	93	70	63	69	73	78	76	...	82
Chemical properties:									
SiO_2, Fe_2O_3, Al_2O_3, per cent.....	72.69	70.0	86.76	85.14	93.54	86.94	86.24	85.47	85.47
MgO, per cent................	...	1.6	1.56	0.96	2.35	0.20	0.21	0.59	0.59
Loss on ignition, per cent........	0.67	0.8	2.59	5.06	0.28	4.73	5.05	3.79	3.79
SO_3, per cent................	...	1.7	2.38	0.01	0.33	0.01	0.04	0.06	0.06
28-day alkali release, per cent....	0.30	1.07	1.03	1.05	0.84	1.56	1.26	1.49	1.49
Moisture, per cent............	0.25	...	0.34	0.17	0.01	1.35	0.58	0.38	0.38
Compressive strength of 2- by 2-in. cubes:									
Mass cure, 28 days, psi..........	5110	5780	5433	5558	5967	6742	5697	6650	6400
Mass cure, 90 days, psi..........	5670	5880	6433	5975	6425	6825	5625	6792	6508

strength, durability, volume change, adiabatic temperature rise, and permeability of concrete. Laboratory test results provide valuable indications of the potential behavior of an agent under consideration. However, it is desirable to supplement these tests with field tests using project materials under project conditions before selecting an agent for extensive use.

TABLE III.—SAND AND AGGREGATE GRADINGS, EXPRESSED AS PER CENT RETAINED.

Series	Maximum Size Aggregate	Sand									Aggregate						
		Pass 100 Pan	No. 50–100	No. 30–50	No. 16–30	Between Nos. 8–16	Retained on No. 8	Fineness Modulus	Specific Gravity	Absorption, 30 min, per cent	3/8—3/16	3/4—3/8	1½—3/4	3—1½	Over 3	Specific Gravity	Absorption, 30 min, per cent
I (Clear Creek	1½	3	16	30	30	13	8	2.58	2.66	0.60	20	33	47	0	0	2.64	0.70
II (Monticello Dam)	3/4	4	18	32	17	15	14	2.63	2.66	1.10	40	60	0	0	0	2.65	1.10
	1½	4	18	32	17	15	14	2.63	2.66	1.10	22	33	45	0	0	2.65	1.10
	3	4	18	32	17	15	14	2.63	2.66	1.10	15	25	28	32	0	2.65	1.10
II Ainsworth Canal	1½	1	12	35	23	18	11	2.78	2.64	0.30	22	33	45	0	0	2.40	3.30
III (Monticello Dam)	6	4	18	32	17	15	14	2.63	2.66	1.10	10	16	20	26	28	2.65	1.10
III Kirwin Dam[a]	6	3	17	35	25	14	6	2.48	2.63	0.20	6	20	25	25	24	2.62	1.20
III Glen Canyon Dam	6	6	20	28	12	16	18	2.66	2.62	0.84	11	20	30	26	13	2.59	0.57
	2½	5	20	24	14	19	18	2.76	2.63	0.84	13	18	33	36	0	2.62	0.37
III Gross Dam	6	5	12	23	30	23	7	2.75	2.67	...	23	0	19	28	30	2.69	...
III Flaming Gorge Dam	6	3	20	30	16	18	13	2.65	2.64	0.71	8	12	20	30	30	2.63	0.65

[a] Crushed limestone coarse aggregate with natural sand.

TABLE IV.

Agent	Description of Agents
A	Ammonium lignin sulfonate solution
B	Ammonium lignin sulfonate solution
C	Calcium lignin sulfonate solution
D	Hydroxylated carboxylic acid solution
E	Ammonium lignin sulfonate powder
F	Ammonium lignin sulfonate powder
G	Calcium lignin sulfonate powder
H	Calcium lignin sulfonate powder
I	Calcium lignin sulfonate solution
J	Calcium lignin sulfonate powder
K	Calcium lignin sulfonate powder with accelerator
L	Calcium lignin sulfonate solution

Laboratory Tests:

Physical and chemical properties of the materials used in the laboratory series of mixes are recorded in Tables I, II, III, and IV. Mixes were designed, test specimens fabricated, and tests performed in accordance with appropriate standard procedures (**1**).[2] The terms nominal dosage, overdosage, and severe overdosage are used herein to mean additions of *WR* agents in approximate amounts of 0.3, 0.5, and 1.0 per cent, lignin solids or hydroxylated carboxylic acid solution by weight of cementitious materials.

Laboratory mixes used in this investigation are grouped into three test series:

Series I.—This was designed to determine the effects of seven commercial water-reducing agents on retardation of set, water reduction, strength development, and durability of concrete containing 1½-in. maximum-size aggregates,

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

TABLE V.—SERIES I—SUMMARY OF MIX AND RETARDATION DATA AND COMPRESSIVE STRENGTH RESULTS.

Mix	Agent, per cent[a]	Slump, in.	Air,[b] per cent by volume	Water-cement ratio	Water, lb per cu yd	Cement, lb per cu yd	Time to Reach		Compressive Strength, psi[f]					
							500 psi,[c] hr:min	4000 psi,[c] hr:min	4000 psi[d]	2-day	7-day	28-day	90-day	180-day
TYPE I CEMENT M-2598														
NO AGENT CONTROL														
No. 1.......	none	2.8	6.0	0.51	239	463	7:05	9:55	110	1190	2200	3270	3780	3800
AGENT *E*, M-2578														
No. 2.......	0.5	3.2	8.0	0.45	211	460	10:25	13:30	120	1550	3270	4520	4780	5240
No. 3.......	0.3	2.4	5.5	0.50	237	467	7:05	9:55	120	1750	3450	4680	5320	5480
AGENT *F*, M-2432														
No. 4.......	0.5	1.0	5.5	0.45	217	475	14:50	18:30	130	1320	3750	5280	6360	6010
No. 5.......	0.3	1.9	3.5	0.52	248	471	9:00	12:10	150	1470	3270	4710	5550	5550
AGENT *G*, M-2194														
No. 6.......	0.5	2.2	5.6	0.47	223	470	13:40	17:30	150	1440	3810	5040	6210	6080
No. 7.......	0.3	3.0	3.7	0.53	248	465	8:35	11:00	140	1430	3220	4680	5430	5510
AGENT *D*, M-2211														
No. 8.......	0.5	2.3	5.7	0.51	239	463	+30:00	−45:00	460	650	2950	4670	5070	5520
No. 9.......	0.3	3.2	6.2	0.51	239	462	11:15	15:00	210	1360	2800	3860	4550	4780
TYPE I CEMENT M-2592														
NO AGENT CONTROL														
No. 10......	none	2.5	4.0	0.55	259	474	4:10	6:10	90	1550	3040	4960	4670	4650
AGENT *E*, M-2578														
No. 11......	0.5	2.4	7.4	0.47	217	465	5:45	7:30	90	2000	3950	5400	5650	5950
No. 12......	0.3	2.8	5.5	0.51	241	470	4:35	6:45	110	1810	3570	5280	5750	5810
AGENT *F*, M-2432														
No. 13......	0.5	2.2	5.2	0.49	230	471	7:15	9:40	90	1970	4020	6170	6700	6870
No. 14......	0.3	2.5	4.3	0.53	247	469	5:20	7:55	130	1780	3700	5390	6210	6100
AGENT *G*, M-2194														
No. 15......	0.5	2.5	5.5	0.47	223	472	7:15	9:40	130	2000	4350	5890	6650	6710
No. 16......	0.3	2.6	4.2	0.52	244	470	5:20	7:25	170	1860	3820	5320	6280	6440
AGENT *D*, M-2211														
No. 17......	0.5	2.1	5.0	0.52	242	468	7:55	10:00	100	1740	3560	4950	5540	5780
No. 18......	0.3	3.1	4.6	0.54	253	472	5:50	7:55	100	1580	3230	4610	5350	5180

TABLE V.—*Continued.*

Mix	Agent, per cent[a]	Slump, in.	Air,[b] per cent by volume	Water Cement Ratio	Water, lb per cu yd	Cement, lb per cu yd	Time to Reach		Compressive Strength, psi[f]					
							500 psi,[c] hr:min	4000 psi,[c] hr:min	4000 psi[d]	2-day	7-day	28-day	90-day	180-day
TYPE II CEMENT M-2610														
NO AGENT CONTROL														
No. 19......	none	3.1	5.4	0.52	238	456	5:45	8:20	100	910	2060	3900	5040	5320
AGENT *E*, M-2578														
No. 20......	0.5	3.3	21.0	0.42	185	434	11:05	16:55	130	820	1990	3390	4020	4020
No. 21......	0.3	2.9	7.5	0.51	234	452	6:15	9:15	120	1030	2290	4180	5320	5080
AGENT *F*, M-2432														
No. 22......	0.5	1.5	6.9	0.44	204	460	16:10	23:35	120	470	2470	5190	6590	6080
No. 23......	0.3	2.4	5.5	0.50	232	461	8:00	11:45	100	650	2110	4480	6020	5650
AGENT *G*, M-2194														
No. 24......	0.5	2.2	7.6	0.43	197	456	26:15	53:15	80	...	1290	4710	5830	6060
No. 25......	0.3	2.9	5.7	0.50	230	458	8:05	12:20	90	630	2140	4820	6120	6340
AGENT *D*, M-2211														
No. 26......	0.5	4.0	5.6	0.49	226	461	26:05	31:00	160	420	2080	4610	6120	6450
No. 27......	0.3	3.0	5.5	0.50	230	460	11:20	14:20	130	930	2250	4890	6080	6260
TYPE II CEMENT M-2595														
NO AGENT CONTROL														
No. 28......	none	2.2	5.2	0.52	263	502	5:30	7:45	110	1310	2900	5120	5800	5860
AGENT *E*, M-2578														
No. 29......	0.5	3.2	13.0	0.42	185	439	11:35	16:15	90	890	2000	3480	3840	3930
No. 30......	0.3	3.0	8.2	0.44	202	461	7:10	9:50	90	1440	3220	5100	5570	5850
AGENT *F*, M-2432														
No. 31......	0.5	3.9	8.0	0.42	196	465	15:00	33:05	110	460	2580	5050	6090	6120
No. 32......	0.3	2.1	4.6	0.45	216	476	7:45	10:15	90	1580	3720	6260	7260	7430
AGENT *G*, M-2194														
No. 33......	0.5	3.6	8.5	0.41	190	461	22:50	48:00	200	510[e]	2060	4690	5470	5390
No. 34......	0.3	2.0	4.8	0.49	232	472	8:05	11:10	100	1520	3600	6150	6760	6920
AGENT *D*, M-2211														
No. 35......	0.5	3.0	5.3	0.49	234	473	23:20	26:30	90	700	2440	5140	5710	5870
No. 36......	0.3	3.3	5.5	0.50	239	472	12:15	14:55	130	1160	2820	5090	5660	5650

TABLE V.—*Concluded.*

Mix	Agent, per cent[a]	Slump, in.	Air,[b] per cent by volume	Water Cement Ratio	Water, lb per cu yd	Cement, lb per cu yd	Time to Reach		Compressive Strength, psi[f]					
							500 psi, hr:min	4000 psi,[c] hr:min	4000 psi[d]	2-day	7-day	28-day	90-day	180-day
TYPE II CEMENT M-2400														
NO AGENT CONTROL														
No. 37......	none	3.5	5.3	0.53	248	470	6:45	9:15	97	1200	2500	4160	5160	5370
AGENT *H*, M-2997														
No. 38......	0.5	2.8	5.0	0.44	206	470	13:35	16:05	106	2160	4460	6300	7110	7440
No. 39......	0.3	2.2	4.3	0.47	224	475	8:00	11:00	120	1975	3780	5850	6770	6930
AGENT *I*, M-2889														
No. 40......	0.5	2.3	8.0	0.41	195	474	13:05	16:50	89	1520	3890	5720	6540	6440
No. 41......	0.3	2.5	4.5	0.48	235	489	10:30	12:35	174	1780	3850	5820	6450	6840
AGENT *J*, M-2977														
No. 42......	0.5	3.4	3.5	0.47	221	475	13:00	16:45	112	1500	3680	5630	6550	6870
No. 43......	0.3	2.8	5.3	0.49	227	464	11:25	14:40	184	1550	3460	5200	6280	6520
TYPE II CEMENT M-3100														
NO AGENT CONTROL														
No. 44......	none	2.2	4.1	0.52	245	470	4:40	7:05	55	1270	2710	4530	...	...
AGENT *H*, M-2997														
No. 45......	0.3	2.9	4.9	0.50	227	458	6:50	9:10	109	1720	3420	4990	...	...
AGENT *K*, M-3451														
No. 46......	0.5	2.5	4.7	0.50	228	459	4:10	6:15	64	2280	3700	5080	...	...

[a] By weight of cement; solid basis (except agent *D*).

[b] Per cent by volume of concrete; ¼-cu ft air meter.

[c] Time in hours and minutes when wet screened mortar shows resistance of 500 and 4000 psi to penetration by standard Proctor needle.

[d] Compressive strength of 6- by 12-in. concrete cylinders when companion wet-screened mortar has reached a penetration resistance of 4000 psi.

[e] Three days.

[f] Average of two 6- by 12-in. cylinders at each age.

when added in various dosages with a variety of cements at a constant cement factor. Results of this series are shown in Table V.

Series II.—In this series 4 lignin-type and 1 hydroxylated carboxylic acid *WR* agents were used in concrete containing ¾-, 1½-, 3-, and 6-in.-maximum-size aggregates of relatively good quality. A single type II cement was used, with and without pozzolan replacement. Effects of the agents on compressive, tensile, and shearing strengths were determined from concrete containing various size aggregates and having various water to cement-plus-pozzolan ($w/c + p$) ratios. Also, the use of a lignin-type agent with aggregates of marginal or poor quality was studied. Results of this series are shown in Tables VI and VII.

TABLE VI.—SERIES II—CONCRETES CONTAINING 1½-IN. AGGREGATES.
With and Without Pozzolans at Various $w/c + p$ Ratios

Mix	Water-Cement Ratio or $w/c + p$ Ratio	Agent[a]		Slump, in.	Air[b]	Water, lb per cu yd	Pozzolan,[c] per cent	Compressive strength, psi Standard cured 6- by 12-in. cylinders[d]							
		Per cent	Type					3-day	7-day	28-day	90-day	180-day	1-yr	2-yr	5-yr
MONTICELLO DAM—CEMENT, M-2005—POZZOLAN, M-2017 NO POZZOLAN, NO AGENT															
No. 47..........	0.45	...	...	2.4	5.0	190	0	1590	2130	3720	4850	5220	5590	5530	6030
No. 48..........	0.51	...	...	2.3	5.3	188	0	1040	1810	3260	4100	4130	4520	4280	4880
No. 49..........	0.58	...	...	2.2	5.7	188	0	890	1380	2580	3390	3750	3780	4010	4100
NO POZZOLAN AND AGENT *A*															
No. 50..........	0.45	0.1	*A*	1.5	4.4	169	0	1630	2620	3940	4790	5680	5730	5820	6610
No. 51..........	0.51	0.1	*A*	1.3	4.3	176	0	1390	2030	3650	4500	5040	5500	5330	5480
No. 52..........	0.58	0.1	*A*	1.8	4.8	174	0	1000	1450	2700	3620	3790	3810	4210	4300
POZZOLAN, NO AGENT															
No. 53..........	0.45	...	...	1.8	3.0	220	30	1380	2210	5050	5490	5720	6400	5950	6900
No. 54..........	0.51	...	...	1.9	4.0	219	30	960	1590	3740	5000	4540	4950	5740	5700
No. 55..........	0.58	...	...	2.8	6.9	210	30	510	790	2410	3250	3510	4000	3960	3960
POZZOLAN AND AGENT *A*															
No. 56..........	0.45	0.1	*A*	1.2	3.5	197	30	1320	2180	4730	5750	6010	6600	6530	7220
No. 57..........	0.51	0.1	*A*	1.5	3.8	197	30	930	1460	3680	4750	5120	5060	5610	5870
No. 58..........	0.58	0.1	*A*	1.6	4.2	196	30	650	1010	3020	4020	4600	4640	4960	4990
AINSWORTH CANAL (MARGINAL AGGREGATE)—CEMENT, M-1700 NO POZZOLAN AND AGENT *G*															
No. 59..........	0.51	...	...	2.8	6.0	199	0	...	2140	3420	3840	...	...	...	...
No. 60..........	0.53	0.2	*G*	2.2	8.0	182	0	...	2080	3160	...	...	...	...	...
No. 61..........	0.52	0.4	*G*	2.2	6.4	180	0	...	2530	3900	...	...	...	...	...

[a] Per cent agent by weight of total cementitious material, solid basis.
[b] Air per cent by volume, air meter.
[c] Per cent by weight of total cementitious materials.
[d] Average of two 6- by 12-in. cylinders at each age.

Series III.—One hydroxylated carboxylic acid *WR* agent and several lignin-type *WR* agents with good water-reducing effects were selected for use in the mass concretes, series III, reported in Tables VIII and IX. The effect of the agents on volume change, temperature rise, and permeability, considered to be particularly important properties of mass concrete, was determined. In addition, effect of these agents on workability, strength, and durability of mass concrete was determined.

Cylinders 18 by 36 in. in size contain-

TABLE VII.—SERIES II—CONCRETES WITH $\frac{3}{4}$-, $1\frac{1}{2}$-, 3-, AND 6-IN. AGGREGATES WITH POZZOLAN.

Mix	Agent[a]		Slump, in.	Air[b]	Water, lb per cu yd	Pozzolan,[c] per cent	Time to Reach[d]		Compressive Strength, psi[e] Standard Cured 6- by 12-in. Cylinders								Tensile Strength, psi									
																	Standard cured 6- by 12-in. cylinders[f]					Standard briquettes[g]				
	Per cent	Type					500 psi, hr: min	4000 psi, hr: min	3-day	7-day	28-day	90-day	180-day	1-yr	2-yr	5-yr	3-day	7-day	14-day	28-day	90-day	3-day	7-day	14-day	28-day	90-day
MONTICELLO DAM																										
$\frac{3}{4}$-IN. AGGREGATE—$w/c + p$, 0.55																										
No. 62....	0	...	3.0	6.3	254	20	6:15	8:55	910	1400	3620	4080	4280	4200	4990	...	101	139	182	258	318	236	340	441	506	591
No. 63....	0.2	*C*	3.5	7.8	225	20	7:10	9:40	875	1460	3510	3940	4540	4720	5250	...	107	160	179	249	362	226	279	415	467	555
No. 64....	0.2	*D*	3.5	5.9	246	20	7:30	10:30	1030	1660	4030	4870	5360	5710	5520	...	118	145	223	278	362	264	371	448	548	633
$1\frac{1}{2}$-IN. AGGREGATE—$w/c + p$, 0.55																										
No. 65....	0	...	2.3	4.6	215	20	5:45	8:55	980	1500	3740	4220	4960	5360	5330	...	92	149	220	237	332	264	313	417	531	588
No. 66....	0.2	*C*	3.5	6.7	192	20	7:20	10:30	820	1240	3100	3920	4220	4020	4510	...	112	148	226	265	322	173	257	334	445	530
No. 67....	0.2	*D*	3.0	5.1	208	20	8:05	10:15	940	1450	3370	4230	4590	4870	4980	...	115	156	223	279	293	205	280	359	477	593
3-IN. AGGREGATE—$w/c + p$, 0.55																										
No. 68....	0	...	2.6	4.0	200	30	6:25	9:20	810	1330	3530	4020	5110	4640	4380	...	98	143	207	245	298	228	297	438	527	616
No. 69....	0.2	*C*	4.2	4.8	179	30	7:30	10:40	790	1280	3340	4210	4600	5310	5580	...	101	135	217	262	328	201	303	407	533	643
No. 70....	0.2	*D*	3.3	3.7	192	30	8:05	10:55	880	1470	3170	4730	5040	5600	5740	...	100	130	206	273	319	217	310	457	579	598
6-IN. AGGREGATE—$w/c + p$, 0.62 (AVERAGE)																										
No. 71....	0	...	2.8	5.8	149	30	7:20	10:30	400	790	2330	3260	3650	4340	4580	...	21	52	134	178	112	129	183	264	393	440
No. 72....	0.2	*C*	2.0	5.6	132	30	7:20	10:35	520	960	2640	3810	4260	4660	5140	...	78	110	176	207	308	125	196	303	426	501
No. 73....	0.2	*D*	2.6	5.7	140	30	7:40	10:40	460	810	2580	3800	4160	4620	4870	...	71	100	174	237	343	107	147	249	396	479
No. 74....	0.2	*B*	2.3	5.5	134	30	...	...	530	810	2470	3710	4540	4900	5000	...	66	96	157	230	325	120	175	237	392	515
NOTE.—Compressive strength 18 by 36-in. cylinders—mix 74.											2850	3360	3670	3840	4460	4760										

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[a] Per cent agent by weight of total cementitious material, solid basis (except agent *D*).

[b] Per cent by volume air meter test on 3- and 6-in. handpicked to $1\frac{1}{2}$-in. maximum size.

[c] Cement type II, laboratory No. M-2005, specific gravity 3.17; pozzolan, calcined diatomaceous clay, laboratory No. M-2017, specific gravity 2.44.

[d] Time in hours and minutes when wet-screened mortar resisted penetration, by standard Proctor needles, of 500 and 4000 psi.

[e] Average of two 6- by 12-in. cylinders at each age. Cylinders from 3- and 6- in. concrete wet-screened to $1\frac{1}{2}$ in. maximum.

[f] Average of three 6- by 12-in. cylinders at each age. Cylinders from 3- and 6-in. concrete wet-screened to $1\frac{1}{2}$-in. maximum.

[g] Average of three specimens wet screened to $\frac{3}{16}$-in. maximum.

TABLE VIII.—SERIES III—MASS CONCRETE WITH MATERIALS FROM VARIOUS PROJECTS.

Mix	Water-Cement Ratio or $w/c + p$ Ratio	Agent		Slump, in.	Air[b]	Water, lb per cu	Pozzolan per cent[c]	Compressive Strength, psi[d] 6- by 12-in. Standard Cured Cylinders								Compressive Strength, psi, 18 by 36-in. mass cured cylinders					
		Per cent[a]	Type					3-day	7-day	28-day	90-day	180-day	1-yr	2-yr	5-yr	28-day	90-day	180-day	1-yr	2-yr	5-yr
MONTICELLO DAM MATERIALS—3 SACKS CEMENTITIOUS MATERIALS—M-2005 AND M-2017 AND M-1236																					
No. 75......	0.50	0	...	3.1	4.8	137	0	1240	1690	3040	4150	4680	4630	5210	5200	3030	3400	3830	3540	4090	4400
No. 76......	0.53	0	...	2.7	4.0	149	30	750	1160	3370	4250	4190	4450	4640	5180	3030	3480	3790	3950	3950	4720
No. 77......	0.44	0.1	*A*	2.5	5.4	122	0	1710	2150	3730	4790	5160	5530	5480	5800	3580	3830	4340	4050	4840	5620
No. 78......	0.50	0.1	*A*	1.6	3.0	142	30	920	1420	3730	4900	5100	5720	6000	6390	2910	3990	4500	4390	4760	4910
No. 79......	0.43	0.1	*A*	2.2	3.9	121	30[e]	1220	1660	2930	5130	5860	6640	7010	6790	3470	3760	4300	4890	5210	5500
KIRWIN DAM MATERIALS—3 SACKS CEMENT—M-1779																					
No. 80......	0.58	0	...	2.5	3.4	167	0	...	2040	3680	4440	4830	4990	...	...	3890	4850	5090	5090	...	...
No. 81......	0.52	0.25	*L*	3.3	6.0	148	0	1535	2485	4080	4890	5480	5570	5520	...	4460	4280	4860	5270	5330	...
No. 82......	0.50	0.20	*A*	1.4	3.8	146	0	1670	3000	5040	5430	5760	5930	6490	...	5720	5500	...	6720	6560	...
GROSS DAM MATERIALS—2½ SACKS CEMENT—M-1219																					
No. 83......	0.66	0	...	1.3	3.7	155	0	1270	2000	3380	3540	3600	3450	3690	3870	2930	3170	2890	3200	3580	3480
No. 84......	0.62	0.2	*A*	0.8	3.7	148	0	1340	2190	3750	4020	3920	3910	4090	4810	3320	3580	3850	3870	3950	4050
FLAMING GORGE DAM AGGREGATE—3 SACKS CEMENTITIOUS MATERIALS—M-3100 AND M-3233 AND M-3053																					
No. 85......	0.62	0	...	1.7	4.8	175	0	...	2320	3390	4180	4230	...	...	...	...	3400	3860	...	...	...
No. 86......	0.60	0	...	1.7	4.1	167	33.3[e]	...	1530	2610	3400	3670	...	...	...	...	3100	3050	...	...	...
No. 87......	0.57	0.3	*J*	1.8	4.3	161	0	...	2630	3750	4700	5220	...	...	...	...	4190	4390	...	...	...
No. 88......	0.56	0.3	*J*	2.0	4.5	160	33.3[e]	...	1860	2930	4330	4740	...	...	...	...	3700	3970	...	...	...
No. 89......	0.61	0	...	2.0	3.0	173	0	...	2670	3960	5040	5360	...	...	...	...	...	...	...	...	...
No. 90......	0.60	0	...	2.4	5.5	168	0	...	2470	3560	4430	4870	..	...	...	...	3420	3060	...	...	...
No. 91......	0.61	0	...	2.5	4.8	174	0	...	...	3440	4240	4840	...	...	...	...	3340	...	...	...	...
No. 92.....	0.60	0	...	2.2	4.9	170	33.3	...	...	2860	3750	4170	...	...	...	...	2870	...	...	...	...
No. 93.....	0.56	0.37	*G*	2.0	3.9	157	33.3	...	...	4350	5110	5690	...	...	...	...	4150	...	...	...	...
No. 94.....	0.56	0.37	*J*	1.9	4.4	157	33.3	...	...	3660	4730	4950	...	...	...	...	3280	...	...	...	...

FLAMING GORGE DAM MATERIALS—3 SACKS CEMENTITIOUS MATERIALS—M-3389 AND M-3364

No. 95......	0.53	0	...	1.7	4.7	152	33.3	...	...	3950	5080	5840	...	...	...	3540	4130	...	...	...	...
No. 96......	0.54	0	...	2.0	5.1	154	33.3	...	...	3890	4940	5250	...	...	...	2970	3620	...	...	...	...
No. 97......	0.50	0.37	*G*	2.6	4.8	142	33.3	...	...	4800	5850	6300	...	...	...	3890	4340	...	...	...	...

GLEN CANYON DAM AGGREGATES—3½ SACKS CEMENTITIOUS MATERIALS—M-3100 AND M-3337

No. 98......	0.51	0	...	2.0	4.4	169	42.8	2-day[f]	...	3780	5440	6220	...	...	...	2950	3770	4320	...	...	...
No. 99......	0.46	0.37	*G*	1.9	4.5	152	42.8	...	...	4700	6680	7510	...	...	...	3620	5320	6130	...	...	...

GLEN CANYON DAM AGGREGATES—3 SACKS CEMENTITIOUS MATERIALS—M-3100 AND M-3337

No. 100......	0.56	0	...	2.1	4.2	159	33.3	570	1520	3560	4890	5510	...	...	...	3030	3970	4400	...	...	...
No. 101......	0.49	0.37	*G*	2.0	3.9	140	33.3	830	2090	4710	6370	7190	...	...	...	4420	5440	6330	...	...	...
No. 102......	0.56	0	...	1.6	4.0	157	0	...	...	4480	5390	5750	...	...	...	...	...	...	...	...	...
No. 103......	0.51	0.37	*G*	1.8	4.3	145	0	...	...	5370	6270	6640	...	...	...	...	...	...	...	...	...

GLEN CANYON AGGREGATES—2½ SACKS CEMENTITIOUS MATERIALS—M-3100 AND M-2942B

No. 104......	0.64	0	...	1.7	4.9	152	0	730	1840	3010	3625	3970	...	...	...	2610	...	...	...	...	...
No. 105......	0.60	0.27	*G*	1.7	4.9	139	0	990	2270	3410	4310	4440	...	...	...	3020	...	...	...	...	...
No. 106......	0.56	0.54	*G*	1.5	4.9	130	0	970	2450	3880	4780	5020	...	...	...	3070	...	...	...	...	...
No. 107......	0.66	0	...	1.5	4.6	153	20	570	1410	3010	4080	4410	...	...	...	2360	...	...	...	...	...
No. 108......	0.63	0.27	*G*	2.0	5.1	147	20	585	1560	3260	4315	4910	...	...	...	2950	...	...	...	...	...
No. 109......	0.61	0.54	*G*	2.4	4.6	142	20	570	1730	3640	4680	5310	...	....	...	3140	...	...	...	...	...
No. 110......	0.67	0	...	2.1	4.7	159	20	...	...	2680	3980	4240	...	...	...	2850	3420	3640	...	...	...
No. 111......	0.61	0.37	*G*	2.2	4.7	145	20	...	...	2840	4090	4410	...	...	...	3240	4360	4770	...	...	...
No. 112......	0.65	0	...	1.8	5.1	155	0	710	1430	2690	3600	3850	...	...	...	2750	3160	3690	...	...	...
No. 113......	0.60	0.37	*G*	1.7	4.8	142	0	930	2130	3550	4370	4740	...	...	...	3260	3810	4220	...	...	...

GLEN CANYON DAM MATERIALS—3 SACKS CEMENTITIOUS MATERIALS (LESS 5 PER CENT)—M-3329, M-3439A AND M-3439B

No. 114......	0.56	0	...	1.8	3.8	157	33.3	910	1710	3840	...	...	...	...	...	2990	...	...	...	...	...
No. 115......	0.53	0.37	*G*	2.0	4.2	141	33.3	1130	1990	4510	...	...	...	...	...	3650	...	...	...	...	...
No. 116......	0.56	0	...	1.6	3.6	159	33.3	950	1840	4270	...	...	...	...	....	...	...	...	...	...	....
No. 117......	0.53	0.37	*G*	1.7	3.8	144	33.3	1150	2050	4850	...	...	...	...	...	...	...	...	...	...	...

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[a] Per cent agent by weight of total cementitious material, solid basis (except agent *D*).
[b] Air per cent by volume. Air meter test on 3- and 6-in. concrete handpicked to 1½-in. maximum.
[c] Per cent by weight of total cementitious material.
[d] Average of two 6- by 12-in. cylinders cast from material wet-screened to 1½-in. maximum.
[e] Fly ash used as pozzolan.
[f] 2-day strengths on mixes Nos. 98 to 113 only.

TABLE IX.—SUMMARY OF MIX DATA.

Results of Retardation and Compressive Strength Tests for Mass Concretes Placed at 52 F, Cured at 50, 75, and 100 F for 48 hr

MONTICELLO DAM

Mix	Water-Cement Ratio or $w/c + p$ Ratio	Agent		Slump, in.	Air[b]	Water, lb per cu yd	Pozzolan, per cent[c]	Compressive Strength, psi[e]														
		Per cent[a]	Type					6- by 12-in. cylinders cured for 48 hr at 50, 75, and 100 F then standard cured until break date														
								At 4000 psi[d]			2-day			7-day			28-day			90-day		
								50 F	75 F	100 F	50 F	75 F	100 F	50 F	75 F	100 F	50 F	75 F	100 F	50 F	75 F	100 F
No. 118	0.60	0	...	0.9	3.8	151	30	41	33	62	320	610	720	1170	1210	1350	3380	3210	2650	4780	4010	3330
No. 119	0.60	0.3	*C*	1.1	4.5	146	30	39	50	60	260	550	770	1060	1170	1310	3360	3320	3060	4720	4310	3870
No. 120	0.60	0.5	*C*	0.9	4.6	142	30	51	35	37	250	580	800	1140	1310	1350	3340	3280	3070	4910	4620	4160
No. 121	0.60	0.75	*C*	0.9	5.7	131	30	26	29	42	200	530	730	940	1130	1330	3150	3170	2790	4710	3680	4500
No. 122	0.60	0	...	2.1	5.3	157	30	35	37	45	250	460	690	950	1000	1150	3180	3050	2820	4370	4120	3410
No. 123	0.60	0.2	*D*	1.4	5.3	146	30	35	30	53	230	480	680	900	1010	1140	2910	2970	2640	4300	4260	3400
No. 124	0.60	0.3	*D*	1.1	5.4	141	30	29	32	43	230	460	700	900	1010	1150	3090	2990	2750	4490	4420	3710
No. 125	0.60	0.4	*D*	1.1	5.5	136	30	23	46	35	230	460	720	930	990	1220	3050	3060	2750	4530	4380	3610

[a] Per cent agent by weight of total cementitious material, solid basis (except Agent *D*).

[b] Per cent by volume, air meter test on material handpicked to 1½-in. maximum size.

[c] Per cent by weight of cementitious material.

[d] Compressive strength of 6- by 12-in. cylinders when penetration resistance to Proctor needle is 4000 psi.

[e] Average of two cylinders at each age. Wet-screened to 1½-in. maximum size.

ing full mass mix materials from Monticello Dam, Calif.; Denver Water Board's Gross Dam, Colo.; Kirwin Dam, Kans.; Flaming Gorge Dam, Utah; and Glen Canyon Dam, Ariz., were made for compressive strength tests up to 5 yr of age. However, results of tests on specimens at 5 yr of age are presently available for only the first two projects.

TABLE X.—COMPARISON OF FIELD CONTROL TESTS WITH AND WITHOUT LIGNINS.

Properties	Clear Creek Tunnel				Glen Canyon Dam				Fremont Canyon Power Conduit				Navajo Dam			
	2½-in. maximum				2½-in.maximum				1½-in. maximum				2½-in. maximum			
	Control		Agent *H*		Control		Agent *G*		Control		Agent *G*		Control		Agent *J*	
Compressive strength, psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi	Number of ~~cycles~~ CYLINDERS	psi
7 days of age	1	1920	1	2745	...	...	2	2770	69	2370	50	2800	12	2350	11	2960
28 days of age	...	...	...	...	22	4750	186	4340	73	4090	30	4190	17	4220	8	5280
90 days of age	...	...	...	...	...	...	8	6100	...	...	...	...	...	...	...	...
Coefficient V, per cent	...	...	...	...	...	7.3	...	9.8	...	15.9	...	13.7	...	11.6	...	2.6
Control, per cent	...		...		91.3				102.4				125.1			
Slump	6.3		5.0		4.7		5.0		4.0		4.4		4.7		5.3	
Air (meter), per cent	4.2		4.4		3.3		3.5		4.2		4.5		3.0		3.8	
Temperature, deg Fahr.	46		53		68		70		56		67		64		74	
Water	233		221		225		206		283		262		256		224	
Cement	487		454		441		401		531		500		446		432	
Water-cement ratio	0.48		0.49		0.51		0.51		0.53		0.52		0.57		0.52	
Sand, per cent	27		27		36		36		45		45		34		34	
Water reduction, per cent	5				8.4				7.4				12.5			
Cement reduction, per cent	7				9.1				5.8				3.1			

meet coarse aggregate specifications, is being used in the concrete lining of Fremont Canyon power conduit near Casper, Wyo. The continuous tunnel-lining method is being used here and initial retardation is desirable to avoid cold joints. Observations were made to determine the effects of a *WR* agent on appearance of the completed tunnel lining, as well as the ability of the agent to control the set of the concrete.

Field Tests and Observations:

The ability of a lignin-type *WR* agent to improve the pumpability of concrete placed in the diversion tunnels at Glen Canyon Dam, Ariz., was studied by observing the frequency of plugged lines and the power required for pumping comparable concretes with and without an agent. Also, observations were made of the influences of *WR* agents on the finishing characteristics of concrete placed in floor slabs exposed to the desert climate of this project.

Crushed tunnel muck, processed to

Recently, tests were made to determine whether a *WR* agent could prevent an aggregate-induced rapid slump loss in tunnel concrete being placed at Prineville Dam, Ore. Other tests to determine the effects of *WR* agents on slump loss were performed at Navajo Dam, N. Mex.; Flaming Gorge Dam; Fremont Canyon power conduit; and Clear Creek tunnel, Calif.

At Anchor Dam, Wyo., a 375-cu-yd block of mass concrete was placed with one half containing, the other half omitting a *WR* agent. This permitted an evaluation of the agent under field conditions. Field control tests of concrete with and without *WR* agents used on several Bureau of Reclamation projects are reported in Table X.

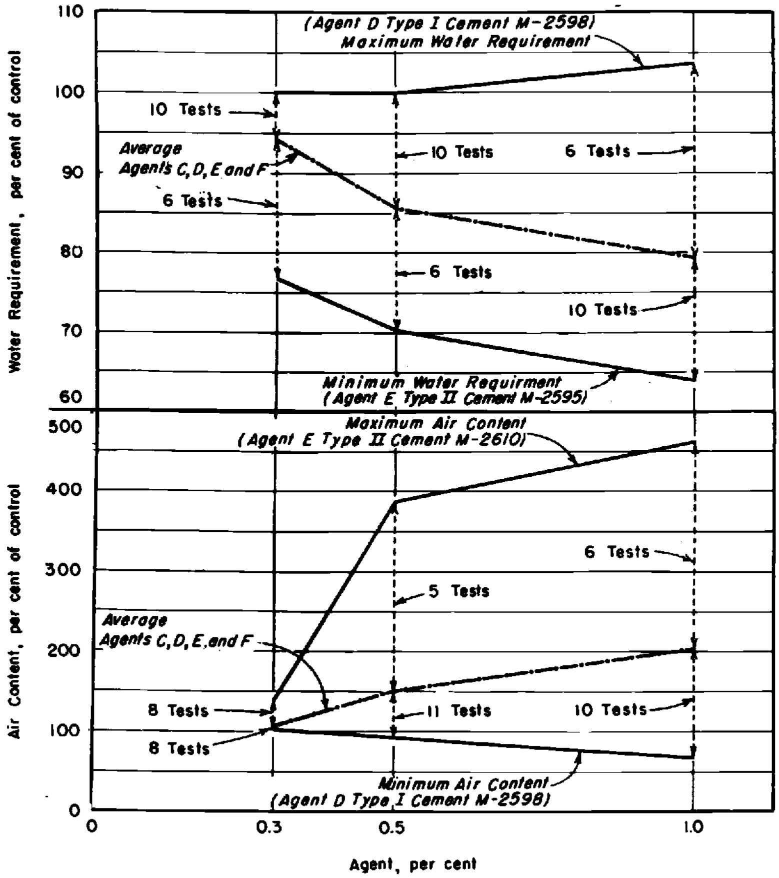

FIG. 1.—Influence of Lignin and Hydroxylated Carboxyic Acid Agents on Water Requirement and Air Content of Structural Concrete.

Four different cements—four different agents—1½-in. maximum size—Clear Creek, Colo., aggregate.

MIX DESIGN

Economical proportioning of concrete mixes containing *WR* agents to meet specified limits of slump, air content, time of set, and strength development requires a series of laboratory or field trial mixes under job conditions. Trial adjustments may be minimized by foreknowledge of the effects of a given agent on other project materials. The value of such information is apparent in light of the wide variations in water and air content that may be produced, as shown in Fig. 1, by various agents used with different cements.

In general, partial doses of air-entraining agents were necessary and were added to the mixes containing nominal dosages of *WR* agents, to raise the air content to that of the mixes without a *WR* agent (control mixes) which utilized a normal amount of air-entraining agent. On the other hand, several lignin-type *WR* agents entrained excessive amounts of air when used alone, that is, without addition of an air-entraining agent. In these cases, no attempt was made to reduce the air content by the use of an air-detraining agent.

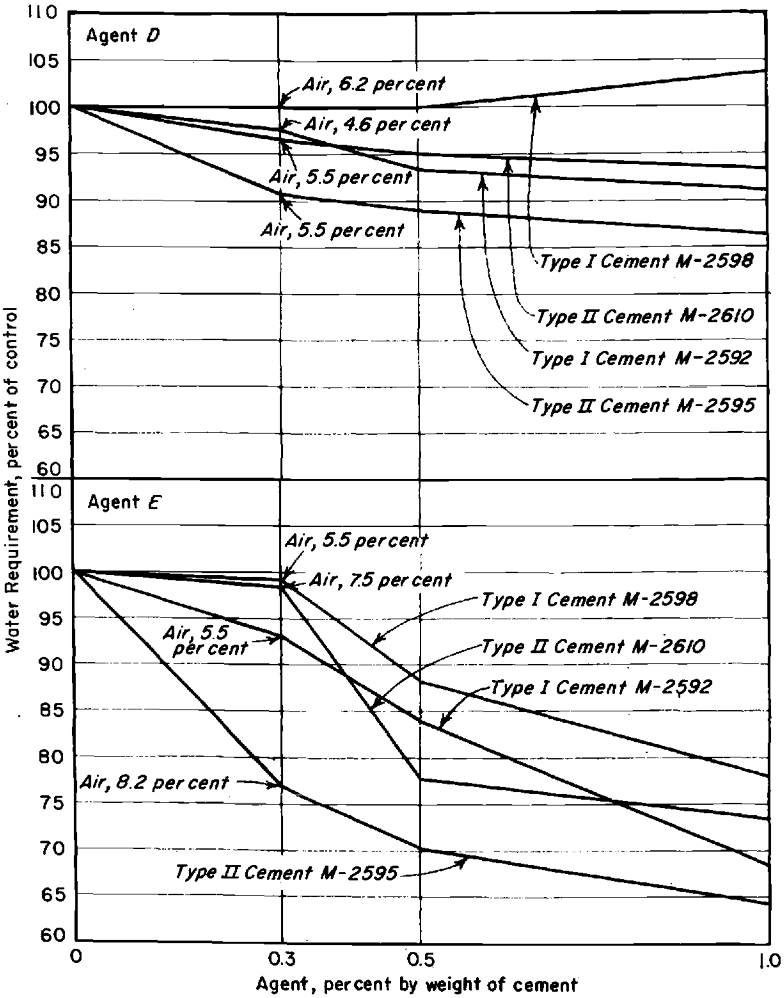

FIG. 2.—Influence of Lignin and Hydroxylated Carboxylic Acid Agents on Water Requirements of Structural Concrete.

1½-in. maximum size—Clear Creek, Colo., aggregate—four different cements.

Water Content:

Water reduction resulting from the use of nominal dosages of the four *WR* agents used with four cements in structural concrete, based on 16 comparisons in mixes Nos. 1 through 36, ranged from 0 to 23 per cent of the water requirement of the control mixes. In general, the lignin-type agents were most efficient in this respect, producing greater water reductions than the hydroxylated carboxylic acid agent in comparable concretes having essentially equal air contents. The average reductions for nominal dosages of the lignin-type and hydroxylated carboxylic acid agents were approximately 6 per cent and 4 per cent, respectively.

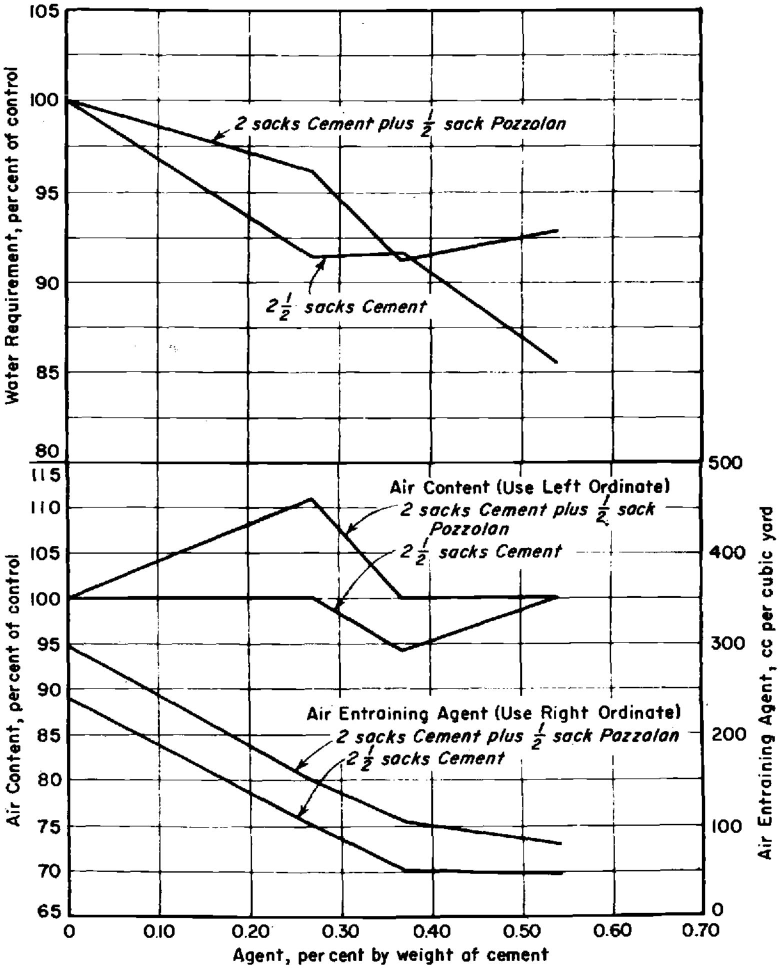

Fig. 3.—Influence of Lignin Agent on Water Requirement and Air Content of Mass Concrete.

Wahweap Creek aggregate—6-in. maximum size—type II cement M-3100—pozzolan M-2942B—agent *G*.

Figure 2 shows that the ability of a *WR* agent to reduce water is markedly affected by the particular cement with which it is used. For example, nominal dosage of 0.3 per cent agent *E* gave a large water reduction when used with cement M-2592, but was much less effective with cement M-2598. Both of these mixes contained type I cement and 5.5 per cent air.

The average water reduction produced

by optimum amounts of lignin-type agents used in the mass concretes for various projects represented by mixes Nos. 80 through 117, Table VIII, was about 8 per cent. Water requirement, air content, and air-entraining agent requirement using Glen Canyon Dam aggregates in mass mixes with various amounts of a lignin agent are shown in Fig. 3.

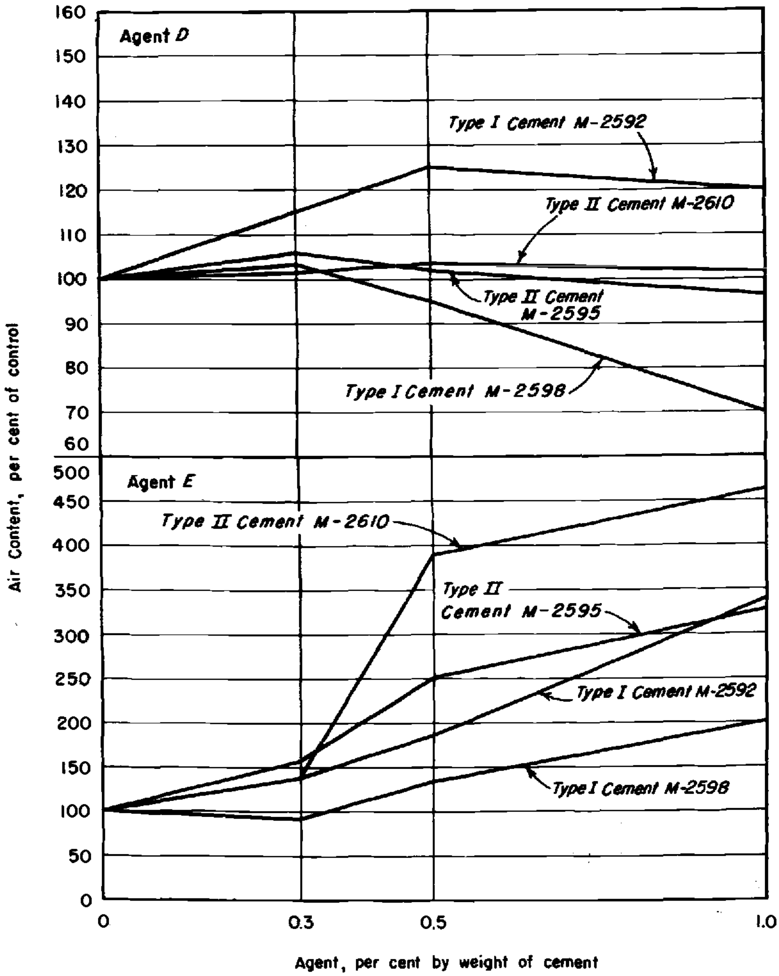

FIG. 4.—Influence of Lignin and Hydroxylated Carboxylic Acid Agents on Air Content of Structural Concrete.

1½-in. maximum size—Clear Creek, Colo., aggregate—four different cements.

Air Content:

Figure 4 shows that the amount of air entrained by a given amount of a *WR* agent varies considerably when used with different cements. To maintain design air content, the normal air-entraining agent requirement of control mixes was reduced 60 to 100 per cent in the mixes containing nominal dosage of lignin-type agents and 0 to 25 per cent for mixes with hydroxylated carboxylic acid agents.

Objectionably high air contents were obtained with overdosages of all lignin-type agents. The same trend was not noted when hydroxylated carboxylic acid was used in overdoses or severe overdoses, indicating that the latter agent can be safely used in large quantities when extended retardation is desired without fear of entraining an excessive amount of air. On the other hand, where prolonged retardation is required and obtained through the use of large quantities of lignin-type agent, a defoaming agent added at the batch plant would be required to control the amount of air entrained.

WORKABILITY

The influence of *WR* agents on the workability of concrete is often discussed by producer representatives and consumers alike in a very intangible way. Actually, workability characteristics are tangible properties of concrete, measurable by tests of fresh concrete and appearance of the concrete upon completion of the work. Characteristics include: (*a*) mobility of concrete as measured by slump and flow tests; (*b*) pumpability as measured by frequency of plugged lines and power consumption; (*c*) ease with which concrete can be screeded, floated, and troweled, plus appearance of the finished concrete surfaces; and (*d*) length of time concrete can be handled and consolidated by vibration, as measured by rate of hardening tests.

All four of these characteristics have, to some extent, been investigated to determine the influence of various *WR* agents on the workability of concrete. The chief benefit to workability accruing from the use of *WR* agents lies in their ability to extend the time that the concrete can be vibrated. This is a very important contribution, not fully appreciated by a consumer who also expects a reduced rate of slump loss through use of *WR* agents. This does not occur.

Retardation:

The terminology, nominal dosage, overdosage, and severe overdosage is very descriptive of the degree of retardation of structural concrete, as induced at 70 F by the majority of *WR* agents studied (without accelerators), when added in amounts 0.3, 0.5, and 1.0 per cent, respectively.

Average and limiting rate of hardening curves for the structural concretes of series I, plus 5 additional tests, are shown in Fig. 5. Nominal dosages of the lignin and hydroxylated carboxylic acid agents extend the average time to reach vibration limit about 25 per cent and 40 per cent, respectively, beyond the average vibration limit of the control concretes shown in Fig. 5. However, the range of time intervals to reach vibration limit produced by various *WR* agents with different cements is very broad, ranging from 4½ to 12¾ hr for concretes with lignin agents and from 5¾ to 17 hr for concretes with the hydroxylated carboxylic acid agent. Hydroxylated carboxylic acid agents may be better adapted for occasions requiring extended retardation because they have not been observed to induce premature stiffening as has occurred in a few instances with lignin agents. Concretes with hydroxylated carboxylic acid agents remain plastic until the setting cycle commences and thereafter execute a normal hardening cycle.

Dosages of 0.37 per cent lignin agents used in the series III mass mixes of the Glen Canyon investigation extended the average interval to reach vibration limit about 35 per cent beyond the vibration limit period of the control mix, as shown in Fig. 6. Comparison of Figs. 6(*a*) and 6(*b*) shows that somewhat more retarda-

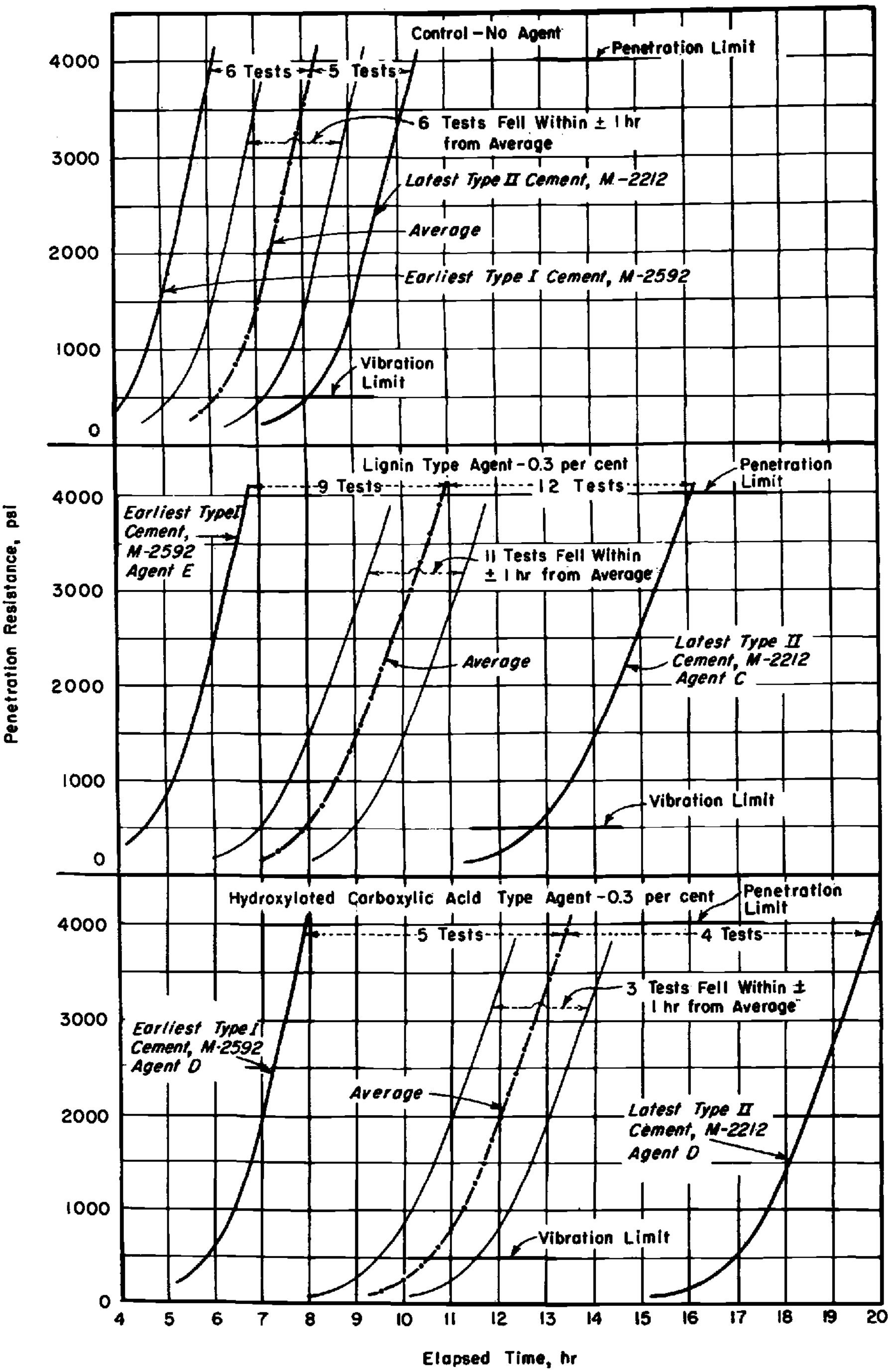

FIG. 5.—Rate of Hardening by Proctor Needle.

Clear Creek, Colo. aggregate—1½-in. maximum size—11 type I and type II cements—temperature of concrete 70 F. Average values taken at 500 psi.

NOTE.—4 type II cements of series I
2 type I cements of series I
3 type II cements of previous tests[1]
2 type I cements of previous tests[1]

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[1] L. H. Tuthill and W. A. Cordon, "Properties and Uses of Initially Retarded Concrete," *Proceedings*, Am. Concrete Inst., Vol. 52, p. 273 (1955–1956).

tion is obtained by concretes with pozzolan than without pozzolan. Figure 6(*c*) shows retardation obtained by similar concretes containing the same pozzolan ground to different finenesses, and indicates the lignin agent to be more effective with the coarser ground pozzolan. Figure 6(*d*) shows that retardation can be reduced or eliminated entirely by adding triethanolamine, a common accelerating agent, to the lignin-type *WR* agent. Water reduction alone would be a desirable feature in cold weather.

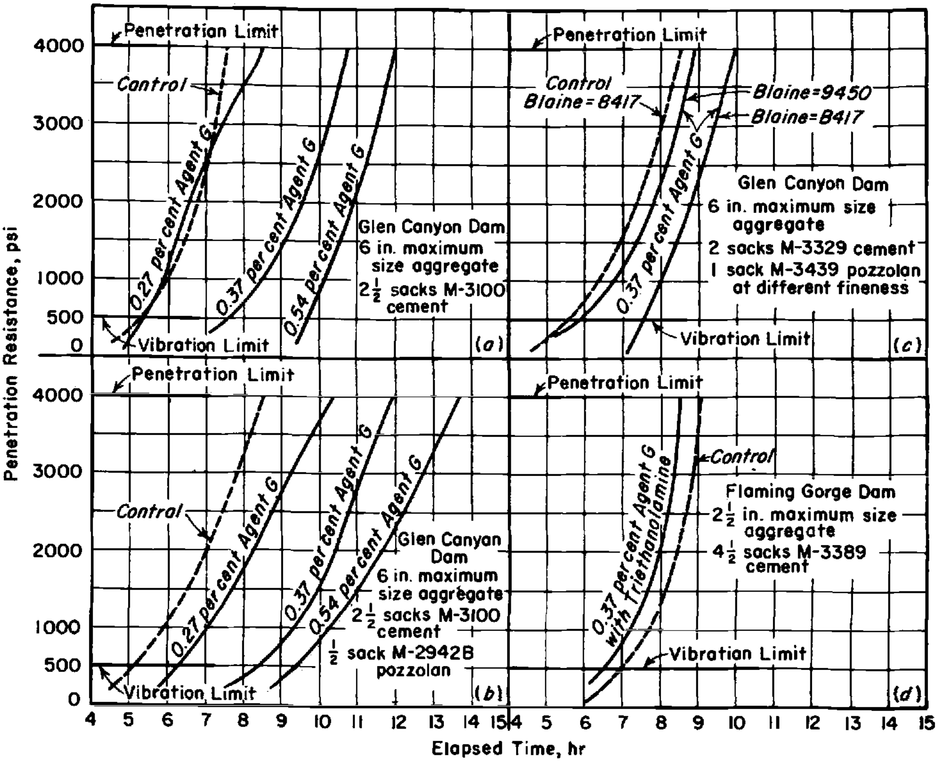


FIG. 6.—Influence of Agent on Rate of Hardening of Mass Concrete as Shown by Proctor Needle Test.

Three type II cements—initial temperature of concrete 50 F—tests performed at 73.4 F.

Mass concrete in Bureau of Reclamation dams is usually placed at an initial temperature of about 50 F, then proceeds through a period of rising temperature. Tests performed on samples of concrete at the batch plant do not reflect the influence of the increasing temperature occurring within massive blocks in the dam. To determine the effect of rising temperatures on the rate of hardening of mass concrete with and without lignin and hydroxylated carboxylic acid agents, the mixes reported in Table IX and Fig. 7 were made. The average initial temperature of the mass concrete was 52 F. Mortar samples, wet screened from mass concrete, were immediately taken into each of three rooms wherein the air temperature was maintained at 50, 75, and 100 F, while rate of hardening tests were performed.

The influence of predictable temperature cycles for various job conditions on

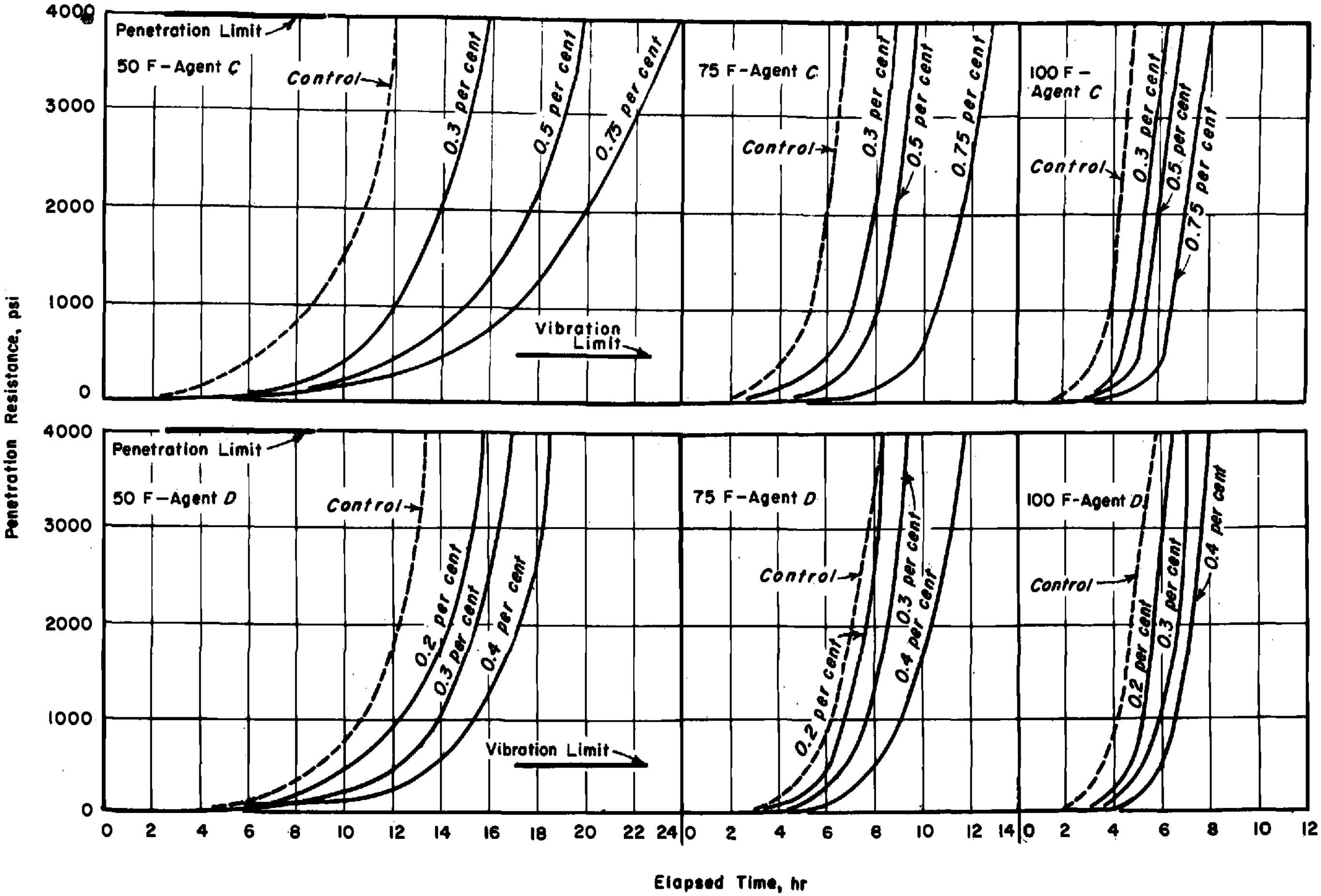
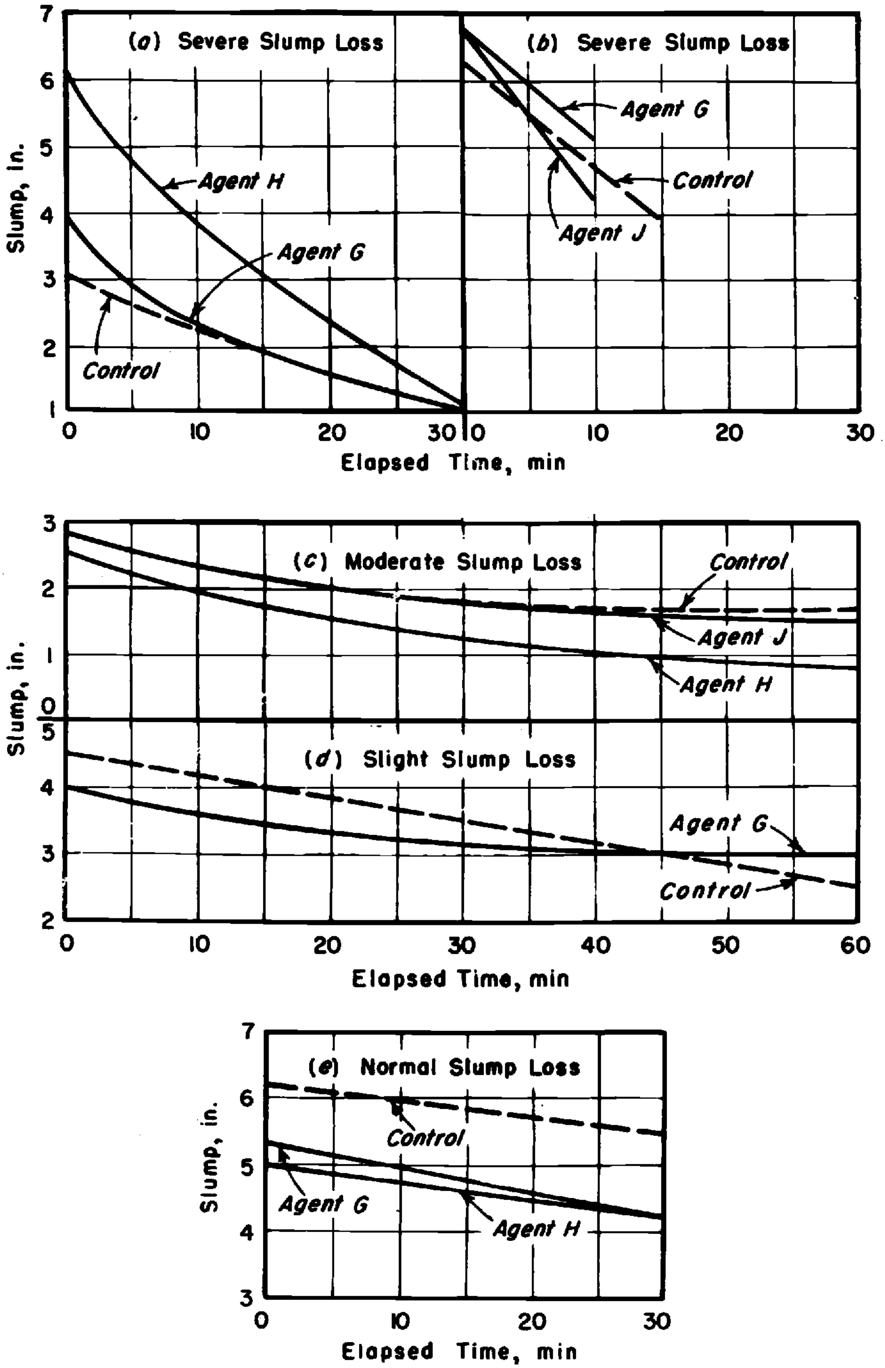


FIG. 7.—Influence of Various Quantities of Lignin and Hydroxylated Carboxylic Acid Agents on Hardening Characteristics of Mass Concrete Placed at 52 F and Cured at 50, 75, and 100 F.

Monticello Dam—Constant $w/c + p$ of 0.60, 30 per cent pozzolan.



(*a*) Prineville Dam—laboratory tests.
(*b*) Navajo Dam—field tests.
(*c*) Flaming Gorge Dam—field tests.
(*d*) Fremont Canyon power conduit—field tests.
(*e*) Clear Creek, Colo., tunnel—field tests.

FIG. 8.—Influence of Lignin Agents on Rate of Slump Loss of Concrete for Various Projects.

the rate of hardening of mass concrete may be estimated from the data in Fig. 7. The figure indicates that larger dosages of *WR* agents may be used without objectionable retardation when the temperature of the concrete is ascending than would be permissible if the concrete remained at the placing temperature of approximately 50 F. The acceleration of hardening and early strength development of mass concrete due to rising temperature tend to reduce form pressures and facilitate early removal of forms without damaging the formed concrete surfaces.

TABLE XI.—PIPELINE PRESSURES AND POWER REQUIRED FOR PUMP OPERATION

Mix	Slump, in.	Air Content, per cent	Placing Rate, cu yd per min	Maximum Average Pipeline Pressure, psi	Kilowatts, per cu yd	Length of Line, ft	Total Volume Pumped, cu yd
No. 1—Control	5.2	2.9	1.21	70	0.269	77	182
No. 2—Agent *G*	4.1	3.4	1.05	70	0.296	77	180
No. 3—Control with interruptions	4.0	3.1	0.91	76	0.415	96	123

Slump Loss:

Although, as indicated by rate of hardening tests, *WR* agents extend the length of time during which concrete can be placed and consolidated, the ease of handling concrete after various intervals of time following discharge from the mixer is not similarly affected. Rate of slump loss is the measure used to gage this characteristic.

Figure 8 shows rate-of-slump-loss curves depicting conditions encountered on five projects. At Prineville Dam, severe slump loss induced by the sand caused difficulty in pumping operations. As shown in Fig. 8(*a*), the addition of lignin agents *H* and *G* apparently increased the rate of slump loss. At Navajo Dam, where cement has occasionally exhibited false set, slump loss was not alleviated by agents *G* and *J*, as shown in Fig. 8(*b*). A moderate rate of slump loss encountered at Flaming Gorge Dam was not corrected by the addition of agents *H* and *J*, as shown in Fig. 8(*c*). Concretes with normal and only slightly higher-than-normal slump loss were encountered at Glen Canyon, Clear Creek, and Fremont Canyon tunnels. The addition of lignin agents to the Clear Creek and Fremont Canyon concretes did not appreciably change the rate of slump loss, as shown in Figs. 8(*d*) and (*e*).

In three of the six jobs cited above, the contractors elected to continue using the *WR* agents because there was a decrease in the frequency of plugged pumplines due to the presence of the lignin in the concretes.

Pumpability:

In an attempt to gain more tangible data regarding the effect of lignin agents on the pumpability of concrete, special tests were performed at Glen Canyon Dam on tunnel lining concrete containing 2½-in. maximum-size aggregates, which was being placed with a pumpcrete machine. Comparable concretes with and without a lignin agent were pumped through the same pipeline. Pressures in the pipeline and the power required to operate the pumps were measured. Frequency of plugged lines was to be tabulated, but none occurred during the tests. Results of the first two tests, which are summarized in Table XI, show that the maximum pressures developed in the line were equal for concretes made with and without the lignin agent.

Concrete containing the lignin agent was pumped with 1 in. (20 per cent) less slump than the control mix for approximately the same expenditure of power. A second control mix, No. 3, was made and tested in which the slump was nearly equal to that of the lignin mix. The power requirement to pump this mix was 40 and 54 per cent more than that required to pump the lignin and the first control mixes, respectively. However, a part of this increased power expenditure must be attributed to the fact that flow through the pipeline was interrupted briefly on four occasions during the test and that the pipeline was 25 per cent longer, necessitating 8.5 per cent more pressure to move the concrete. More tests are needed to fully evaluate the benefits of *WR* agents on the pumpability of a variety of concretes.

Finishing Characteristics:

During construction of the community facilities at Glen Canyon Dam, difficulty was encountered in finishing concrete slabs exposed to the hot desert climate. The concrete surfaces dried out and became encrusted before troweling could be completed. Addition of a lignin agent did not prevent formation of a dehydrated surface crust but did retard concrete in the base of the slabs. When a heavy mechanical trowel was applied to a slab, the retarded base rolled under this weight and caused the surface crust to crack. All observers, including a representative of the admixture producer, agreed that in this instance, retardation was not desirable.

Several 2 by 2-ft slabs were made in the laboratory, with and without a lignin agent, to evaluate the effect of the agent on hand screeding, floating, and troweling. The slabs were covered with wet burlap between screeding and troweling operations. The available period between screeding and troweling operations on the surface of the concrete containing the lignin agent was appreciably longer than the corresponding time for the control concrete. This was not important in finishing the small laboratory slabs but could be very important on large slabs, or when the number of skilled finishers is insufficient for the job.

A marked improvement in the metal-formed finish of continuously placed tunnel lining for Fremont Canyon power plant was obtained by the addition of a lignin agent. In this case, initial retardation produced by the agent was primarily responsible for the improved appearance of the concrete surface. By this means, the long, advancing concrete slope inherent in this continuous construction method remained plastic enough to respond to vibration several hours after discharge from the slickline, thereby reducing the number of cold joints and rock pockets.

STRENGTH

Results of the strength tests made during this study substantiate the long recognized theory that compressive strength, tensile strength, and shearing strength of concrete are all more or less related. An increase or decrease in one is generally reflected in the others, though not to the same degree. The addition of nominal dosages of most of the *WR* agents tested improved the compressive, tensile, and shearing strengths, as shown in Figs. 9 through 24. The improvements are diminished if cement is reduced to offset the cost of the agents.

Compressive Strength:

More tests were performed to evaluate the influence of *WR* agents on compressive strength than were made for any other property of concrete. Data reported in this paper are based on compressive

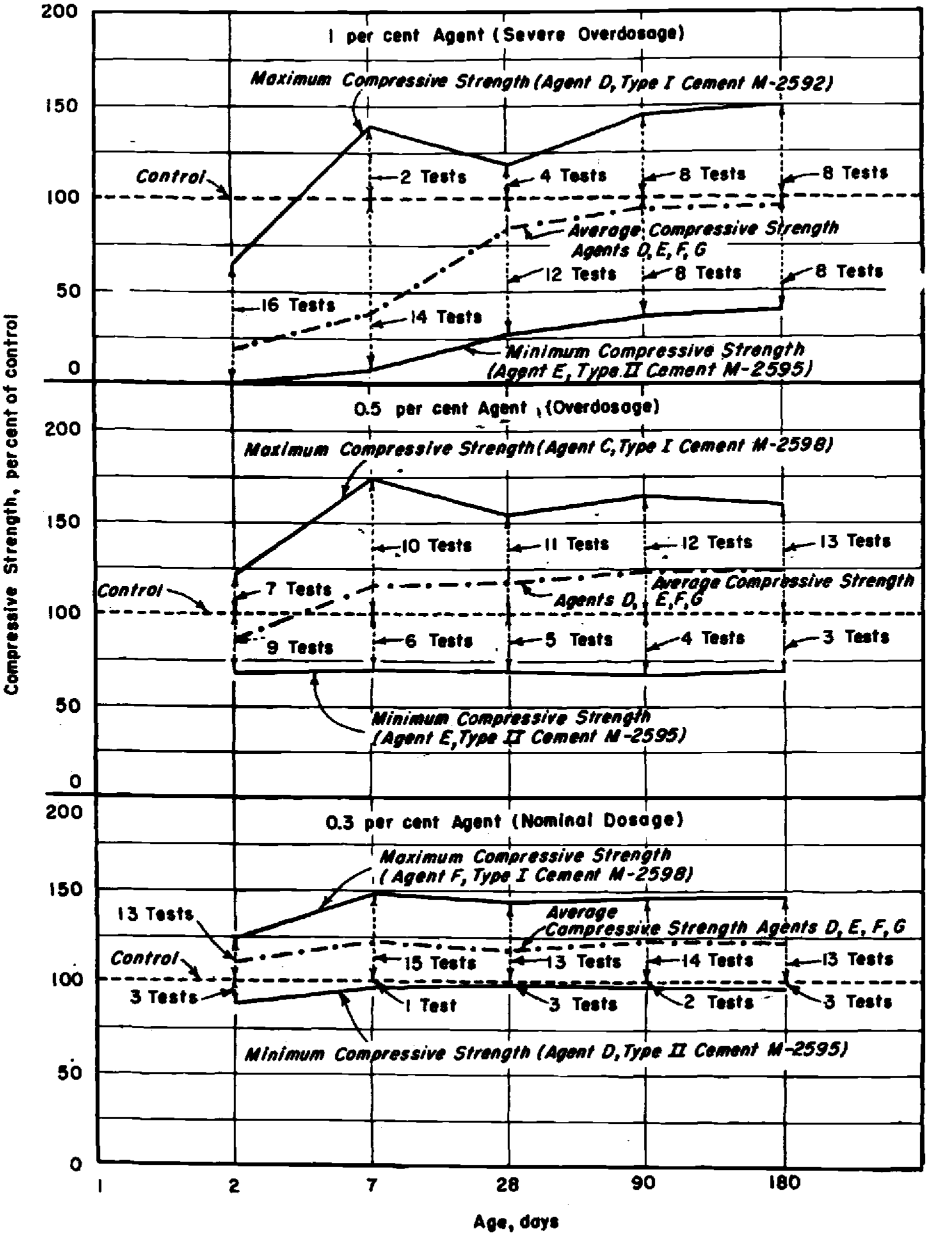


FIG. 9.—Influence of Lignin and Hydroxylated Carboxylic Acid Agents on Compressive Strength of Structural Concrete.

Clear Creek, Colo., aggregate—1½-in. maximum size—6 by 12-in. cylinders—standard cured—four different cements at 5 sacks per cu yd—four different agents.

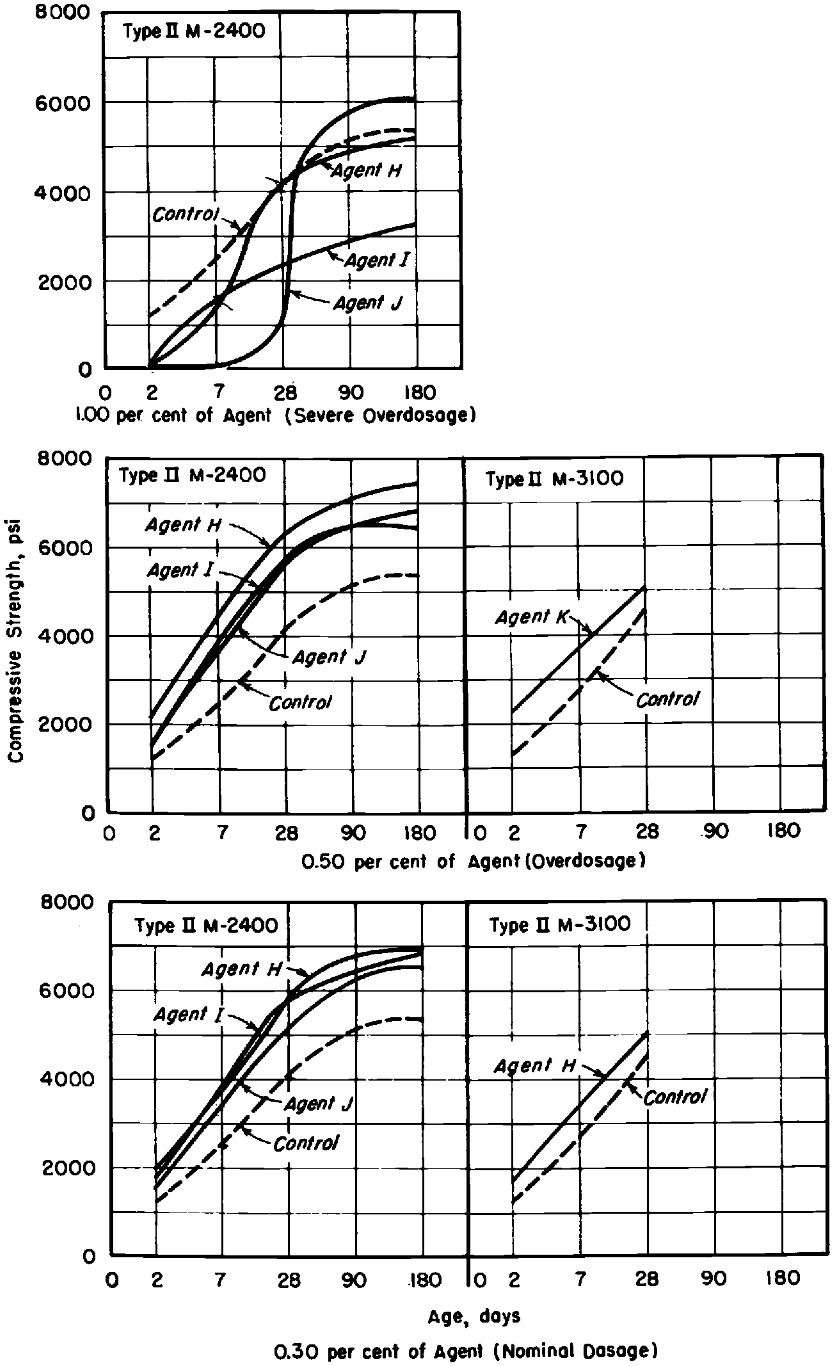


FIG. 10.—Influence of Lignin Agents on Compressive Strength of Structural Concrete.

Clear Creek, Colo., aggregate—1½-in. maximum size—6 by 12-in. cylinders—standard cured two blends of type II cement—cement content: 5 sacks per cu yd—four lignin agents.

strength test results of 1820 6 by 12-in. cylinders and 111 18 by 36-in. cylinders made in the laboratory, and 591 6 by 12-in. cylinders made for field control tests. The test for compressive strength was emphasized because experience has shown that this test provides a good over-all index of the quality of air-entrained concrete.

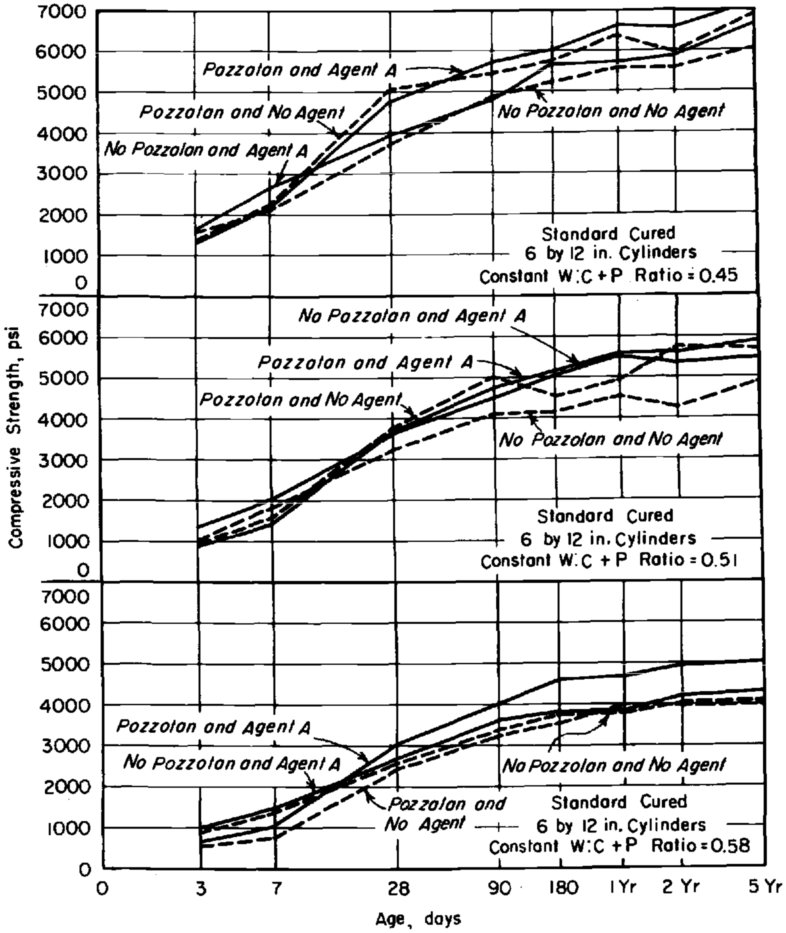


FIG. 11.—Influence of Lignin Agent on Compressive Strength of Structural Concrete With and Without Pozzolan, Monticello Dam Series.

Cache Creek aggregate—1½-in. maximum size—type II cement M-2005—calcined clay pozzolan M-2017—agent used in the amount of 0.10 per cent by weight of cement and pozzolan.

Laboratory Tests of Structural Concrete.—Figure 9 graphically summarizes data derived from 52 mixes and 520 compressive strength tests of 6 by 12-in. cylinders of series I. Each graph portrays the pattern of strengths obtained for a given admixture dosage. In each case, maximum and minimum compressive strengths are delineated to illustrate the range of strengths which may occur when various combinations of admixtures and cements are used.

Considering tests at all ages, 85 per

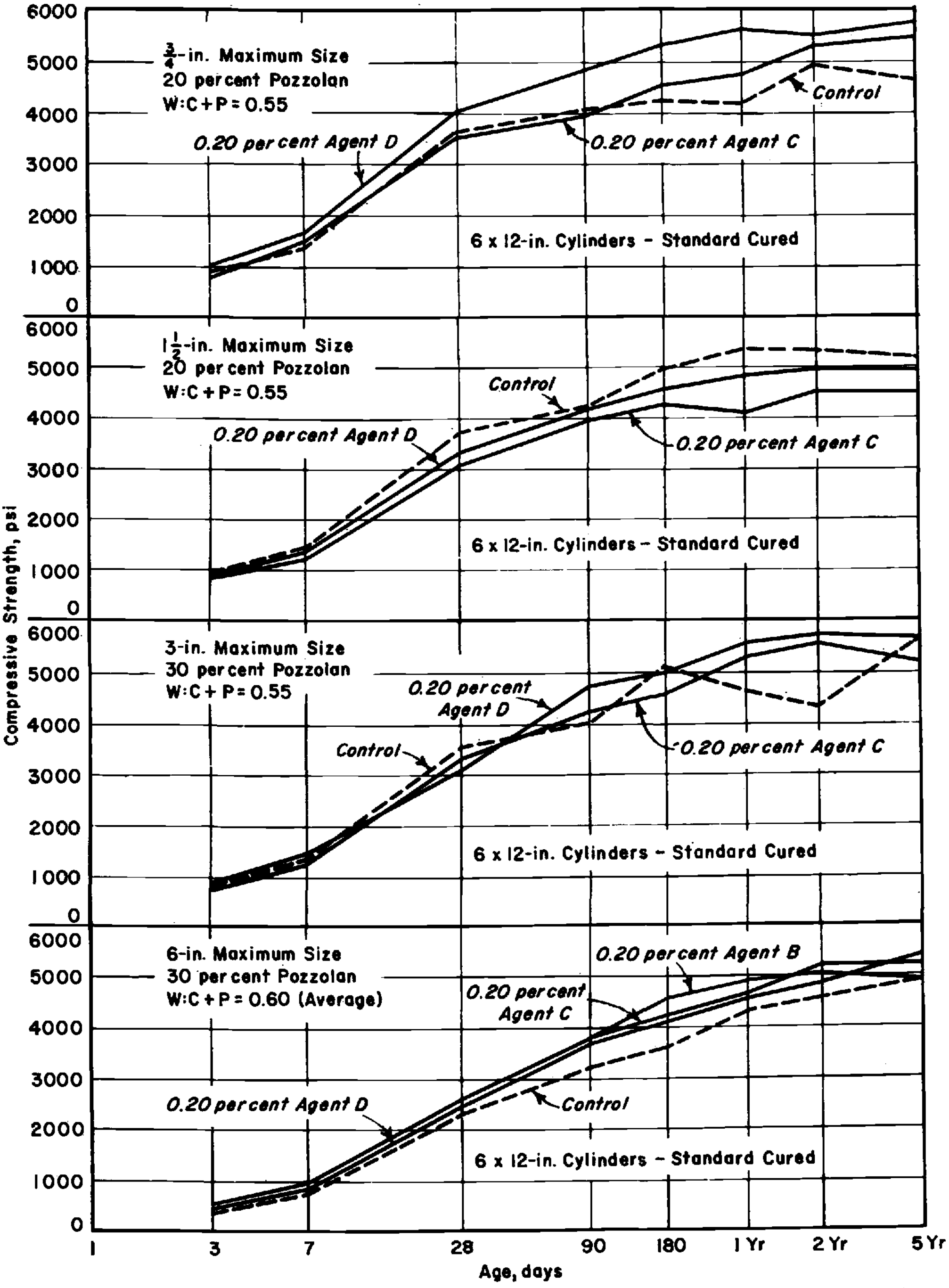


FIG. 12.—Influence of Lignin and Hydroxylated Carboxylic Acid Agents on Compressive Strength of Concrete at Constant $w/c + p$, Monticello Dam Series.

Cache Creek aggregate—calcined diatomaceous clay pozzolan M-2017—type II cement M-2005.

cent of the specimens containing nominal dosages of the *WR* agents developed greater compressive strength than their companion control specimens, the agents increasing the over-all average compressive strength by 18 per cent. Overdosage decreased to 66 per cent the number of specimens developing compressive strength greater than control specimens; the over-all average compressive strength increases equaling 12 per cent. Severe overdosage caused 72 per cent of the specimens to develop less compressive strength than the companion control specimens, and accounted for a decrease of 25 per cent in the average compressive strength.

Since the above-mentioned tests were completed, several admixture producers have placed newer and reportedly improved products on the market. Water-reducing retarding agents *H*, *I*, and *J*, and water-reducing accelerating agent *K*, are among these newer agents. Compressive strengths of specimens containing nominal dosages and overdosages of these newer agents exceeded the companion control cylinder strengths in every case, as shown in Fig. 10. Nominal dosages and overdosages increased the over-all average compressive strength by 36 and 41 per cent, respectively. Percentage-wise, strength increases were slightly higher than average at early ages and slightly lower than average at later ages.

Unlike most of the lignin agents used in the previous mixes, agents *H* and *J* did not produce excessively high air contents when used in severe overdoses, and therefore did not adversely affect ultimate development of compressive strength which, at 90 and 180 days of age, exceeded that of the companion control specimens by 4 per cent. However, on the detrimental side, severe overdosage of these agents did produce excessive retardation of set and slow early strength development, which would necessitate serious delays in form removal and greatly increase the possibilities for damage to structures during construction operations.

The key questions in the mind of a potential user of a *WR* agent are probably these:

What will be the effect of the agent on the quality of the concrete at later ages?

Will the agent-induced strength increases obtained at ages of 28, 90, and 180 days be reflected by similar increases after the concrete has aged for several years?

If cement content is reduced to offset the cost of the agent and maintain the water-cement ratio, will the strength of the concrete after several years of aging be as good as it would have been with the richer mix and no agent?

Results of series II compressive strength tests, shown graphically in Figs. 11 and 12, indicate that these questions may be answered in the affirmative. The figures provide a comparison of mixes with and without *WR* agents, when the ratio of water to cementitious materials was held constant. To maintain this constant ratio in the agent concretes, the quantity of cementitious materials was reduced 7 to 13 per cent for mixes containing lignin agents and 3 to 6 per cent for mixes with hydroxylated carboxylic acid agents. Even with lower cement content, concretes incorporating the *WR* agents generally had higher strengths than companion control specimens at all ages through 5 yr. Although, as shown in Fig. 11, the strength increase was not great, it should be emphasized that the lignin agent was added in a very slight dosage (0.1 per cent) and greater benefits than those shown in this figure would no doubt be obtained by using nominal dosages. The small quantity of agent produced the greatest and most consistent compressive strength gains with lean concrete having a $w/c + p$ of 0.58 and

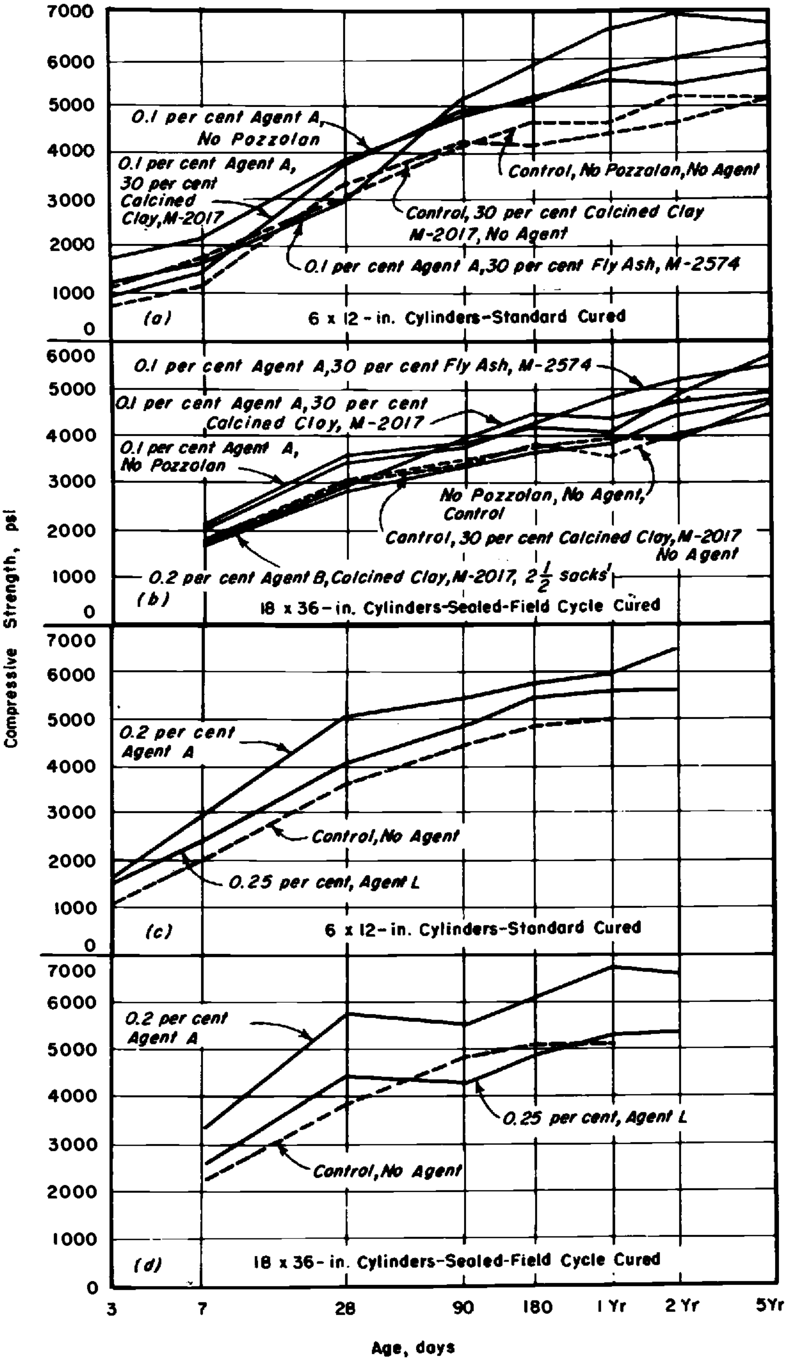


FIG. 13.—Influence of Lignin Agents on Strength of Mass Concrete.

(*a*) and (*b*) Monticello Dam-Cache Creek aggregate—6-in. maximum size—3 sacks cementitious materials (exception[1])—type II cement M-2005.

(*c*) and (*d*) Kirwin Dam—crushed limestone aggregate—6-in. maximum size—3 sacks type II cement M-1779.

NOTE.—All 18 by 36-in. data is extrapolated prior to 28 days of age.

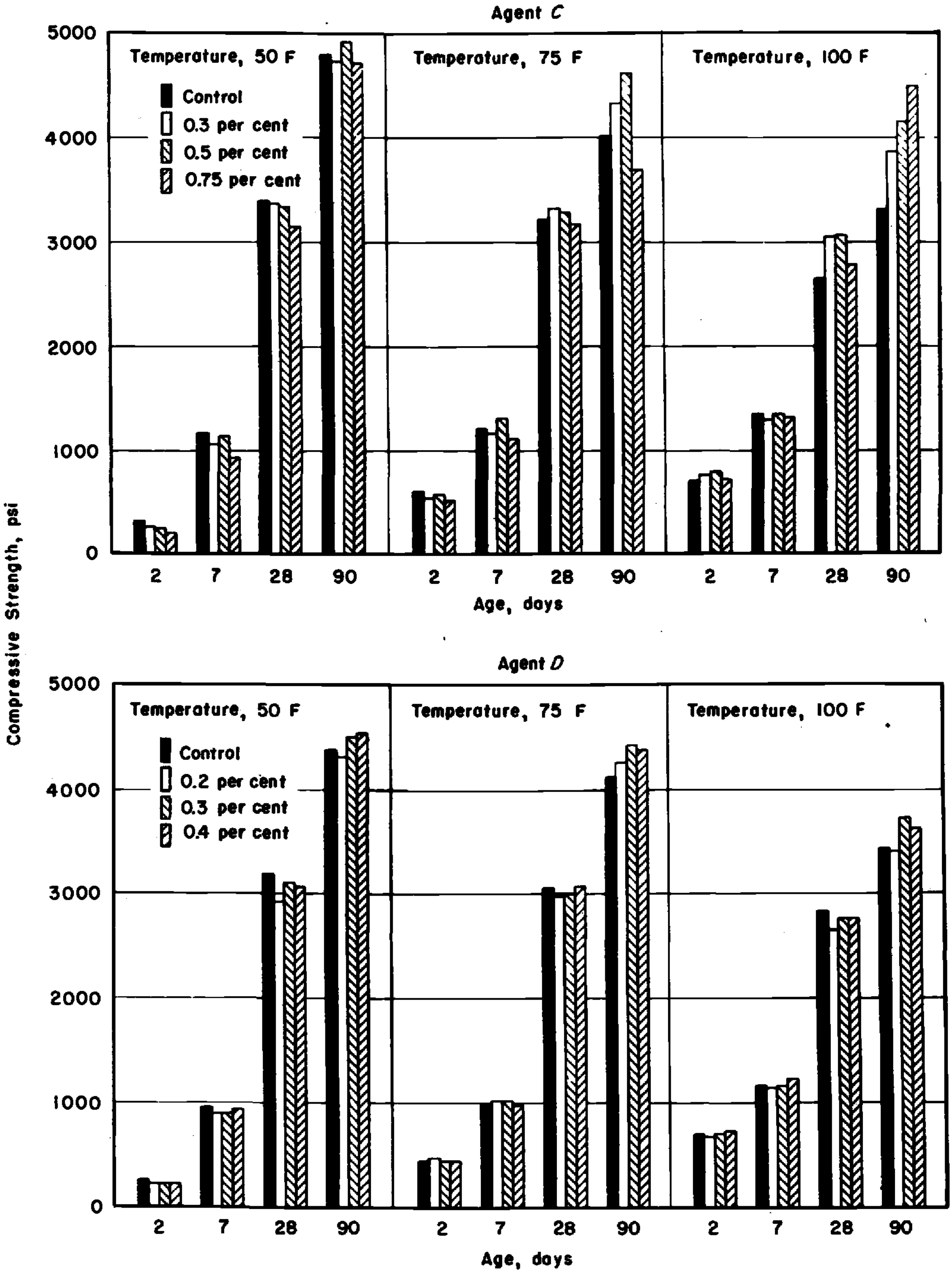


FIG. 14.—Influence of Various Quantities of Lignin and Hydroxylated Carboxylic Acid Agents on Compressive Strength of Mass Concrete Placed at 52 F, Moist Cured 48 hr at 50, 75, and 100 F, then Standard Cured. Monticello Dam.

Cementitious materials varied from 217 to 263 lb per cu yd—type II cement M-2005—30 per cent pozzolan M-2017—constant $w/c + p$ of 0.60—6 by 12-in. cylinders.

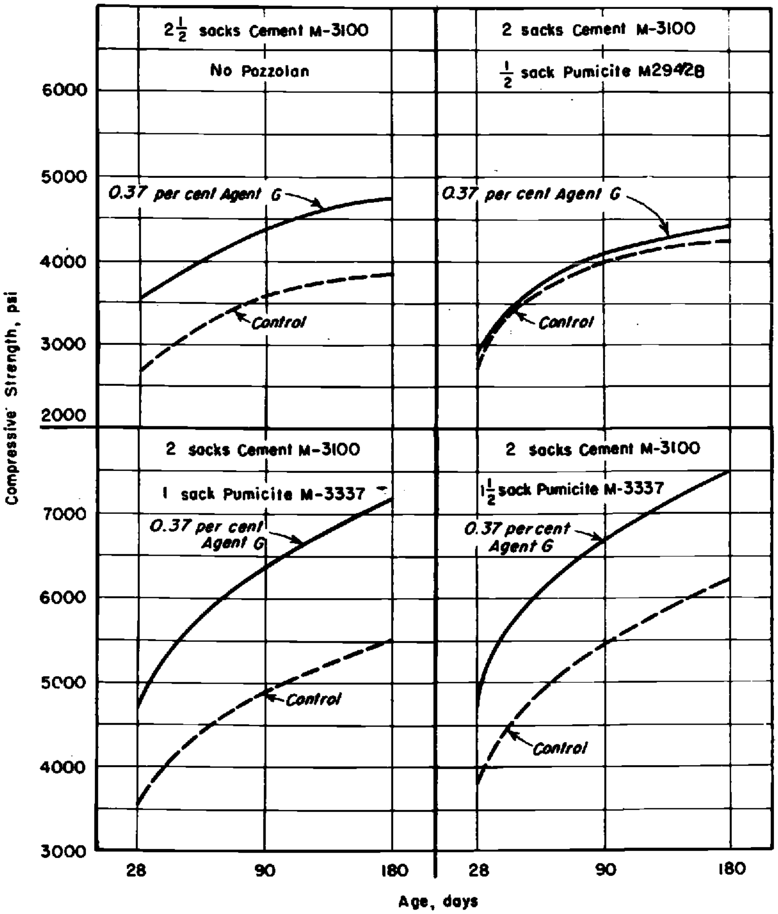


FIG. 15.—Influence of Agent on Compressive Strength of Mass Concrete for Glen Canyon Dam. Wahweap Creek aggregate—6-in. maximum size—6 by 12-in. cylinders—standard cured.

containing 30 per cent pozzolan. This agrees with observations by Doidge (2) that plasticizers, possessing the power of deflocculation, appear to increase the pozzolanic activity. Results of tests on concretes having $w/c + p$ ratios of 0.45 and 0.51 and representing the richer concretes containing pozzolan do not support this theory, although other tests of lean mass concretes, to be discussed later, do verify Doidge's findings.

Figure 12 compares graphically the age-compressive strength development of concretes containing various maximum size aggregate, with 20 and 30 per cent pozzolan replacements, and with and without addition of lignin and hydroxylated carboxylic acid agents. These concretes had a constant ratio of water to cementitious materials of 0.55, except for an average value of 0.60 for the mass concrete. Thus, cement content was reduced for the mixes containing *WR* agents. Control specimens from the concretes designed for 1½-in. maximum-size aggregates had considerably less slump and air content than did the comparison specimens with *WR* agents, creating an impression which is inconsistent with the generally indicated agent-induced gain

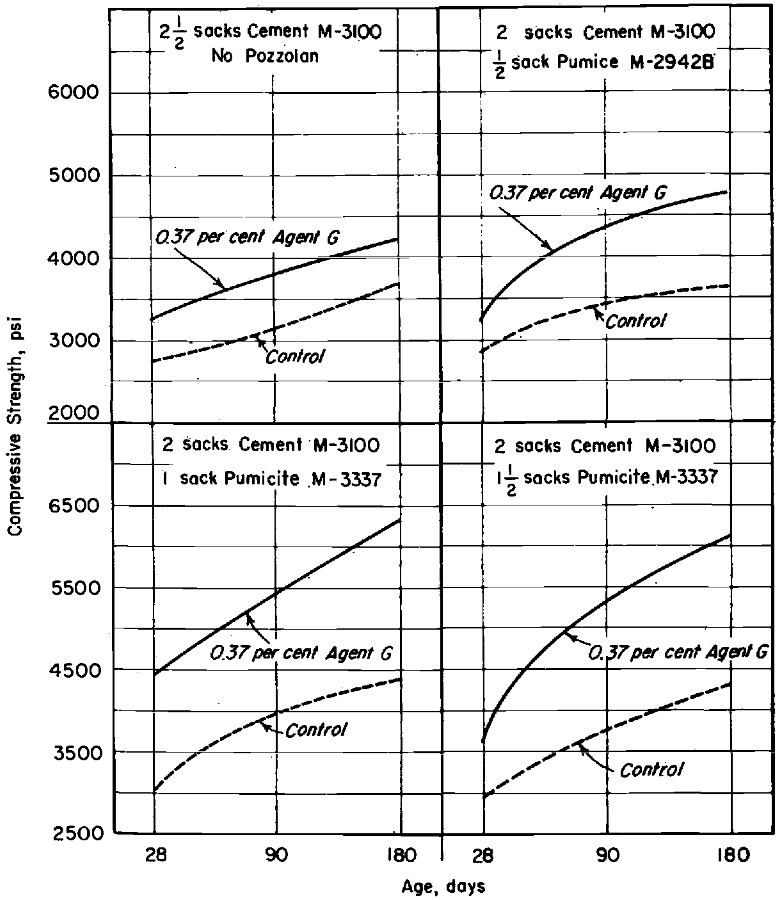


FIG. 16.—Influence of Agent on Strength of Mass Concrete for Glen Canyon Dam. Wahweap Creek aggregate—6-in. maximum size—18 by 36-in. cylinders—field cycle cured.

of compressive strength. In general, other results indicate agent-induced gains in compressive strength, particularly at ages 1, 2, and 5 yr.

Laboratory Tests of Mass Concretes.—The influence of *WR* agents on the properties of mass concrete is becoming of increasing interest to the Bureau of Reclamation and others who design and construct large concrete dams. Figures 13 through 21 show the influence of *WR* agents on the compressive strength of mass concretes made with materials from four Bureau of Reclamation projects. The figures reflect test results from 52 sets of 18 by 36-in. mass concrete specimens, each set consisting of 2 specimens for comparison, 1 with and 1 without a lignin agent. Included in the comparisons are specimens made with and without pozzolans, having various dosages of lignin agent, and tested at various intervals of time from 2 days through 5 yr of age. Early age strength development of concrete in massive blocks is accelerated by rising temperatures due to heat released by hydrating cement. To reflect the influence of increasing temperatures, and prevent loss of moisture, all 18 by 36-in. cylinders were sealed in metal molds and

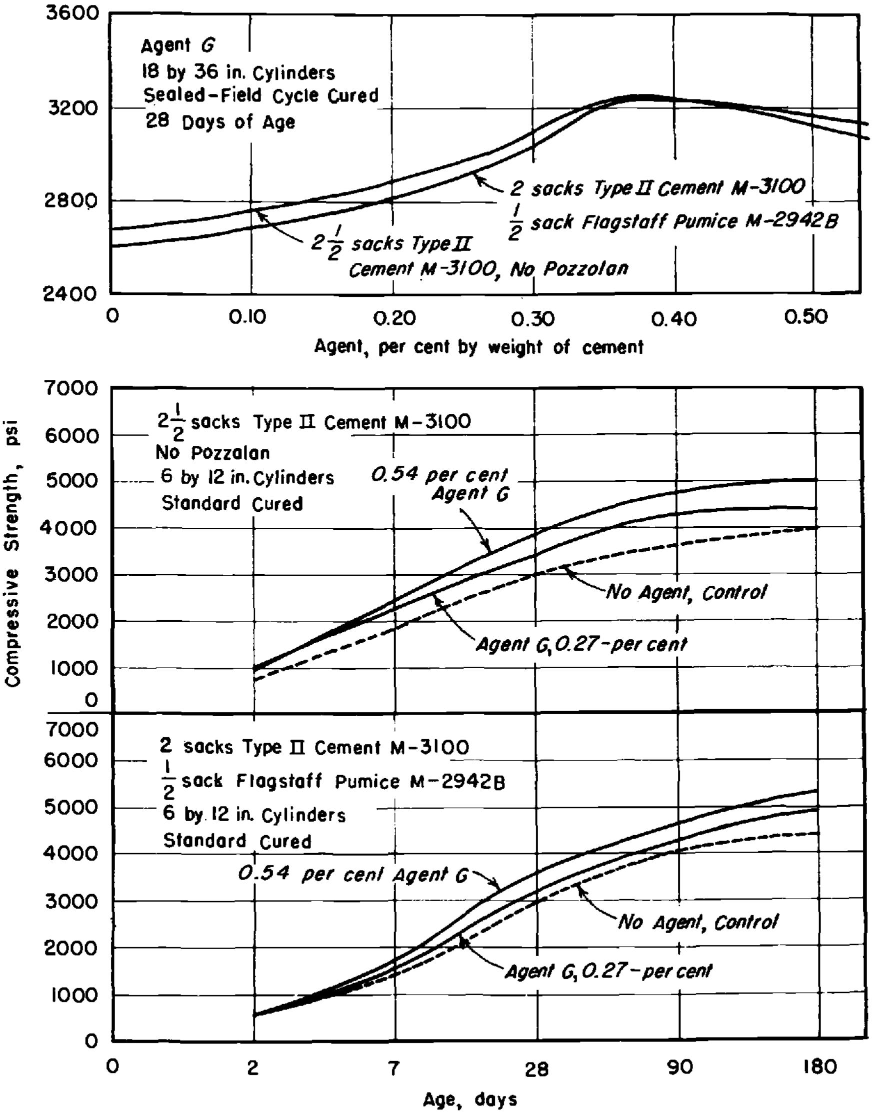


FIG. 17.—Influence of Quantity of Agent on Compressive Strength of Mas; Concrete—Glen Canyon Dam Studies.

Wahweap Creek aggregate—6-in. maximum size—average per cent air = 3.0 (±0.1)—average slump = 1.9 in. (±0.1).

cured at a temperature cycle predicted for mass concrete in the particular dam under consideration. In 49 of 52 comparisons, the compressive strength of the specimens containing the lignin agent exceeded, by an average of 21 per cent, that of the control specimen. The three exceptions were: 28-day strength, mix No. 74; 90- and 180-day strengths, mix No. 81. It is noteworthy that in mix No. 81 the specimens with agents contained 2.6 per cent more air and had 0.8 in. more

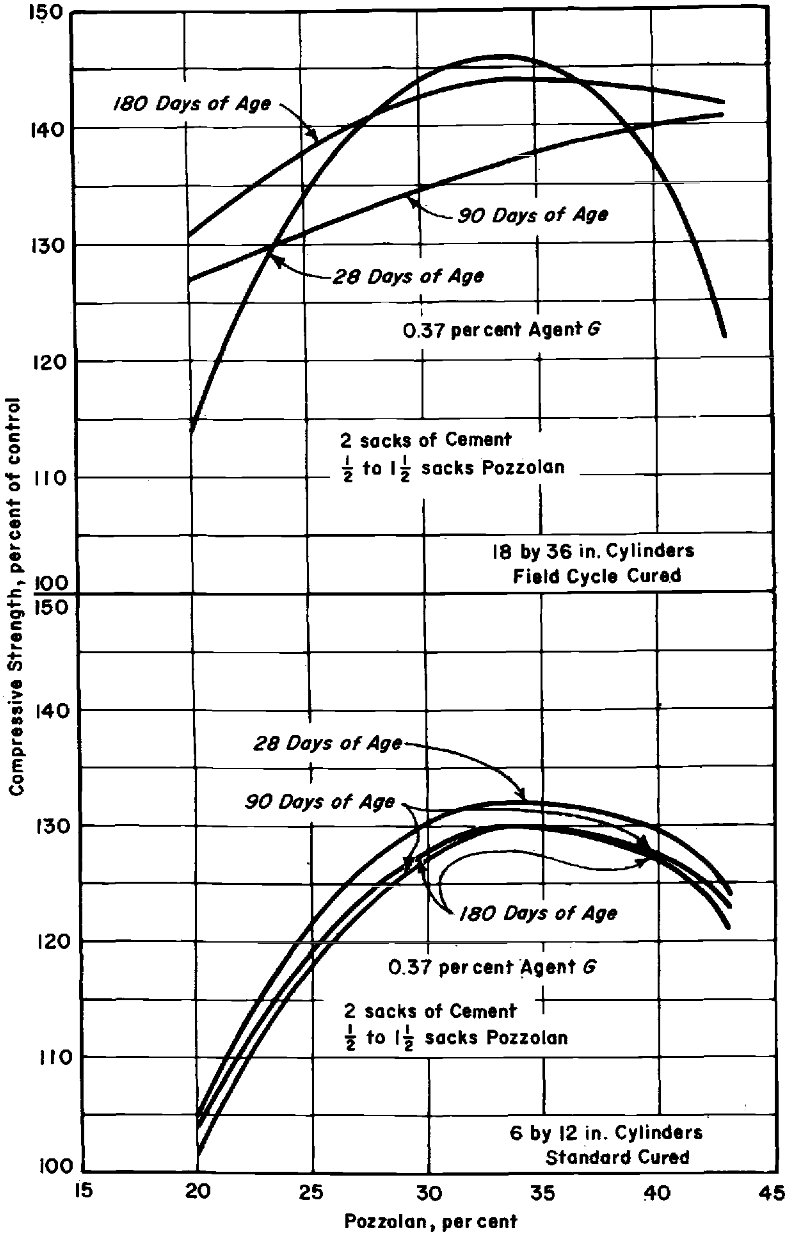


FIG. 18.—Influence of Lignin Agent on Cementing Activity of Glen Canyon Dam Mass Concrete. Wahweap Creek aggregate—6-in. maximum size—type II cement M-3100 Dam Flagstaff pumice.

slump than the companion control cylinders, which would be expected to reduce strength. Even so, the maximum strength decrease was only 12 per cent at 90 days' age. This apparent reduction in compressive strength was reduced to 4.5 per cent at 180 days and at later ages a strength increase was registered.

To help answer the question, "What is the effect of lignin agents on mass concrete after extended periods?" the results of later age tests on 18- by 36-in. specimens are tabulated in Table XII. Reference to the table shows that, on the average, compressive strength of the later age specimens containing lignin agent is 28 per cent higher than that of the companion control specimens. The average dosage of agent in these specimens is 0.28 per cent. Compared to control, the compressive strength was increased an average of 40 per cent for those specimens, referred to in Table XII, that contained more nearly an optimum dosage (0.37 per cent). These results indicate that the benefits produced by use of lignin agents in mass concrete are not temporary in nature, as is the case with some accelerating agents.

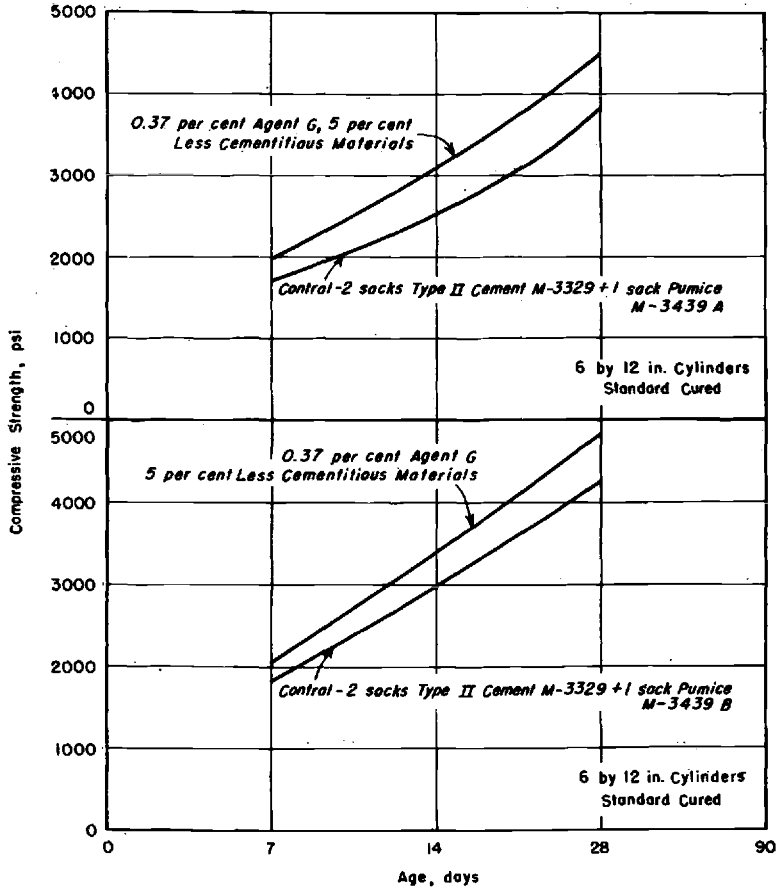


FIG. 19.—Cement Reduction with Lignin Agent—Glen Canyon Dam Mass Concrete.

Wahweap Creek aggregate—6-in. maximum size—average per cent air = 2.5 (±0.1)—average slump = 1.7 in. (±0.1).

Figure 13 shows compressive strength development of mass concrete containing various dosages of lignin agents and materials from Monticello and Kirwin Dams for ages up to 5 yr. Results of tests on 18 by 36-in. cylinders containing the full mass mix and 6 by 12-in. cylinders con-

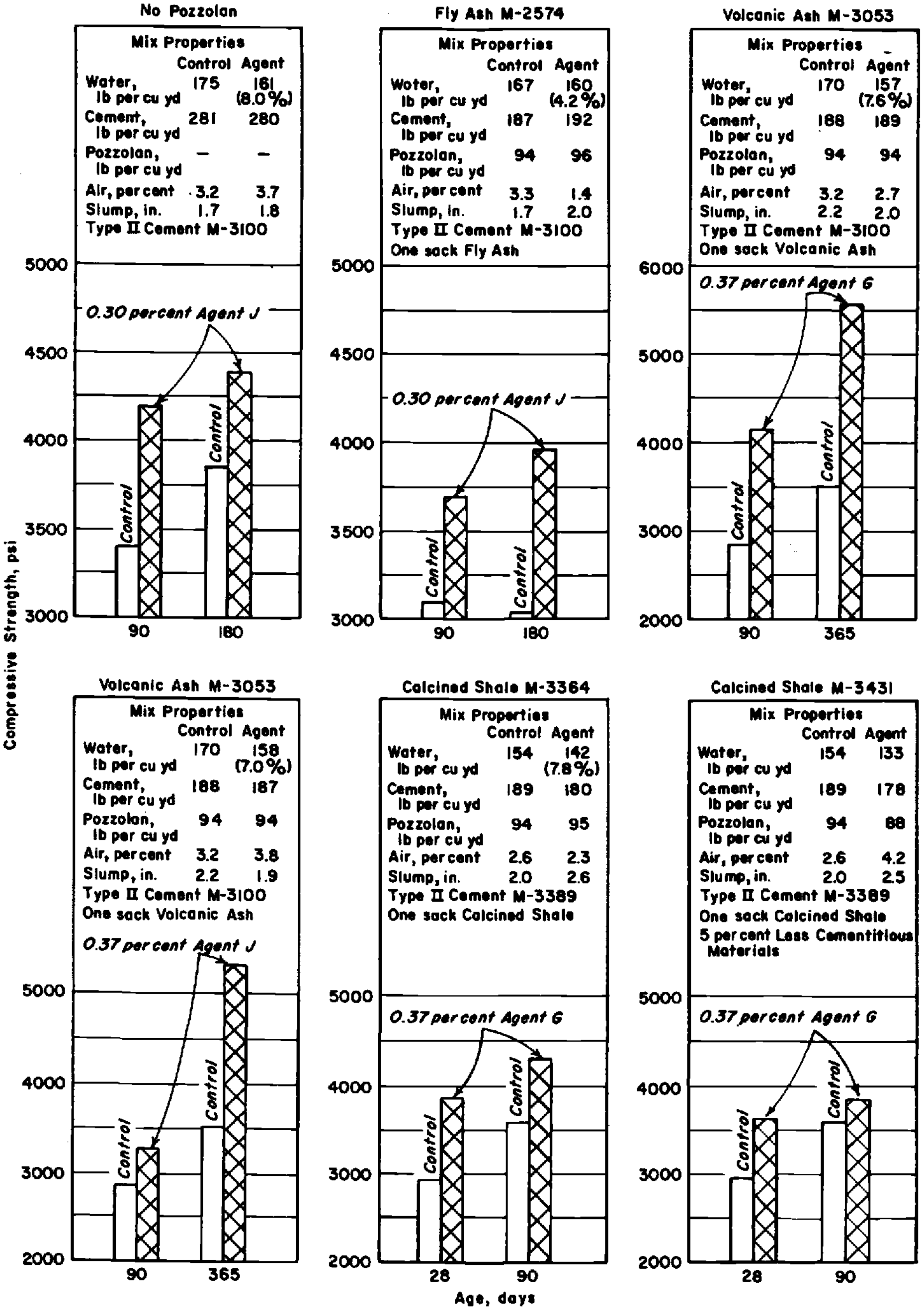


FIG. 20.—Influence of Lignin Agents on Compressive Strength of Mass Concrete.

Flaming Gorge Dam-river aggregates—6-in. maximum size—18 by 36-in. cylinders—field cycle cured.

NOTE.—Average water reduction due to use of lignin = 8.0 per cent.

taining concrete from the mass mix wet screened to 1½-in. maximum-size aggregate are shown in this figure. All but one of the concretes contained a total of 3 sacks of cementitious materials per cu yd of concrete. The one exception contained 0.20 per cent agent *B* with 2½ sacks of cementitious materials per cu yd of concrete. Results from this mix are plotted with results of tests on the control concrete without an agent containing 3 sacks of cementitious materials per cu yd. Strength development for the 2 concretes is practically identical throughout the 5 yr of tests.

TABLE XII.—EFFECTS OF LIGNIN AGENTS ON COMPRESSIVE STRENGTH OF MASS CONCRETE AT LATER AGES.

Project	Age	Cementatious Materials, sacks per cu yd	Pozzolan, per cent	Agent		Compressive Strength
				Type	Per cent	Control, per cent
Monticello Dam	5 yr	3 3	0 30	*A* *A*	0.10 0.10	128 104
Gross Dam	5 yr	2½	0	*A*	0.20	116
Kirwin Dam	1 yr	3 3	0 0	*A* *L*	0.20 0.25	132 104
Glen Canyon Dam	180 days	3½ 3 2½ 2½	43 33 20 0	*G* *G* *G* *G*	0.37 0.37 0.37 0.37	142 144 131 114
Flaming Gorge Dam	1 yr	3 3	33 33	*G* *J*	0.37 0.37	158 152
	180 days	3 3	0 33[a]	*J* *J*	0.30 0.30	114 130
Average compressive strength, per cent of control						128

[a] Fly ash used instead of project pozzolan.

The effect of rising temperature on the compressive strength development of 6 by 12-in. cylinders with and without lignin and hydroxylated carboxylic acid agents is indicated by tests results shown in Table IX and Fig. 14. These cylinders were fabricated from the minus 1½-in. fraction of mass concretes. A constant $w/c + p$ ratio of 0.60 and an initial placing temperature of 52 F were maintained. The specimens were divided into three groups and each group cured under wet burlap for 48 hr at different temperature conditions. One group was cured at the approximate placing temperature (50 F), one at 75 F, and the third at 100 F.

Compared to curing at 50 F, the higher curing temperatures accelerated early strength and reduced ultimate strength development. This was true of concretes with and without *WR* agents. However, these effects were offset by retardation at early ages and increased ultimate strength development induced by the agents. Apparently, the detrimental effect on ultimate strength produced by elevated early curing temperature may be substantially offset by use of larger-than-normal dosages of *WR* agents.

The specimens with the larger dosages

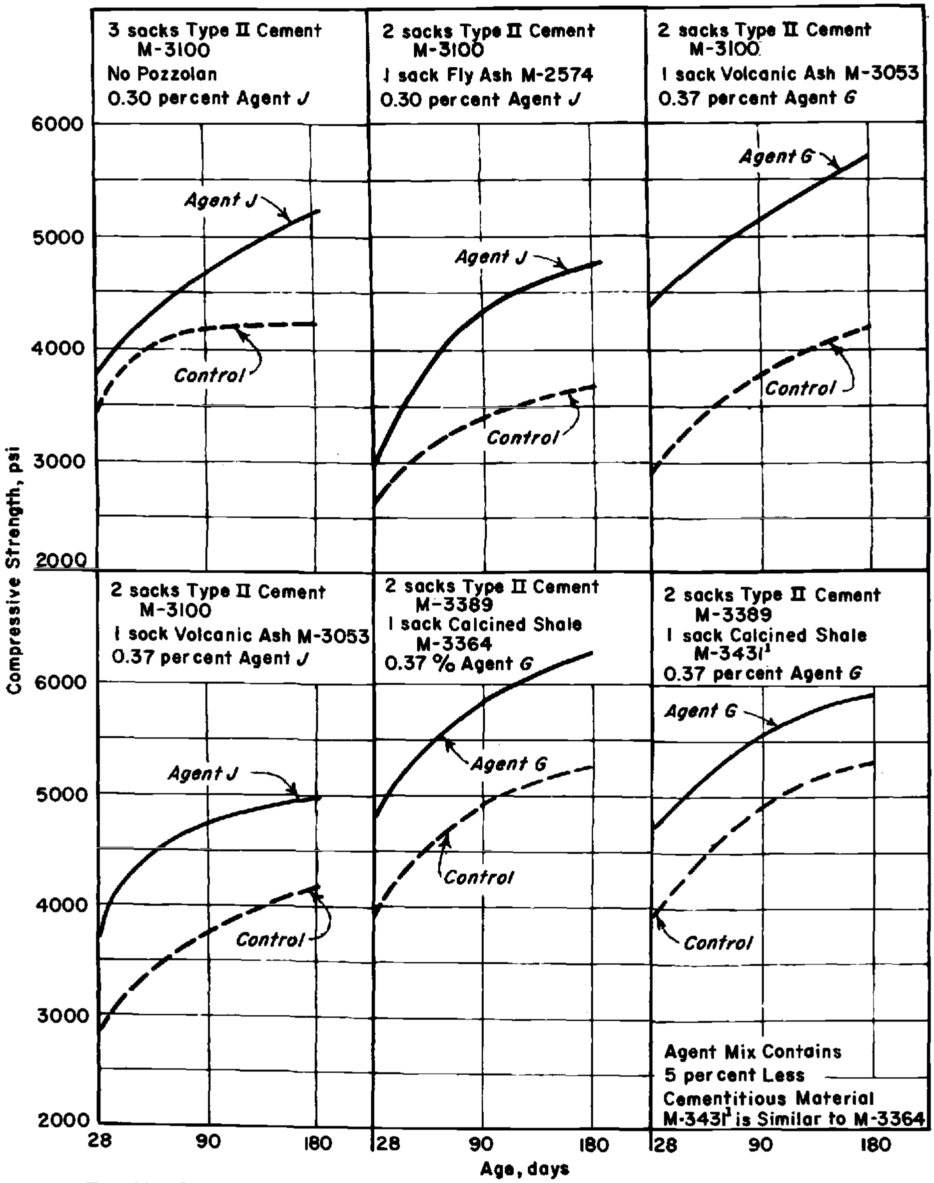


FIG. 21.—Influence of Lignin Agents on Compressive Strength of Mass Concrete.

Flaming Gorge Dam-river aggregates—6-in. maximum size—6 by 12-in. cylinders—standard cured—average per cent air = 2.9 ± 0.5—average slump = 2.0 in. ± 0.5.

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[1] M-3431 is similar to M-3364.

of *WR* agents contained about 13 per cent less water and cement than the companion control specimens. Even so, the average 90-day compressive strengths of the agent specimens exceeded those of the control specimens.

Compared to the effect of 50 F curing temperature on control specimens tested

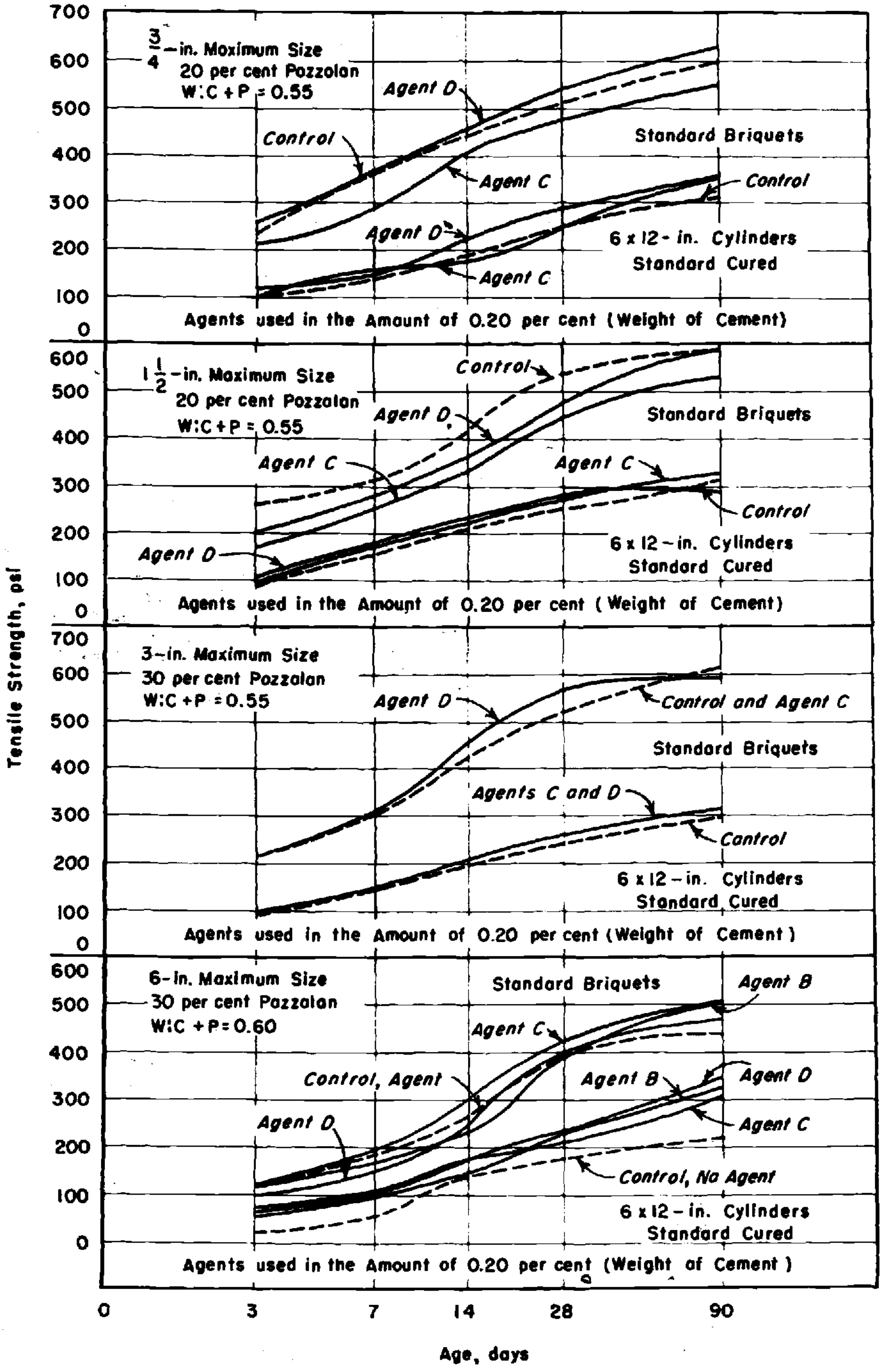


FIG. 22.—Influence of Lignin and Hydroxylated Carboxylic Acid Agents on Tensile Strength of Concrete at Constant $w/c + p$, Monticello Dam.

Cache Creek aggregate—calcined diatomaceous clay pozzolan M-2017—type II cement M-2005.

at 90 days' age, the rising temperature induced a loss of compressive strength of about 30 per cent in companion control specimens cured at 100 F. Addition of 0.75 per cent lignin agent to a mix having the same water-cement ratio (13 per cent less cement) decreased the temperature-induced loss of compressive strength to only 6 per cent.

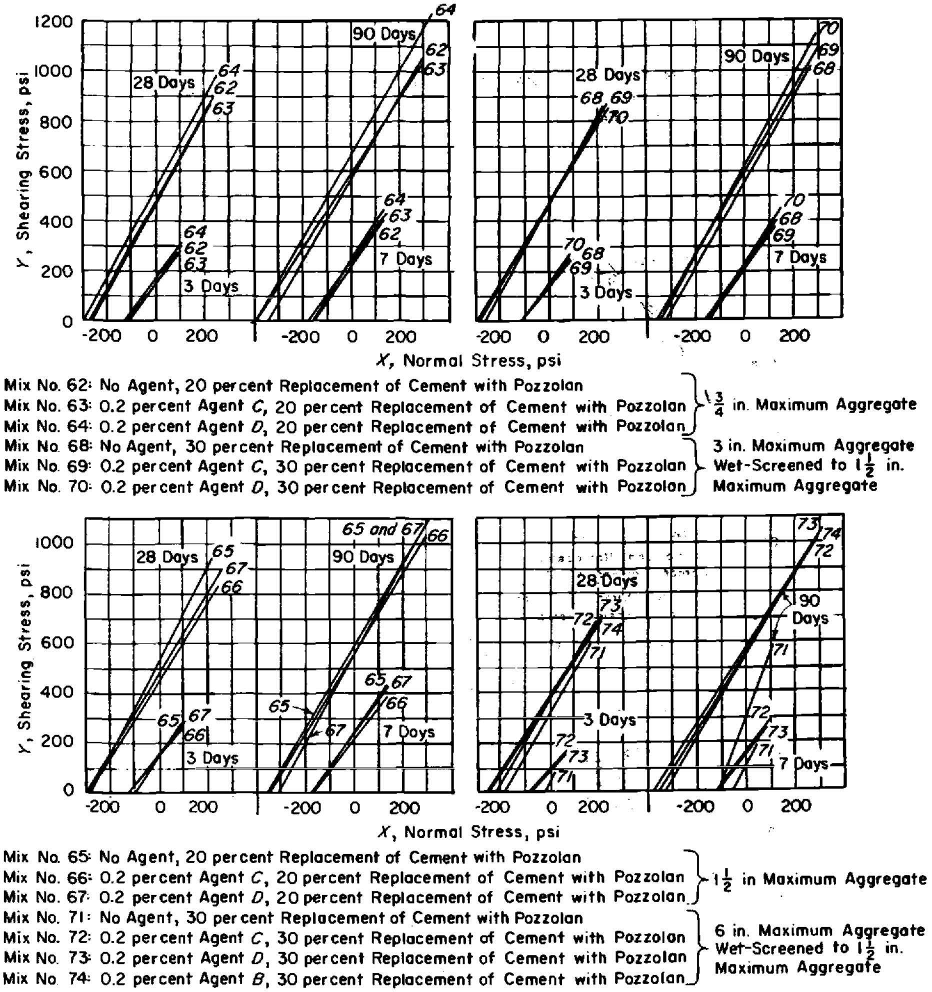


FIG. 23.—Influence of Lignin and Hydroxylated Carboxylic Agents on Shearing Relationships at Zero Lateral Pressure.

NOTE.—Intercept value on Y axis of $C_{tc} = \sqrt{rR}$ and slope of $\tan \theta_{tc} = \dfrac{R - r}{2\sqrt{rR}}$ where r and R are the radii of the tension circle and compressive circle, respectively.

Compressive strengths of mass concretes made with materials from Glen Canyon Dam, as obtained by tests of 6 by 12-in. and 18 by 36-in. cylinders, are shown graphically in Figs. 15 and 16. Figure 16 indicates that, without exception, the compressive strengths of mass specimens with lignin agents are significantly higher at all ages than strengths

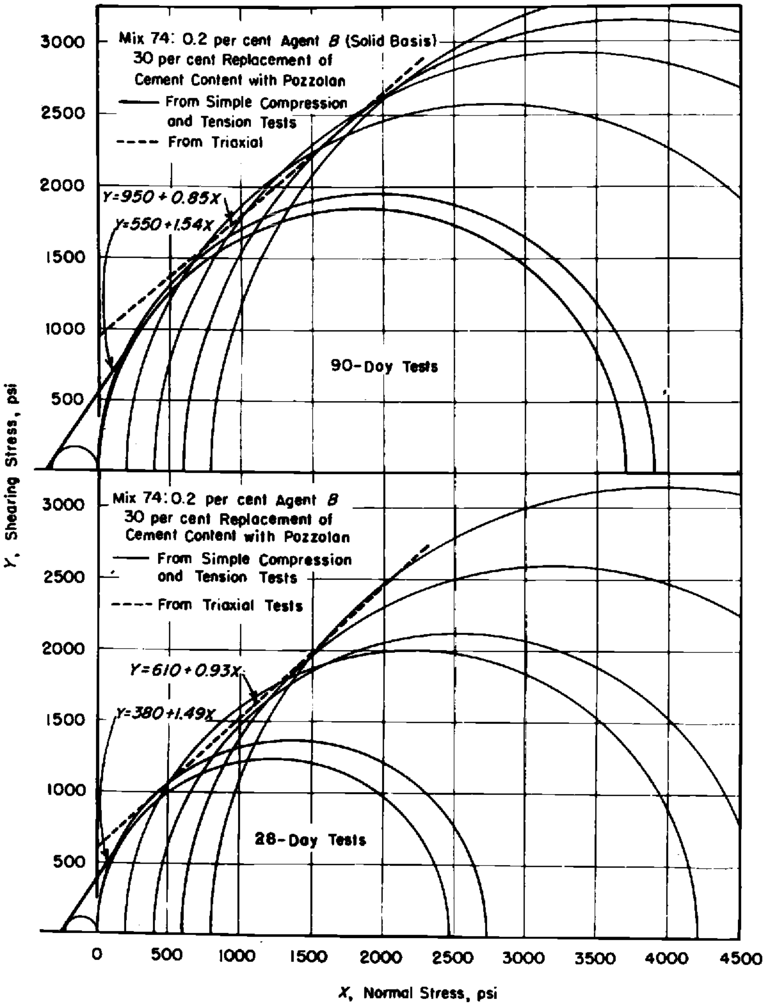


FIG. 24.—Comparison of Shearing Relationships Obtained from Triaxial Tests and from Simple Compression and Tension Tests.

of companion control cylinders. This is true for concrete proportioned with 2½, 3, and 3½ sacks total cementitious materials with 0, 20, 33, and 43 per cent pozzolan replacements. Figure 17 shows the relationship between compressive strength and quantity of lignin agent in concrete made with Glen Canyon materials. Results of 28-day tests on 18 by 36-in. cylinders indicate that 0.35 lb (that is, 0.37 per cent) of agent per sack of cement produced the maximum compressive strength in mass concrete made with these materials. However, the compressive strength was only slightly lower for concrete containing 0.50 lb of agent per sack of cement. Furthermore, this quantity of agent did not produce an objectionable amount of retardation. A greater amount of lignin agent per cu yd of mass concrete is required for optimum results than would be required by structural concrete.

Comparison of the effects of lignin agent on mixes with and without pozzolans, shown in Fig. 16, indicates that the agent was more effective in producing strength increases in the concretes containing pozzolan. Figure 18 was prepared to quantify the activating influence of lignin agents on pozzolans. Compressive strength test results of both 18- by 36-in. and 6- by 12-in. cylinders show that agent-induced strength gains are greater for concretes containing increasing amounts of pozzolan up to a maximum amount of 33 per cent.

The data portrayed graphically in Fig. 13 and tabulated in Table VIII indicate that significant and lasting benefits are derived by use of lignin agents in mass concrete. Are the tangible benefits worth more than the cost of the agent? It should be obvious to the admixture producer that his customer will not be interested in purchasing a *WR* agent unless a net gain is realized when cement and other savings are balanced against the expenses encountered in purchasing, storing, handling, and dispensing the agent and in processing extra aggregates to compensate for the reduced volume of water and cement. *WR* agents provide extra time for concrete surface finishing, but this is not an important factor in constructing massive concrete blocks. Agents assist in preventing the formation of cold joints, but these can usually be avoided without retardation by careful scheduling and provision of extra equipment and labor. However, in many cases, the added period of workability imparted by a retarding agent does permit savings in equipment and labor cost. If these savings balance the cost of handling, storing, and dispensing an agent, and if slight cement reduction will pay for the cost of the agent and costs of additional aggregates, then the consumer may, at no increased cost, obtain a higher strength, better quality concrete. These factors will no doubt be considered by all parties concerned in deciding whether or not a *WR* agent will be used in mass concrete for future construction of multimillion cubic yard structures.

The possibility of obtaining both cement reduction and higher quality concrete is indicated by tests performed with Glen Canyon materials. In these tests, the addition of a lignin agent more than offsets the strength diminishing effect of a 5 per cent cement reduction. The 28-day compressive strength of 18 by 36-in. cylinders containing lignin agent and 5 per cent less cement exceeded that of the control cylinders by 22 per cent. Results of tests on companion 6 by 12-in. cylinders shown in Fig. 19 indicate a corresponding strength increase of 10 to 15 per cent. In the case under consideration, it is estimated that the 5 per cent savings in cost of cement will equal the cost of the agent and the extra aggregate. In some cases, the cost of handling, storing, and dispensing agents may be offset by savings realized in handling and placing the concrete. A *WR* agent was approved and used in the tunnel concrete at Glen Canyon Dam. Here, the cost of handling, storing, and dispensing the *WR* agent used in the tunnel lining was largely borne by the contractor, and the cost of the agent was borne by the Government.

Figures 20 and 21 depict the influence of lignin agents on the compressive strength of mass concrete made with materials tested in connection with Flaming Gorge Dam. Here again, without exception, significant individual increases in compressive strength were obtained by use of the agents, the average gain being 25 per cent.

Field Control Tests.—Although their permanent benefits have been shown through laboratory tests, *WR* agents have not as yet been required in specifications for Bureau of Reclamation construction. Two steps must be taken to establish the necessary confidence for specifying use of these agents in construction contracts. First, field experience must verify that the benefits obtained in the laboratory can be duplicated in the field. Second, a specification is needed to permit an evaluation of agents supplied on the job against acceptable standards. Advancements are being made toward the fulfillment of these needs.

Results of field control tests comparing concretes with and without *WR* agents are summarized in Table X. Average water and cement reduction obtained by using *WR* agents on the four projects referred to in the table was about 8 per cent. The mean of each project average revealed that compressive strength of specimens made with *WR* agents was 5 per cent greater than that of the control specimens. The cement reduction of 9 per cent used for Glen Canyon tunnel lining concrete containing a *WR* agent was somewhat excessive since the average compressive strength of specimen representatives of this concrete was below that of the control specimens. Coefficients of variation shown in the table indicate that the addition of *WR* agents does not prevent production of uniform concrete. The coefficient of variation of 9.8 per cent for the 186 specimens, tested at 28 days' age over a period of approximately 1 yr during the construction of Glen Canyon Dam tunnel lining, is considered to be excellent.

Results of field control tests and mix data for mass concretes, with and without a lignin agent, placed at Anchor Dam, Wyo., are shown in Table XIII. The downstream half of a 375-cu-yd block of mass concrete was placed with the control concrete and the upstream half with concrete containing agent *G*. The agent concrete was designed for a 5 per cent cement reduction, but due to low air content in the resulting concrete, a reduction of only 2½ per cent occurred. With this reduction and low air content, agent-induced compressive strength gains of 29, 41, and 32 per cent were obtained for specimens tested at 7, 28, and 90 days of age, respectively.

TABLE XIII.—ANCHOR DAM—FIELD TRIALS OF LIGNIN-TYPE WATER-REDUCING RETARDING AGENT IN MASS CONCRETE.

6-in. maximum-size aggregate

Mix Data	Control Mix	Lignin Mix (Agent *G*)
Water, lb per cu yd....	174	166
Cement, lb per cu yd..	287	280
Sand, per cent........	23	22
TESTS ON FRESH CONCRETE		
Air content (minus 1½-in. fraction).....	5.0	3.8
Slump, in.............	1¾	2.0
Temperature, deg Fahr	48	42
COMPRESSIVE STRENGTHS, PSI		
2-day..............	620	680
7-day..............	1800	2330
28-day..............	3250	4600
90-day..............	4260	5610
DURABILITY		
Cycles of freezing and thawing...........	300	300
Weight loss (6 by 12-in. cylinders)........	No appreciable loss in weight from either control or agent specimens	

Workability and Retardation.—Good workability was maintained with both mixes. Aided by cool temperatures, the control mix did not reach the vibration limit for approximately 7 hr. Vibration limit of lignin mix was at about 9 hr. No difficulty was encountered from increased form pressures or early stripping of forms.

Tensile Strength:

Tensile strengths, listed in Table VII, for standard briquets and 6 by 12-in.

cylinders fabricated from concretes containing $\frac{3}{4}$-, $1\frac{1}{2}$-, 3-, and 6-in. aggregates; 20 and 30 per cent pozzolan; and 0.2 per cent agents B, C, and D, are plotted on Fig. 22. A $w/c + p$ ratio of 0.55 was maintained except for the mass mixes where the $w/c + p$ ratio varied from 0.57 to 0.64. Tensile strength as shown by the results of tests on 6 by 12-in. cylinders was, in general, equal or greater for the specimens containing agents B, C, and D than for control specimens without these admixtures at all test ages and for all maximum size aggregates. Tensile strength values for briquet specimens were erratic with no definite trend resulting. However, the general trend of all tests indicates that the concretes containing agents generally develop equal or greater tensile strengths than similar concretes without the agents.

Shearing Strength:

Shearing strength relationships for concretes containing various maximum size aggregates and pozzolan replacements are shown in Table XIV and Fig. 23. These are linear relationships determined from results of simple compressive and tensile strength tests of unconfined specimens having a constant $w/c + p$ ratio. This method is generally used when triaxial compressive strength data are not available. Shearing relationships are more comprehensively determined by triaxial compression tests from which Mohr's diagrams are plotted, as shown in Fig. 24. This figure shows a comparison of shearing relationships determined by both methods for specimens wet screened from mass concrete containing a lignin agent. It can be seen that the shearing relationships determined by the tangents to the unconfined tension and compression circles are somewhat different than those derived from Mohr's envelopes constructed from the triaxial shear tests. The true shearing relationships are curvilinear, whereas both of the above methods produce linear expressions. True cohesive strength of concrete lies between the values obtained from the triaxial and unconfined tests.

Generally, the shearing stress at zero normal stress was greater for specimens containing agents B, C, and D than for the control specimens.

DURABILITY

A fundamental principle in concrete mix design pertains to the fact that, in addition to having suitable strength, the concrete must be so proportioned that it will adequately withstand the destructive forces of freezing and thawing, wetting and drying, and attack by sulfate salts contained in the water or soil in contact with the concrete.

To evaluate the ability of concretes containing *WR* agents to resist these destructive forces, specimens were subjected to accelerated tests in the laboratory; these tests simulated the cyclic variations in weathering as well as exposure to sulfate-bearing soils.

Effect on Void Parameters:

Microscopic examinations of void systems were made on sections of 6 by 12-in. cylinders representing concretes incorporating air-entraining agents derived from a sodium salt of processed resin and a sodium and potassium soap of wood resin, to compare with air-entrainment accomplished by lignin-type retarding agent C (3). Void systems of concretes employing the air-entraining agents alone are characterized by small bubbles (specific surfaces 851 and 1081 in.$^{-1}$) and excellent spacing factors ($\bar{L}$ of 0.0052 and 0.0047 in.), as shown in Table XV.

Concretes in which air was entrained by the lignin-type retarding agent contained voids of moderate size (specific surfaces 702 and 635 in.$^{-1}$). These moderate size voids have also been encoun-

TABLE XIV.—SHEARING STRENGTH RELATIONSHIPS—SERIES III—MONTICELLO DAM.

Age, days	Mix	Compressive Strength, psi, average of 2	Tensile Strength, psi, average of 3	Shearing Strength, Relationships	Agent	
					Per cent	Type
Concretes Containing ¾-in. Aggregate						
3........	No. 62	910	101	$Y = 150 + 1.33X$	none	...
3........	No. 63	875	107	$Y = 150 + 1.25X$	0.2	*C*
3........	No. 64	1030	118	$Y = 175 + 1.31X$	0.2	*D*
7........	No. 62	1405	139	$Y = 220 + 1.43X$	none	...
7........	No. 63	1460	160	$Y = 240 + 1.34X$	0.2	*C*
7........	No. 64	1660	145	$Y = 245 + 1.54X$	0.2	*D*
29........	No. 62	3615	258	$Y = 480 + 1.74X$	none	...
29........	No. 63	3510	249	$Y = 465 + 1.74X$	0.2	*C*
29........	No. 64	4025	278	$Y = 530 + 1.77X$	0.2	*D*
90........	No. 62	4080	318	$Y = 570 + 1.65X$	none	...
90........	No. 63	3935	362	$Y = 595 + 1.50X$	0.2	*C*
90........	No. 64	4865	362	$Y = 665 + 1.70X$	0.2	*D*
Concretes Containing 1½-in. Aggregate						
3........	No. 65	980	92	$Y = 150 + 1.48X$	none	...
3........	No. 66	820	112	$Y = 150 + 1.17X$	0.2	*C*
3........	No. 67	940	115	$Y = 165 + 1.25X$	0.2	*D*
7........	No. 65	1500	149	$Y = 240 + 1.43X$	none	...
7........	No. 66	1245	148	$Y = 215 + 1.28X$	0.2	*C*
7........	No. 67	1450	156	$Y = 240 + 1.36X$	0.2	*D*
29........	No. 65	3740	237	$Y = 470 + 1.86X$	none	...
29........	No. 66	3095	265	$Y = 455 + 1.56X$	0.2	*C*
29........	No. 67	3370	279	$Y = 485 + 1.59X$	0.2	*D*
90........	No. 65	4215	332	$Y = 590 + 1.64X$	none	...
90........	No. 66	3915	322	$Y = 560 + 1.60X$	0.2	*C*
90........	No. 67	4230	293	$Y = 555 + 1.77X$	0.2	*D*
Concretes Containing 3-in. Aggregate						
3........	No. 68	805	98	$Y = 140 + 1.26X$	none	...
3........	No. 69	790	101	$Y = 140 + 1.22X$	0.2	*C*
3........	No. 70	875	100	$Y = 150 + 1.31X$	0.2	*D*
7........	No. 68	1325	143	$Y = 220 + 1.36X$	none	...
7........	No. 69	1275	135	$Y = 205 + 1.37X$	0.2	*C*
7........	No. 70	1470	130	$Y = 220 + 1.53X$	0.2	*D*
28........	No. 68	3530	245	$Y = 465 + 1.77X$	none	...
28........	No. 69	3340	262	$Y = 470 + 1.65X$	0.2	*C*
28........	No. 70	3165	273	$Y = 465 + 1.56X$	0.2	*D*
91........	No. 68	4020	298	$Y = 545 + 1.70X$	none	...
91........	No. 69	4210	328	$Y = 590 + 1.65X$	0.2	*C*
91........	No. 70	4730	318	$Y = 615 + 1.80X$	0.2	*D*
Concretes Containing 6-in. Aggregate						
3........	No. 71	400	21	$Y = 45 + 2.07X$	none	...
3........	No. 72	525	78	$Y = 100 + 1.10X$	0.2	*C*
3........	No. 73	460	72	$Y = 90 + 1.07X$	0.2	*D*
7........	No. 71	785	52	$Y = 100 + 1.81X$	none	...
7........	No. 72	960	110	$Y = 160 + 1.31X$	0.2	*C*
7........	No. 73	810	100	$Y = 140 + 1.25X$	0.2	*D*
28........	No. 71	2325	178	$Y = 320 + 1.67X$	none	...
28........	No. 72	2635	207	$Y = 370 + 1.64X$	0.2	*C*
28........	No. 73	2580[a]	237	$Y = 390 + 1.50X$	0.2	*D*
28........	No. 74	2470	230	$Y = 380 + 1.49X$	0.2	*B*
91........	No. 71	3260	112	$Y = 300 + 2.61X$	none	...
91........	No. 72	3810	308	$Y = 540 + 1.62X$	0.2	*C*
91........	No. 73	3800	343	$Y = 570 + 1.51X$	0.2	*D*
90........	No. 74	3710	325	$Y = 550 + 1.54X$	0.2	*B*
Triaxial Series						
28........	No. 74	...	...	$Y = 610 + 0.93X$	0.2	*B*
90........	No. 74	...	...	$Y = 950 + 0.85X$	0.2	*B*

[a] One test only.

tered in other tests, not reported herein. Spacing factors of 0.0053 and 0.0063 in. compare favorably to spacing factors created by the air-entraining agents, despite the moderate size of the average entrained bubble.

Studies of void characteristics were also made for Glen Canyon Dam and Flaming Gorge Dam concretes with pozzolans and with and without *WR* agents. In these concretes, small amounts of air-entraining agents were used with the *WR* agents; hence, void characteristics reflect this combination rather than the individual *WR* agent, as was the case in the first group of mixes reported above. Spacing factors for these concretes were but slightly greater than for concretes containing air which was entrained by use of an air-entraining agent alone. The difference is not considered significant.

TABLE XV.—SUMMARY OF VOID CHARACTERISTIC STUDIES.

Mix	Mix Data								Void Characteristics					
	Agent, per cent, type	Water-cement ratio	Cementitious Materials, lb per cu yd	Water, lb per cu yd	Slump, in.	Sand, per cent	Air Content, air meter	Paste Content, per cent by volume	Air Content, per cent	Average Chord Intercept, in.	Specific Surface, in.$^{-1}$	Number of Voids Intercepted, per in.	Paste-Air Ratio	Spacing Factor, $\bar{L}$, in.
VOID CHARACTERISTIC MIXES														
No. I[a]......	none	0.50	493	247	3.0	36	5.4	23.87	4.8	0.0047	851	10.158	4.97	0.0052
No. II......	0.3, *C*	0.50	433	217	1.5	36	5.7	20.97	5.7	0.0057	702	9.474	3.70	0.0053
No. III[b].....	none	0.50	500	250	2.7	36	4.7	24.18	4.0	0.0037	1081	10.810	6.04	0.0047
No. IV......	0.3, *C*	0.50	436	218	2.4	36	5.5	21.08	5.2	0.0063	635	8.206	4.06	0.0063
FLAMING GORGE DAM														
No. 96......	none	0.54	285	154	2.0	20	5.1	26.09	5.39	0.0041	976	13.161	4.84	0.0047
No. 97......	0.37, *G*	0.50	284	142	2.6	20	4.8	25.38	3.95	0.0039	1026	10.045	6.43	0.0050
GLEN CANYON DAM														
No. 98......	none	0.51	331	169	2.0	20	4.4	23.59	4.04	0.0039	1026	10.372	5.84	0.0048
No. 99......	0.37, *G*	0.46	338	152	1.9	20	4.5	21.79	3.69	0.0042	952	8.791	5.91	0.0053
No. 100......	none	0.56	284	159	2.1	20	4.2	22.08	6.46	0.0050	800	12.991	3.42	0.0042
No. 101......	0.37, *G*	0.49	286	140	2.0	20	3.9	20.77	5.19	0.0062	645	8.331	4.00	0.0062
No. 110......	none	0.67	237	159	2.1	20	4.7	22.57	5.14	0.0047	851	10.844	4.39	0.0051
No. 111......	0.37, *G*	0.61	238	145	2.2	20	4.7	21.35	5.25	0.0051	784	10.329	4.07	0.0052

[a] Air-entrained with neutral sodium salt of processed resins.
[b] Air-entrained with sodium and potassium soaps of wood resins.

Freezing and Thawing:

Results of freezing-and-thawing tests for the various concretes made in connection with investigations for Gross, Kirwin, Monticello, Glen Canyon, Flaming Gorge Dams, and Ainsworth canal are shown in Table XVI. Comparable specimens having approximately the same cement and air content, with and without *WR* agents, were subjected to freezing-and-thawing tests. The measure of concrete resistance to freezing and thawing is the number of cycles to which the concrete is subjected to obtain a weight loss of 25 per cent, based on the original weight. Eighty-eight per cent of the specimens containing *WR* agents which received 28 days' standard (fog) curing proved more resistant to freezing and thawing than companion control

TABLE XVI.—RESUME OF FREEZING-THAWING TEST RESULTS.

Mix	Water-Cement Ratio	Agent		Pozzolan, per cent	Cycles of Freezing-and-Thawing to 25 per cent Weight Loss	
		Per cent	Type		28-day fog cure	14-Day Fog plus 76-Day 50 per cent Relative Humidity
Ainsworth Canal—4 Sacks Cementitious Materials—M-1700						
No. 59	0.51[a]	0	...	0	570	780
No. 60	0.53[a]	0.2	*G*	0	750	720
No. 61	0.52[a]	0.4	*G*	0	930	850
Monticello Dam—2½ Sacks Cementitious Materials—M-2005 and M-2017						
No. 74	0.57	0.2	*B*	30	620	580
Monticello Dam—3 Sacks Cementitious Materials—M-2005, M-2017, and M-1236						
No. 75	0.50	...	...	0	1180	2900
No. 76	0.53	...	...	30	650	530
No. 77	0.44	0.1	*A*	0	1540	2830
No. 78	0.50	0.1	*A*	30	960	620
No. 79	0.43	0.1	*A*	30[b]	1490	2050
Kirwin Dam—3 Sacks Cementitious Materials—M-1779						
No. 80	0.58	0	...	0	270	...
No. 81	0.52	0.25	*L*	0	430	1050
No. 82	0.50	0.20	*A*	0	350	490
Gross Dam—2½ Sacks Type I Cement—M-1219						
No. 83	0.66	0	...	0	210	1070
No. 84	0.62	0.2	*A*	0	430	1640
Flaming Gorge Dam—3 Sacks Cementitious Materials—M-3389 and M-3364						
No. 96	0.54	0	...	33.3	630	410
No. 97	0.50	0.37	*G*	33.3	670	440
Glen Canyon Dam—3½ Sacks Cementitious Materials—M-3100 and M-3337						
No. 98	0.51	0	...	42.8	550	320
No. 99	0.46	0.37	*G*	42.8	1020	410
Glen Canyon Dam—3 Sacks Cementitious Materials—M-3100 and M-3337						
No. 100	0.56	0	...	33.3	800	400
No. 101	0.49	0.37	*G*	33.3	860	540
Glen Canyon Dam—2½ Sacks Cementitious Materials—M-3100 and M-2942B						
No. 104	0.64	0	...	0	600	900
No. 105	0.60	0.27	*G*	0	660	800
No. 106	0.56	0.54	*G*	0	450	450
No. 107	0.66	0	...	20	530	590
No. 108	0.63	0.27	*G*	20	530	710
No. 109	0.61	0.54	*G*	20	590	810
No. 110	0.67	0	...	20	360	230
No. 111	0.61	0.37	*G*	20	460	250

[a] Water-cement ratios are uncertain because of the highly absorptive aggregate.

[b] Fly ash used as pozzolan.

specimens without agents. The average resistance of agent concretes was 39 per cent greater than that of the control specimens.

The ability of a *WR* agent to provide improved resistance to freezing-and-thawing forces is particularly important in the pozzolan concretes. Here, the net effect is to partially offset the reduction in freezing-and-thawing resistance that occurs when pozzolan is substituted for part of the cement. This might permit use of pozzolan to reduce heat or neutralize effects of aggregate reaction, sulfate attack, or acid attack, when fear of diminishing resistance to freezing and thawing might otherwise void its use.

Control specimens for Kirwin Dam studies, containing crushed aggregates, and control specimens for Gross Dam interior concrete, containing type I cement, had low resistance to freezing and thawing after 28 days' fog curing (less than 300 cycles produced 25 per cent weight loss). Addition of *WR* agents to these mixes increased their resistance, raising them into the satisfactory category (above 300 cycles).

Durability specimens for the Ainsworth Canal investigation were made with marginal aggregates having high absorption values, but the addition of 0.4 per cent agent *G* increased the resistance to freezing and thawing of 28-day fog-cured specimens 63 per cent, compared to control specimens.

There is no established correlation between the results obtained on the 28-day standard-cured specimens and those subjected to 14-day standard cure plus 76 days at 50 per cent relative humidity. The average resistance for the latter cured specimens containing *WR* agents was 31 per cent greater than that of the control specimens, with 4 tests of 14 falling below the resistance exhibited by their respective controls.

The agent-induced increase in resistance to freezing-and-thawing forces may be attributed in large part to reduced water-cement ratio, resulting from the water-reducing ability of the *WR* agents. If the quantity of cementitious materials were reduced to maintain a ratio of water to cementitious material equal to that of the control mix, the resistance to freezing-and-thawing forces would probably be reduced accordingly.

Resistance to Sulfate Attack:

Tests to determine resistance to sulfate attack of concretes made for the Kirwin, Gross, and Monticello Dam investigations are reported in Table XVII. There is also shown the resistance to sulfate attack of concretes reported in Table *D* of the authors' closure to Tuthill and Cordon's paper (4).

Results indicate that agents improve the resistance of concrete to sulfate attack in most cases, the exception being the mass mixes of the Gross Dam investigation. Here, both the agent and control concretes with type I cement had but little resistance to sulfate attack. It should be noted that many of the tests referred to in Table XVII are not complete; that is, the specimens have not yet reached 0.5 per cent expansion.

VOLUME CHANGE

Volume change in this paper refers to expansion and contraction of hardened concrete as a result of wetting and drying.

Drying shrinkage was determined on 4 by 4 by 30-in. prisms fabricated from the minus $1\frac{1}{2}$-in. fraction of mass concrete and dried at 50 per cent relative humidity and 73.4 F.

Autogenous volume change was determined on sealed 18 by 36-in. cylinders containing the full mass mix.

Drying Shrinkage:

Results of drying shrinkage tests performed on concrete with and without

WR agents are shown in Table XVIII and Fig. 25. The range of drying shrinkage at 1-yr age varied from 390 millionths for concrete containing limestone aggregates, agent *L*, and no pozzolan, to a maximum of 998 millionths for concrete without a *WR* agent but containing diatomaceous clay, a known contributor to high shrinkage.

TABLE XVII.—RESISTANCE TO SULFATE ATTACK.

Mix	Remarks	Accelerated Test			
		0.2 per cent expansion		0.5 per cent expansion	
		Cycles	Reduction in E, per cent	Cycles	Reduction in E, per cent
KIRWIN DAM					
No. 80	no agent, control	226	18.4	332	57.6
No. 81	0.25 per cent agent *L*	324	20.4	449	61.9
No. 82	0.2 per cent agent *A*	354	18.7	485	47.0
GROSS DAM					
No. 83	no agent, control	46	6.8	65	21.6
No. 84	0.2 per cent agent *A*	43	10.2	57	25.9
MONTICELLO DAM					
No. 75	no pozzolan, no agent, control	1150	31.8	1725[a]	...
No. 76	30 per cent pozzolan, no agent	310	60.0	554	+90.0
No. 77	no pozzolan, agent *A*	780	18.5	1746[a]	...
No. 78	pozzolan, agent *A*	495	58.8	760	+76.0
No. 79	fly ash, agent *A*	1752[a]	50.0	...	...
PPT SERIES					
No. 8	no agent, control	523	10.0	1480	...
No. 5	0.3 per cent agent *G*	550	6.7	1270	26.1
No. 6	0.6 per cent agent *C*	550	6.5	1120	20.7
No. 7	0.25 per cent agent *D*	660	8.4	1430[a]	...
No. 16	no agent, control	690	6.1	1385[a]	...
No. 12	0.2 per cent agent *D*	662	4.3	1385[a]	...
No. 13	0.3 per cent agent *D*	600	7.2	1385[a]	...
No. 14	0.4 per cent agent *D*	895	7.1	1385[a]	...
No. 15	0.5 per cent agent *D*	720	14.3	1385[a]	...

[a] Cycles to present without expanding to that indicated by the column heading.

Drying shrinkage tests were performed on concretes with 1½-in.-maximum-size, marginal aggregates from the Ainsworth project, with and without agent *G*. Concrete containing 0.2 per cent agent had slightly less shrinkage at 1-yr age (618 millionths) than did the control concrete (661 millionths).

Concretes containing materials for Monticello Dam, including diatomaceous clay pozzolan, experienced excessive shrinkage when made with and without *WR* agents. However, the specimens with agents *A* and *B* did experience slightly less shrinkage at 1-yr age (967 millionths and 927 millionths, respectively) than did the control specimens (998 mil-

TABLE XVIII.—RESULTS OF DRYING SHRINKAGE TESTS.

Project	Glen Canyon Dam[b]					Ainsworth Canal			Monticello Dam						Kirwin Dam	
Mix	DS1	DS2	DS3	DS4	DS5	No. 59	No. 60	No. 61	No. 75	No. 6	No. 77	No. 78	No. 79	No. 74	No. 82	No. 81
Pozzolan, per cent	33	33	33		33	0	0	0	0	30	0	30	30[a]	30	0	0
Agent, per cent	none	0.37	0.37	0.25	0.25	none	0.2	0.4	0.0	0.0	0.1	0.1	0.1	0.2	0.2	0.25
Type	...	*G*	*G*	*D*	*D*	...	*G*	*G*	...	...	*A*	*A*	*A*	*B*	*A*	*L*
Days Drying	Drying Shrinkage—4 by 4 by 30-in. prisms, millionths															
3	90	90	95	85	90	85	100	100	155	180	140	110	73	90	60	45
7	152	152	137	128	134	175	193	197	220	295	235	257	160	220	110	95
14	217	212	201	188	196	285	300	310	320	408	340	397	278	363	165	157
28	303	282	282	262	277	436	435	425	450	538	470	520	413	530	230	235
90	411	381	396	363	375	607	575	561	687	790	695	755	610	780	350	337
180	...	...	...	...	...	637	600	587	793	920	762	892	695	863	395	375
270	...	...	...	...	...	657	614	600	822	970	790	916	723	897	410	390
365	...	...	...	...	...	661	618	607	837	998	795	967	743	927	420	390

[a] Fly ash.

[b] Special series, mix data in Table XIX.

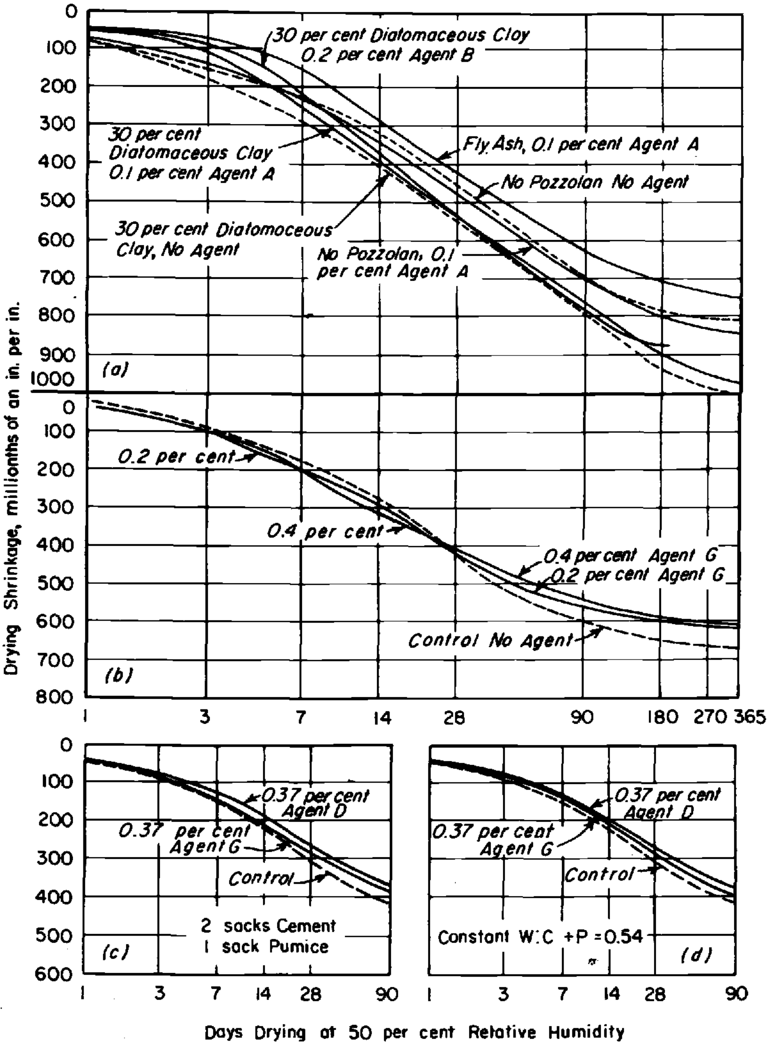
lionths). Shrinkage of concrete without pozzolan was similarly reduced by use of agent *A*.

Drying shrinkage test results for Kirwin Dam investigations, in which agents *A* and *L* were used in mass concrete containing crushed limestone aggregates, are shown in Table XVIII without control data for comparison. One-year shrinkage values for these concretes are 420 millionths and 390 millionths, respectively; this is very close to the average shrinkage of 410 millionths reported by Troxell and Davis (5) for concretes containing limestone aggregates.

A series of tests was made for the specific purpose of studying the effect of lignin and hydroxylated carboxylic acid agents upon drying shrinkage when used with Glen Canyon Dam materials. These mixes were made with agent *G* and agent *D*; each agent was used in a mix at a constant $w/c + p$ ratio and in a mix with a constant cementitious materials factor. Mix designs were identical to those of mixes 100 and 101 (Tables VIII and IX); but, to avoid disruptive effects of wet screening mass concrete, the plus $1\frac{1}{2}$-in. material was not batched. The actual mix quantities per cubic yard of the resulting concrete are presented in Table XIX.

TABLE XIX.—DRYING SHRINKAGE MIXES.

Mix	Agent		Air Entraining Agent, ml	Water, lb	Cement, lb	Pozzolan, lb	Sand, lb	Gravel, lb
	Per cent	Type						
DS-1	none	...	742	218	372	124	965	2266
DS-2	0.37	*G*	448	197	366	121	992	2225
DS-3	0.37	*G*	359	198	337	111	1039	2237
DS-4	0.25	*D*	850	199	369	122	988	2245
DS-5	0.25	*D*	754	198	337	113	1030	2234



(*a*) Monticello Dam—mass concrete wet screened to 1½-in. maximum size aggregate—type II cement M-2005—diatomaceous clay M-2017.

(*b*) Ainsworth canal studies—river sand M-2331—1½-in. maximum coarse aggregate—40 per cent crushed, 60 per cent rounded—type II cement M-1700.

(*c*) and (*d*) Glen Canyon Dam—designed as mass mix—plus 1½-in. aggregates not batched—type II cement M-3329—33 per cent pozzolan M-3439.

FIG. 25.—Drying Shrinkage of 4 by 4 by 30-in. Concrete Beams with and Without Lignin Type Agents.

Results of drying shrinkage tests of these concretes, plotted on Fig. 25, indicate that *WR* agents have no detrimental effect; on the other hand, they do not offer significant reduction of drying shrinkage.

Autogenous Volume Change:

Autogenous volume changes of 18 by 36-in. cylinders for the Monticello Dam investigation are reported in Table XX and shown graphically on Fig. 26. The

TABLE XX.—SERIES III—RESULTS OF AUTOGENOUS LENGTH CHANGE TESTS.
Mass Concrete—Monticello Dam

Mix[a]	No. 75	No. 76	No. 77	No. 78	No. 79	No. 74
Pozzolan, per cent	none	30	none	30	30[b]	30
Agent, per cent	none	none	0.1	0.1	0.1	0.2
Type agent	...	...	*A*	*A*	*A*	*B*
Age in days	Autogenous length change on 18- by 36-in. cylinders, millionths					
1	0	0	0	0	0	0
3	+1	+2	+3	+7	+8	+38
7	+8	+3	+9	+4	+29	+41
14	+14	+17	+7	−6	+18	+28
28	+8	+6	+4	−39	−4	+20
36	0	0	0	0	0	0
90	−6	−15	−2	−12	−2	−1
180	−12	−23	−7	−14	−7	−14
270	−20	−29	−16	−21	−14	−8
365	−29	−38	−20	−20	−21	−11
1½ yr	−29	−36	−25	−31	−29	−24
2 yr	−31	−38	−27	−33	−33	−29
3 yr	−33	−41	−26	−34	−41	−33
4 yr	−33	−41	−26	−34	−45	−33
5 yr	−30	−44	−27	−36	−48	−25

[a] All concrete contained 3 sacks cementitious material per cu yd except mix No. 74, which contained 2½ sacks.

[b] Mix No. 79 contained 30 per cent fly ash in lieu of calcined diatomaceous clay.

Readings 1 through 28 days were movements occurring during field cycle curing. Specimens were reaching stable temperature during period from 28 to 36 days. Thirty-six-day readings taken as new zero.

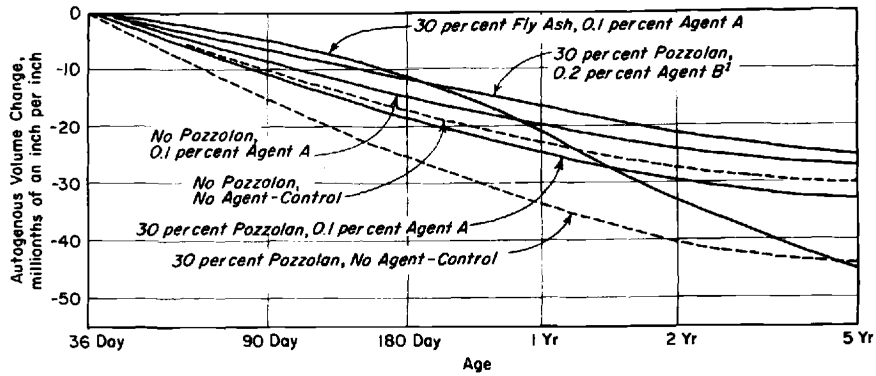


FIG. 26.—Influence of Lignin Agents on Autogenous Volume Change of Mass Concrete, Monticello Dam.

Cache Creek aggregate—6-in. maximum size—18 by 36-in. cylinders—field cycle cured 28 days—3 sacks cementitious materials—cement M-2017—pozzolan M-2005—fly ash M-1236.

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[1] Exception 2½ sacks cementitious materials.

sealed specimens were subjected to a 28-day field temperature cycle and then stored at 73 F. After reaching a stable temperature, autogenous length change measurements were initiated at 36 days' age and continued for a period of approximately 5 yr.

Autogenous volume changes were less

for concretes containing agent *A* than for the control concretes, whether or not the latter contained pozzolan.

Concrete containing 2½ sacks cementitious material, including 30 per cent calcined diatomaceous clay, and 0.2 per cent agent *B* had the smallest autogenous volume change at 5 yr of all the concretes tested. The largest change at this age was registered by a concrete containing 30 per cent fly ash, 3 sacks total cementitious materials, and 0.1 per cent agent *A*. Tests were not made on a control concrete in this case; therefore, the exact effect of the agent is unknown.

Adiabatic Temperature Rise

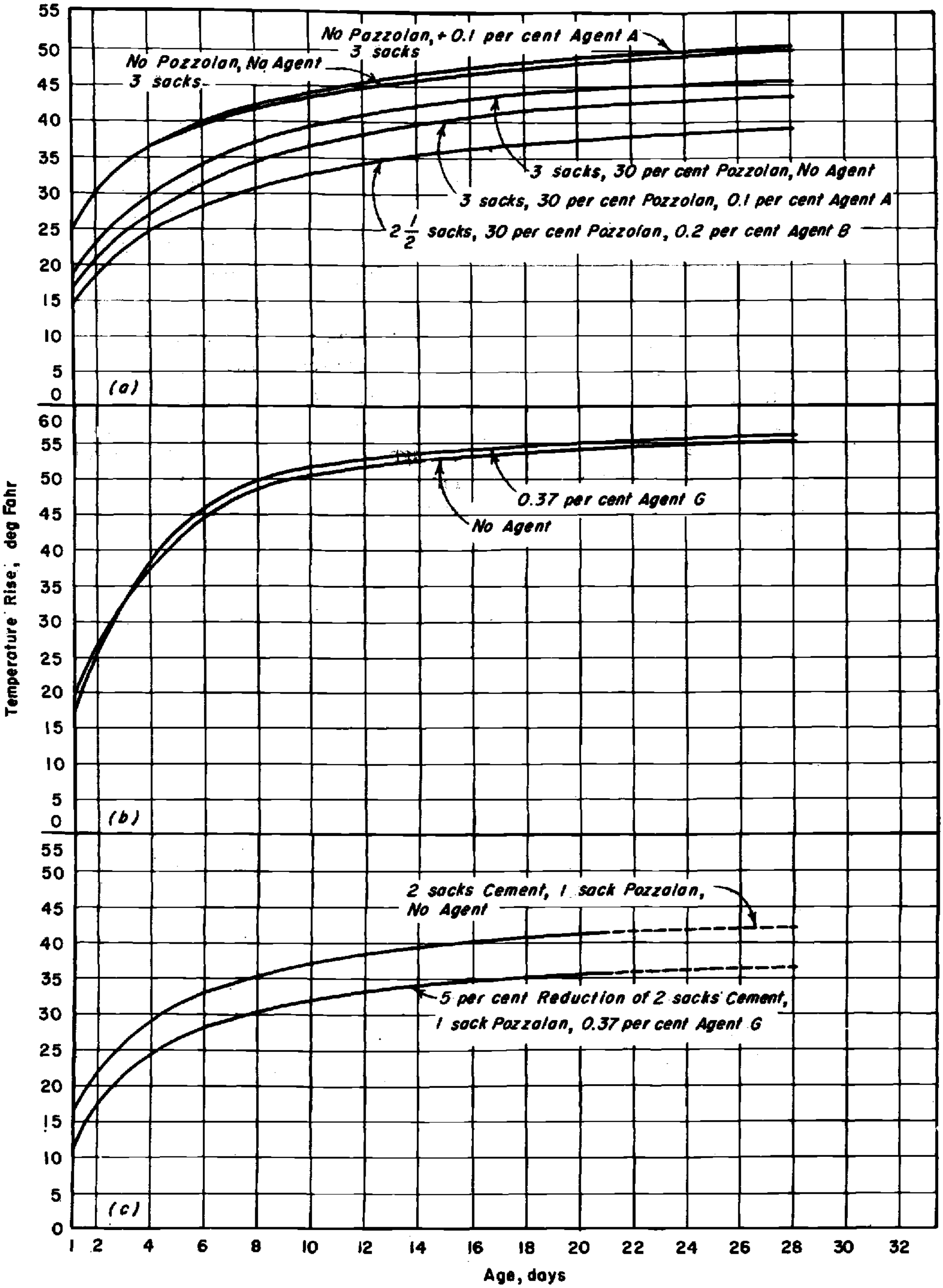
The effects of *WR* agents on temperature rise of mass concretes were investigated by adiabatic temperature rise tests conducted for periods of 28 days using materials from Monticello, Glen Canyon, and Flaming Gorge Dams. Results of these tests are shown in Table XXI and Fig. 27. These graphs serve to illustrate the effect of retarding agents on temperature rise of the test concretes by indicating temperature increases throughout the test period.

TABLE XXI.—EFFECT OF WATER-REDUCING AGENTS ON TEMPERATURE RISE OF MASS CONCRETES, deg Fahr.—SERIES III.

Mix	Agent		Age, days					Remarks
	Per cent	Type	1	3	7	14	28	
Monticello Dam—3 Sacks per cu yd								
No. 75	none	...	24.0	33.7	40.8	45.5	49.8	no pozzolan
No. 76	none	...	18.0	26.6	35.6	41.9	45.4	30 per cent pozzolan
No. 77	0.1	*A*	23.5	34.2	41.9	46.6	50.2	no pozzolan
No. 78	0.1	*A*	16.2	24.2	32.8	39.4	43.2	30 per cent pozzolan
No. 79	0.1	*A*	16.3	25.3	30.6	36.5	42.1	30 per cent fly ash
Monticello Dam—2½ Sacks per cu yd								
No. 74	0.2	*B*	14.3	22.0	28.8	35.1	38.7	30 per cent pozzolan
Glen Canyon Dam—3 Sacks per cu yd								
No. 102	none	...	19	33	47	52	55	no pozzolan
No. 103	0.37	*G*	16	33	48	53	56	no pozzolan
Flaming Gorge Dam—3 Sacks per cu yd								
No. 96	none	*G*	20.8	31.6	39.3	44.2	47.2	33.3 per cent pozzolan
[a]	0.37	*G*	15.3	26.7	34.4	38.9	41.7	

[a] Similar to mix No. 96 with 5 per cent less cementitious materials.

Figure 27 shows that, compared to control concrete, agent concretes with pozzolan exhibited a small decrease in temperature rise, whereas, those without the pozzolan showed a small increase in temperature rise. An examination of Table XXI shows that agent concrete containing fly ash exhibited less temperature rise beyond 7 days of age than any other concrete containing 3 sacks of cementitious material. A maximum difference of 8.1 F was reached in 28 days of age (compare mix No. 77 and mix No.



(*a*) Monticello Dam—6-in. maximum aggregate—cement type II M-2005—pozzolan M-2017.

(*b*) Glen Canyon Dam—6-in. maximum size Wahweap Creek aggregate—3 sacks type II cement M-3100.

(*c*) Flaming Gorge Dam—6-in. maximum size Henry's Fork aggregate—2 sacks type II cement M-3471—1 sack calcined shale M-3431. Cement M-3471 is similar to M-3389. Dotted lines indicate extrapolated portions of curves.

FIG. 27.—Temperature Rise of Various Mass Concretes with and Without Lignin Type Agent.

79). The table also shows that reduction of cementitious materials to 2½ sacks and the addition of 0.2 per cent agent *B* decreases the maximum temperature rise 6.7 F (compare mix No. 74 and mix No. 76).

Composition and quantity of cement and pozzolan are probably much stronger influences on temperature rise than that of an agent, *per se*. The most significant contribution of a *WR* agent toward reducing temperature rise of mass concrete is through cement reduction attendant to its use. This is particularly evident when comparing Flaming Gorge Dam concretes illustrated in Fig. 27, in which a mix containing 2 sacks of cement plus 1 sack of pozzolan is compared to a similar mix containing 0.37 per cent agent *G* and having a 5 per cent reduction in cementitious materials.

TABLE XXII.—HEAT GENERATION, CAL PER G OF CEMENT.

Agent		Age, days					
Per cent	Type	1	3	7	14	28	
None.......	...	32	56	80	90	95	Glen Canyon Dam
0.37........	*G*	27	56	83	93	98	
0.20........	*B*	32.3	49.5	65.0	79.5	87.9	mix 74, Monticello Dam

Reference to Fig. 27 reveals that the adiabatic temperature rise of the agent concrete containing Glen Canyon materials was less at early ages, the same at about 3 days' age, and slightly higher at later ages than that of the control concrete. A summary of heat generated by hydration of cement used in the Glen Canyon Dam and Monticello Dam investigations is summarized in Table XXII.

A study of the data in Table XXII indicates that *WR* agents affect heat generation of cement in a manner very similar to their effect on the temperature rise of mass concrete. Much of the heat is generated during the early age of the concrete, and this may have an important bearing in connection with the ability of agent concretes to withstand stresses induced by the resulting temperature changes. At very early ages, it may be possible to retard the compressive strength development of concretes and in so doing obtain the advantages of increased creep, affording relief to temperature-induced stresses. A fertile field for further development of *WR* agents lies in utilizing stress relief obtained through control of the creep phenomenon, particularly during the period of heat evolution and resulting volume changes.

Permeability

The results of permeability tests, recorded in Table XXIII, show that 30 per cent replacement of cement by the calcined diatomaceous clay reduced the permeability factor[3] from 0.00101 to 0.00082. The addition of 0.1 per cent agent *A* to concrete without pozzolan reduced the permeability factor to 0.00029; this was a greater reduction than that due to diatomaceous clay alone. Agent *A*, added to the concrete with diatomaceous clay, reduced the permeability factor to essentially the same value as that of concrete without pozzolan but with agent *A*. The permeability factor of concrete containing 0.1 per cent agent *A* and 30 per cent fly ash was about half

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[3] Cubic feet of water per square foot area per year per unit hydraulic gradient.

TABLE XXIII.—SERIES III—MONTICELLO DAM—PERMEABILITY TEST RESULTS.

Mix	$w/c + p$, by weight	Quantities per cu yd Concrete			Pozzolan	Agent, per cent cement plus pozzolan	Air Meter, per cent	Slump, in.	Maximum Size Aggregate, in.	Permeability[a]
		Water, lb	Cement, lb	Pozzolan, lb						
No. 75....	0.50	137	276	none	none	none	4.8	3.1	6	0.00101
No. 76....	0.53	149	196	85	diatomaceous clay	none	4.0	2.7	6	0.00082
No. 77....	0.44	122	276	none	none	0.1 agent *A*	5.4	2.5	6	0.00029
No. 78....	0.50	142	198	85	diatomaceous clay	0.1 agent *A*	3.0	1.6	6	0.00028
No. 79....	0.43	121	197	85	fly ash	0.1 agent *A*	3.9	2.2	6	0.00013
No. 74....	0.57	134	165	70	diatomaceous clay	0.2 agent *B*	5.5	2.3	6	0.00011

[a] Corrected to 60 days of age and for end effect.

that of the concrete containing agent *A* with and without the diatomaceous clay.

Although from the foregoing data the use of lignin agents will reduce the permeability factor, this is not an important contribution since excellent permeability factors are commonly obtained.

Conclusions

1. Lasting improvements in lean mass and in structural concretes containing a given amount of cement may be obtained by the addition of optimum dosages of suitable water-reducing retarding agents. The improvements obtained are in the form of increased compressive, tensile, and shearing strength and increased resistivity to freezing and thawing and sulfate-induced expansive forces. These benefits may sometimes be achieved, to a lesser extent, when cement content of the mix is reduced to offset the cost of the agent. To insure obtaining concrete consistently having the desired qualities, it is usually necessary to supplement water-reducing retarding agents with additional air-entraining or detraining agents added at the batch plant as required to produce uniform air content under conditions of varying temperature and changing composition of cement and aggregate.

2. The ease of handling concrete, as gaged by slump loss, is not greatly changed by the addition of water-reducing retarding agents. In fact, in a few cases, these agents have induced an increased rate of slump loss.

The principal contribution of water-reducing retarding agents toward improved workability is through their ability to extend the length of time in which concrete can be consolidated by vibration, thus reducing the risk of obtaining cold joints.

Additional benefits include surface retardation which, under moderate temperature and humidity conditions, permits more time between floating and troweling operations. In some cases, this may be desirable. Furthermore, *WR* agents may lessen the effort required to pump concrete through pipelines.

3. Volume changes due to wetting and drying, and permeability of mass concrete, are not affected by use of water-reducing retarding agents in amount sufficient to warrant changes in design

and construction considerations. However, reduced temperature rise, resulting from a lower cement content achieved through addition of these agents, offers possible savings in cooling mass concrete.

Acknowledgment:

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Special assistance was rendered by engineer Harry F. Avery in reviewing the work for technical accuracy and by Mr. Daniel M. Patterson in coordinating publication activities.

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(5) George Earl Troxell and Harmer E. Davis, "Composition and Properties of Concrete," McGraw-Hill Book Co., Inc., New York, N. Y., p. 236, Table 12.6 (1956).

DISCUSSION

MR. BAILEY TREMPER[1] (*presented in written form*).—This paper is the only one of the symposium that presents data on the effect of water-reducing and set-retarding agents on the drying shrinkage of concrete. The data presented in this paper are not extensive and tend to indicate that the admixtures used did not affect drying shrinkage very much.

The writer has conducted a relatively large number of drying shrinkage tests of concrete containing a variety of water-reducing, set-retarding admixtures. In general, under the conditions of test, such admixtures have tended to increase drying shrinkage significantly. The point it is desired to make at this time is that the results obtained appear to be affected by the particular cement that was used in the test. All of the tests were made with a type II, low-alkali cement manufactured at one mill but different lots were used from time to time. The inference was drawn therefore that minor differences in the composition of the cement might have a pronounced effect on the manner in which the admixtures were functioning in concrete with respect to drying shrinkage. In order to explore such a possibility expeditiously, a series of drying shrinkage tests were made with Ottawa sand mortars.

Test specimens were 1 by 1 by $11\frac{1}{4}$-in. prisms with reference points for length measurement. After 24 hr in the moist room the prisms were removed from the molds and then stored in water at 73.4 ± 3 F to the age of 72 hr. They were then measured for length and subjected to

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[1] Supervising Materials and Research Engineer, Materials and Research Department, California Division of Highways, Sacramento, Calif.

drying at 73.4 ± 3 F and 50 ± 4 per cent relative humidity to the age of 7 days. They were again measured for length. The decrease in length as a percentage of 10 in. was reported as drying shrinkage. The mortar consisted of 1 part by weight of cement to 2 parts by weight of graded Ottawa sand and sufficient water, or water plus admixture, to produce a flow of 100 to 115. Two cements from the same mill were used. They were type II, low-alkali cements containing about 1 per cent SO_3. Blends of the cements and pulverized gypsum were made to increase the SO_3 content by steps of 0.5 per cent over the approximate range of 1.0 to 2.5 per cent.

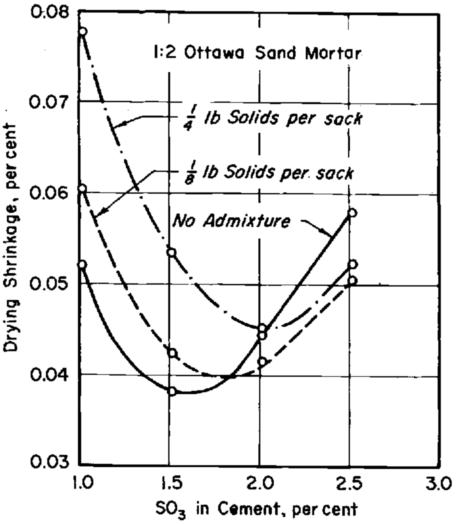

FIG. 28.—Effect of Lignosulfonate Admixture on Drying Shrinkage.

Two water-reducing retarders were used each in two dosages. One was a commercial lignosulfonate product, the other a commercial hydroxylated carboxylic type. Both permitted a reduction in mixing water for constant flow and during drying both retarded the rate at which water was lost from the specimens.

The results of drying shrinkage tests are shown in the accompanying Figs. 28 and 29. The solid curves represent specimens containing the cements without admixture. The effect of varying SO_3 content on drying shrinkage is normal and indicates that the optimum content is about 1.5 per cent. At low SO_3 contents the admixtures increased drying shrinkage significantly. At the higher SO_3 contents the trend was reversed and in most cases resulted in some decrease in drying shrinkage relative to that of the mortar containing no admixture.

It will be noted that the SO_3 content of the cement for minimum drying shrinkage was increased in the presence of the admixtures. It is also noteworthy that the minimum drying shrinkage obtainable with the admixtures was always greater than that obtainable with the cement alone.

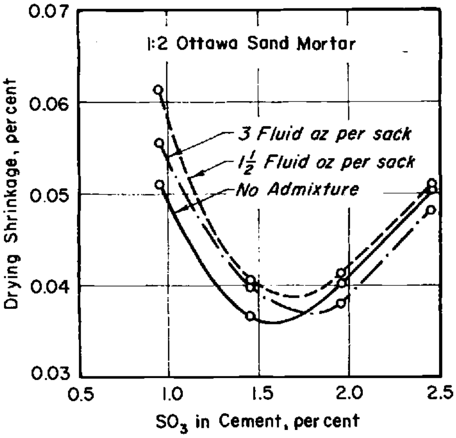

FIG. 29.—Effect of Hydroxylated Carboxylic Admixture on Drying Shrinkage.

It is not intended to imply that the numerical values of these tests are representative of results in normal concretes. It is believed that the trends have been exaggerated by reason of using a rich mortar. Nevertheless the data appear to show clearly that the performance of a water-reducing retarder with respect to drying shrinkage is affected to an important degree by the composition and possibly other characteristics of the cement with which it is used. The effect of SO_3 content of the cement is shown to be particularly pronounced.

Standard specifications for portland cement admit wide latitude in the percentage of SO_3. Among cements with which the writer is familiar, the uniformity of SO_3 in day to day production varies from fair to very poor. In the absence of specific information, concern as to the uniformity of water-reducing and set-retarding admixtures may be justified. Until there is a better understanding of the effects of interactions between cements and admixtures, it does not appear that the potential benefits of water reduction and set retardation can be realized without at the same time producing unknown and possibly harmful effects with respect to drying shrinkage.

Some ideas on the importance of securing low drying shrinkage are contained in the author's closure of a recent paper.[2]

MESSRS. GEORGE B. WALLACE AND ELWOOD L. ORE (*authors*).—It was interesting to note the effect of cements containing various quantities of SO_3 on the drying shrinkage of mortars made with and without *WR* agents.

We also note that you have the impression that our conclusions on the effect of *WR* agents on shrinkage are based on tests which are not extensive. Perhaps, in our effort to summarize all our data, we did treat this section a bit too briefly. However, the data are extensive enough for significance, and include results from concretes made with 4 type II cements, 5 agents, 3 pozzolans, and 4 aggregates. One of the cements (M-1700) was a blend of type II cement from 10 different mills.

The SO_3 content of the four cements ranged from 1.6 to 1.9, which admittedly is not extensive, but it must be remembered that in some cases these cements were used in conjunction with pozzolans having very low SO_3 contents, which might serve to dilute the SO_3 function of the cement, and accentuate this variation.

It was interesting to note that your conclusions are based on the results of tests performed on mortar specimens, as you state. This appears to effectively accentuate the effects of SO_3 used in conjunction with *WR* agents. However, in concrete where the SO_3 concentration is more dilute, this effect may be minimized and other factors, such as reduced water and cement contents will probably be more influential.

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[2] Bailey Tremper, "Control of Gypsum in Portland Cement," *Proceedings*, Am. Soc. Testing Mats., Vol. 59, p. 1101 (1959).

STP266-EB/Jun.1960

OBSERVATIONS IN TESTING AND USE OF WATER-REDUCING RETARDERS

By Lewis H. Tuthill,[1] Robert F. Adams,[1] and John M. Hemme, Jr.[1]

Synopsis

Continuing work in both laboratory and field with water-reducing and set-retarding admixtures has resulted in further helpful knowledge concerning them and has added to confidence in their use on the job. Significant benefits are obtained with these admixtures in job concrete, particularly in warm weather. Through postponement of the vibration limit, cold joints are less a hazard.

Reduction in water requirement to a large extent offsets normal increases in water due to warm weather, and due to higher slumps whatever their cause. At two days and later ages, strength is increased when the dosage is not above normal. At various ages beyond the first few days, the higher strengths achieved are greater than can be ascribed to reduction in water-cement ratio.

Fear of the sugar content of the admixtures is apparently unfounded; troublesome delay in hardening is more likely to be the result of gross overdosage from malfunction of a dispenser. Hence dispensing equipment must be completely reliable and its performance readily verified for each batch. Such equipment is described.

Performance of the admixtures usually varies with concrete temperature and somewhat with various cements. Expected performance should be verified in advance using job materials. Dosages and sometimes the admixture must be changed accordingly, based on such test results and job performance.

The paper discusses these matters with related test data. It also discusses practical aspects of specifications, delivery, and acceptance testing when these are appropriate.

For the past several years the authors have variously taken opportunities to obtain more test data and field experience using water-reducing and set-retardant admixtures. Results have been generally satisfactory although by no means identical. It is our conclusion that use of an acceptable admixture of this type is particularly worthwhile in warm weather, and there may be conditions under which one may be used to advantage at other times. In any case the possible advantage is influenced by the cost of using the admixture.

An earlier paper, (**1**)[2] described the need for a retardant admixture in warm weather to postpone the time when concrete could no longer be vibrated and become monolithic with the next layer of

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[1] Concrete Engineer, Head of Concrete Laboratory, and Engineer, respectively, California Department of Water Resources, Sacramento, Calif.

[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

concrete placed on it. There was also mention of the desirability of offsetting as much as possible the increase in mixing water requirement that is inherent at higher concrete temperatures and which is often further increased to provide greater initial slump as a protection against supposed higher slump loss in hot weather. This was an opportunity for a water-reducing admixture. It takes but little study of many concrete jobs to discern instances when it would be desirable to reduce water content. Some important ones are to:

1. Reduce water when the concrete materials have a higher water requirement than is usual for most similar concretes.
2. Reduce water when slump loss is troublesome and the margin against it is increased.
3. Reduce water when concrete is not dry-batched and mixed at the forms.
4. Reduce water when slump is greater than 3 in.

It is the purpose of this paper to discuss several of the effects of such additives (Table I) on concrete properties and a few of the questions that arise in its use on the job.

TABLE I.—WATER-REDUCING AND RETARDING ADMIXTURES OBSERVED.

Symbol	Condition	Principal Chemical Ingredient	Sugar Content	Where Used
AO	powder	ammonium lignosulfonate	high	laboratory
SO	powder	sodium lignosulfonate	high	laboratory
QA	42 per cent solution	sodium lignosulfonate	high	laboratory and field[a]
RC	liquid	calcium lignosulfonate	high	laboratory
OP	powder	calcium lignosulfonate	low	laboratory and field[a]
DP	powder	calcium lignosulfonate	low	laboratory
AD	liquid	ammonium lignosulfonate	low	laboratory
RW	liquid	modified ammonium lignosulfonate	low	laboratory
HO	powder	ammonium lignosulfonate	low	laboratory
LP	liquid	hydroxylated carboxylic acid or its salt	none	laboratory and field[a]
Sugar	powder	sucrose	100 per cent	laboratory

[a] Choice of these admixtures was by the contractor on each job.

TABLE II.—COMPOSITION OF CEMENTS USED, PER CENT.

Cement	Type	C_3S	C_2S	C_3A	C_4AF	Alkalies
AS	I	43	28	11	9	1.04
DI	I	47	26	11	8	0.94
AC	I	54	25	6	8	0.59
EP	II	54	29	3	9	0.22

Table II shows the general compound composition, and total equivalent alkali content computed as Na_2O, of cements used in the various concretes discussed in this paper.

Standard procedures were followed in laboratory testing. All work was done in an air-conditioned mix room. For concrete at different temperatures, all ingredients were brought to the required temperature before batching. These temperatures were 50 to 55, 70 to 75, and 90 to 95 F. Concrete in test cylinders was held at these temperatures for 24 hr before standard curing. Pertinent data will be reported in connection with each aspect of performance discussed. The plain concrete used as a basis of comparison is in all cases air-entrained concrete.

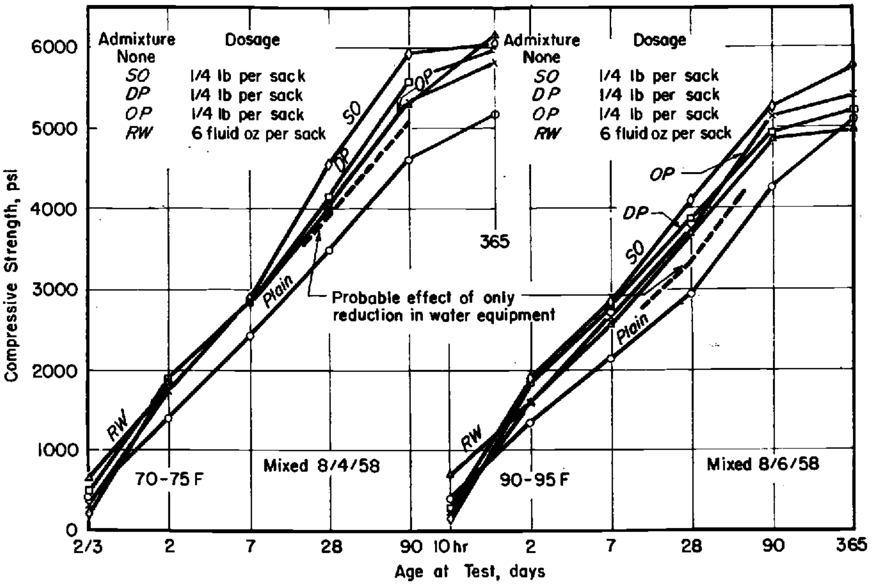

FIG. 1.—Strength of Concrete with Type II Cement *EP* and Different Water-Reducing Admixtures.

1½ in. aggregate, 5½ sack, 3½ to 4½-in. slump, 3½ per cent air, standard cure temperature after 24 hr.

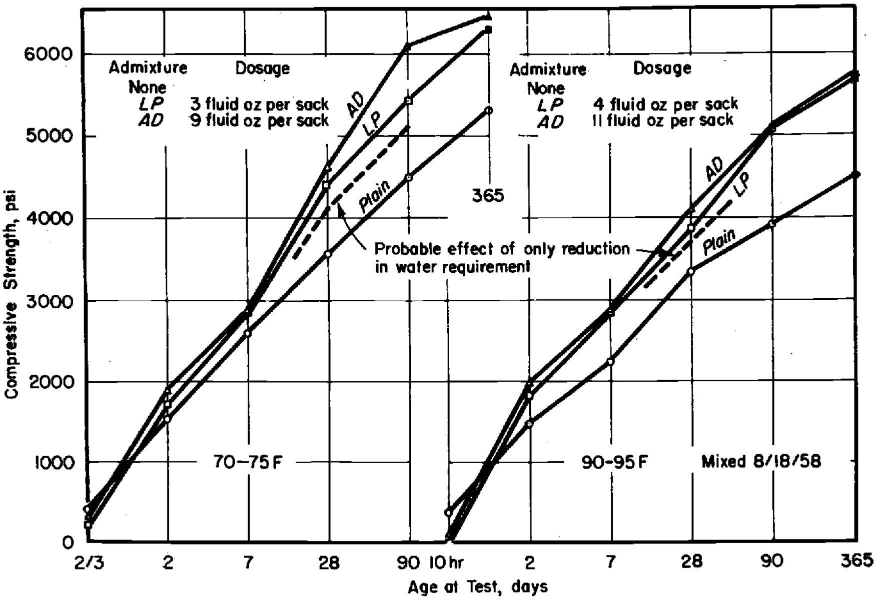

FIG. 2.—Strength of Concrete with Type II Cement *EP* and Different Water-Reducing Retarders.

1½ in. aggregate, 5½ sack, 3½ to 4½-in. slump, 3½ per cent air, standard cure temperature after 24 hr.

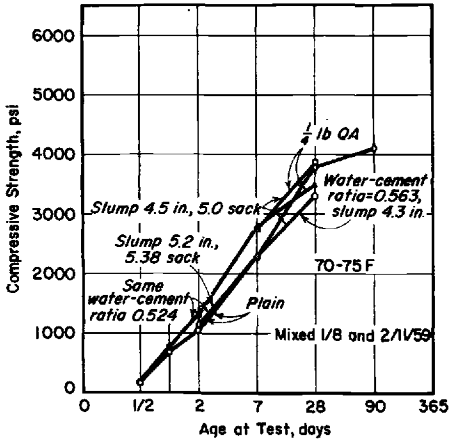

FIG. 3.—Strength of Concrete With and Without Admixture *QA* and With Type I Cement *DI*.

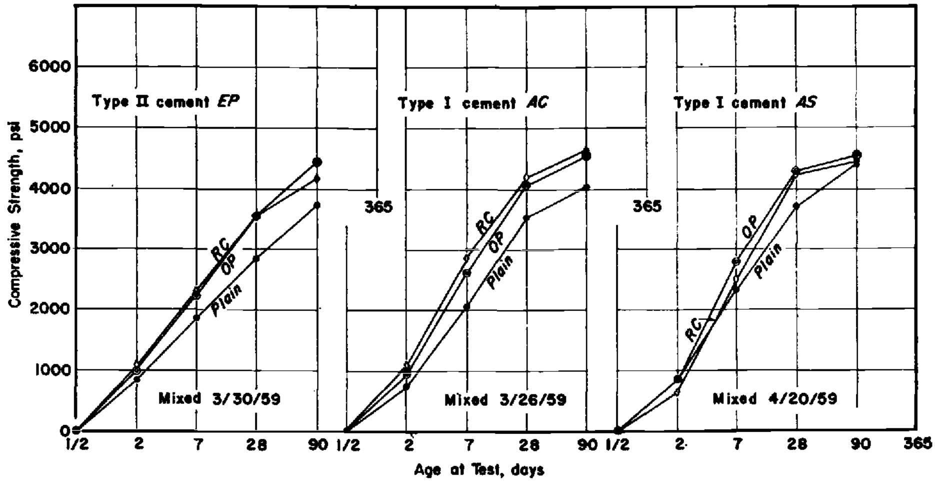

FIG. 4.—Strength of Concrete Mixed at 50 to 55 F with Different Cements and with High *RC* and Low *OP* Sugar Calcium Salt of Lignosulfonic Acid Admixture, $\frac{1}{4}$ lb per sack.

1½ in. aggregate, 5 sack, 3 to 4 per cent air, 3½ to 4½-in. slump, standard cure temperature after 24 hr.

EFFECTS ON STRENGTH AT NORMAL AGES

Ordinarily, at the same cement content and slump, reduction in mixing water is expected to increase strength in accordance with the long recognized strength water-cement ratio relationship. Within the common range of water-cement ratio for good concrete, say 0.45 to 0.58, 28-day strength increases in very round numbers about 100 psi for each reduction of 0.01 in water-cement ratio. An 8 per cent reduction in mixing water requirement would reduce a water-cement ratio of 0.50 to 0.46. According to this "approximate rule," there would be a resulting strength increase of about 400 psi at 28 days.

When such a water reduction is obtained by use of a water-reducing admixture, the increase in strength is usually considerably more than would be expected from the "approximate rule." Twice the expected increase is common and considerably more increase than twice is not unusual. For example, 28-day strength of concrete in the Tecolote Tunnel lining was 5474 psi with a $\frac{1}{4}$-lb per sack dosage of a calcium lignosulfonate in the 7-sack mix, and 4390 psi when the admixture was not used. The water-cement ratio was reduced from 0.44 to 0.41, considerably less than enough to account for the 1084 psi increase or nearly 25 per cent more strength in concrete containing the water-reducing admixture.

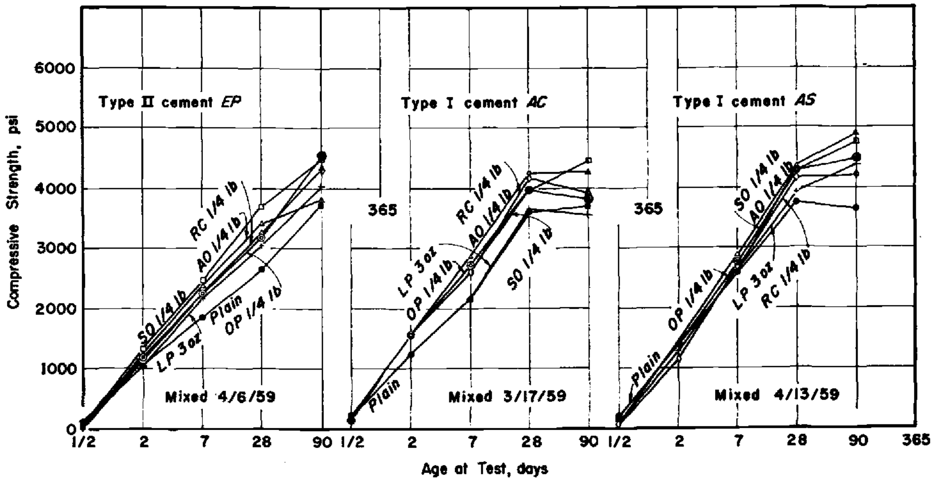

FIG. 5.—Strength of Concrete Mixed at 70 to 75 F with Different Cements and with Various Water-Reducing Admixtures.

1½ in. aggregate, 5 sack, 3 to 4 per cent air, 3½ to 4½-in. slump, standard cure temperature after 24 hr.

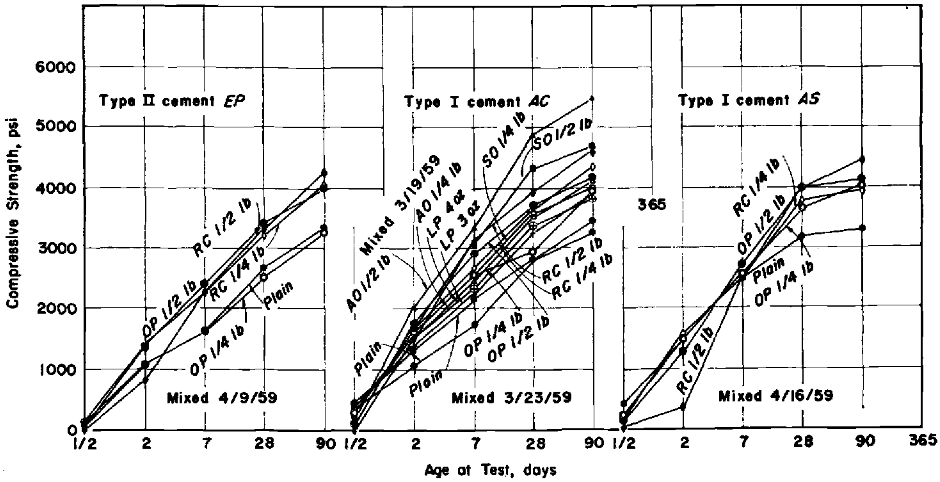

FIG. 6.—Strength of Concrete Mixed at 90 to 95 F with Different Cements and with Various Kinds and Amounts of Water-Reducing Admixtures.

1½ in. aggregate, 5 sack, 3 to 4 per cent air, 3½ to 4½-in. slump, standard cure temperature after 24 hr.

As the curves in Figs. 1, 2, and 3 show, this additional increase in strength, over what might be expected of a reduction in water-cement ratio, is a common property of the principal types of available admixtures when used with favorable cements. Moreover, from Figs. 1 and 2, it is apparently unaffected by the temperature at which the concrete is mixed. In the examples shown, the chemical composition of cement *EP* was nearer type II than type I in that the per cent of C_3A is well below 8; however, it meets requirements of Federal Specifications

SS-C-192b for type II cement. Data in Figs. 3, 4, 5, and 6, particularly that in Fig. 5, indicate that these strength effects may not be as great with a fully type I cement. Whether this is always the case, and whether it is due to the difference in C_3A or in the alkalies, or both, remains to be confirmed.

Figure 3 shows that at approximately the same water-cement ratio and slump, concrete containing one of the lignin-based admixtures still exhibited higher strength than plain concrete containing 0.38 sacks more cement per cu yd. Concretes shown in Fig. 3 were made with type I cement *DI*.

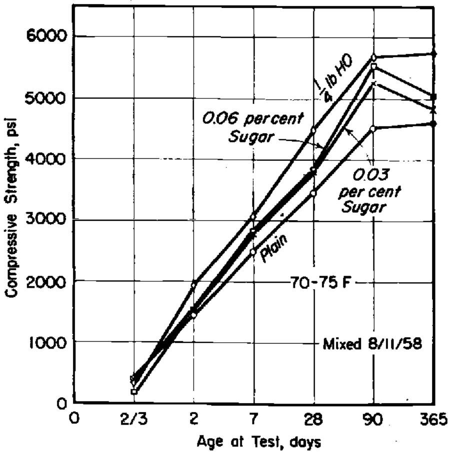

FIG. 7.—Strength of Concrete with Sugar or a Lignin Admixture-Cement *EP*.

1½ in. aggregate, 5½ sack, 3½ to 4½-in. slump, 3½ per cent air, standard cure temperature after 24 hr.

In general, at the higher strengths attained at later ages, the magnitude of the greater strength remains, although it is then a lesser percentage of the control. It is also worth noting that there is no retrogression in strength at later ages in mixes containing water-reducing admixture.

In all cases, even with sugar, Fig. 7, it is interesting to note in Figs. 1, 2, 3, 4, 5, 6, 7, and 8 that, at 2 days, concrete containing normal and often large dosages of water-reducing retarding admixtures developed strength noticeably in excess of the strength of similar concretes without the admixtures.

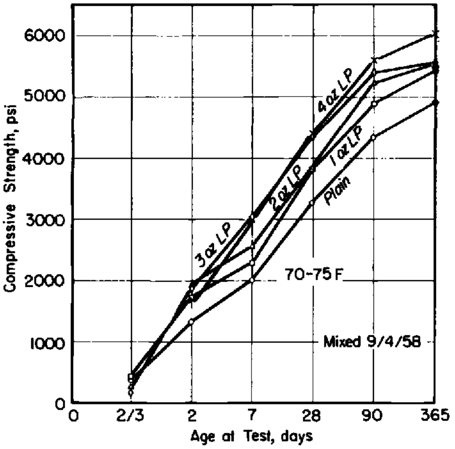

FIG. 8.—Strength of Concrete with Cement *EP* and Different Dosages of Admixture *LP*.

1½ in. aggregate, 5½ sack, 3½ to 4½-in. slump, 3½ per cent air, standard cure temperature after 24 hr.

EFFECTS ON EARLY STRENGTH

Another important aspect of strength development in concretes containing these admixtures is the rate of development of very early strength. On many jobs, the amount of strength attained within 24 hr is not important, since there is usually no need to strip forms earlier than a day or two after placement. However, on many tunnel lining and conduit jobs, it is necessary for the sake of economy to maintain a cycle of operations which entails stripping and reuse of the forms each successive 24 hr. To maintain such a schedule, it is necessary for concrete to be strong enough in about 12 hr to permit removal of forms. Since dead-load stresses in such concrete have been determined to be only from 60 to 150 psi, it is considered that a strength of 200

TABLE III.—EFFECTS OF ADMIXTURES.

Mix	Admixture	Sugars in Admixture	Dosage of Admixture, per sack	Reduction[a] in Water, per cent	Time, hr, to Penetration Resistance of		Compressive Strength, psi	Air Content		
					500 psi	4000 psi		Air, per cent	Air-Entraining Agent	Air-Detraining Agent
									ml per cu yd	
SOME EFFECTS OF ADMIXTURES WITH TYPE I CEMENT *AS*										
INITIAL TEMPERATURE OF CONCRETE—50 to 55 F										
RS50— 1	none	...	...	...	8.4	12.2	32 at 12 hr	3.6	80	0
2	*RC*	high	¼ lb	6.2	12.6	16.8	20 at 12 hr	3.8	0	0
3	*OP*	low	¼ lb	5.8	9.7	12.6	30 at 12 hr	3.7	0	0
INITIAL TEMPERATURE OF CONCRETE—70 to 75 F										
RS— 1	none	...	...	...	5.4	7.2	228 at 12 hr	3.3	100	0
2	*AO*	high	¼ lb	6.8	8.1	10.1	132 at 12 hr	3.4	0	0
3	*SO*	high	¼ lb	5.7	7.2	9.0	158 at 12 hr	4.0	20	0
4	*RC*	high	¼ lb	6.4	8.2	10.6	97 at 12 hr	4.0	10	0
5	*OP*	low	¼ lb	5.7	7.0	9.0	162 at 12 hr	3.7	5	0
6	*LP*	0	3 fl oz	4.1	6.6	8.8	172 at 12 hr	3.9	65	0
INITIAL TEMPERATURE OF CONCRETE—90 to 95 F										
RS90— 1	none	...	...	...	4.3	5.8	473 at 12 hr	4.0	135	0
2	*RC*	high	¼ lb	4.8	6.6	8.2	165 at 12 hr	3.4	30	0
3	*RC*	high	½ lb	8.8	9.5	10.9	47 at 12 hr	3.8	0	0
4	*OP*	low	¼ lb	4.8	5.6	7.3	231 at 12 hr	3.3	30	0
5	*OP*	low	½ lb	8.8	7.9	9.4	114 at 12 hr	3.4	0	0
SOME EFFECTS OF ADMIXTURES WITH TYPE I CEMENT *AC*										
INITIAL TEMPERATURE OF CONCRETE—50 to 55 F										
RC50— 1	none	...	...	...	8.4	12.5	38 at 12 hr	3.0	50	0
2	*RC*	high	¼ lb	9.7	10.4	14.1	21 at 12 hr	3.0	0	0.8
3	*OP*	low	¼ lb	5.8	9.4	12.6	25 at 12 hr	3.5	0	0.5
INITIAL TEMPERATURE OF CONCRETE—70 to 75 F										
RC— 1	none	...	...	...	5.2	6.6	423 at 16 hr	3.5	70	0
2	*OP*	low	¼ lb	8.1	7.2	9.4	355 at 16 hr	3.8	0	0
3	none	...	...	...	5.6	7.7	206 at 12 hr	3.4	91	0
4	*AO*	high	¼ lb	9.2	7.5	10.1	147 at 12 hr	3.4	0	0
5	*SO*	high	¼ lb	8.2	7.0	9.5	190 at 12 hr	3.3	0	0
6	*RC*	high	¼ lb	7.8	7.6	10.0	146 at 12 hr	3.0	0	0
7	*OP*	low	¼ lb	7.0	6.9	8.8	97 at 12 hr	3.1	0	0
8	*LP*	0	3 fl oz	4.8	7.0	8.8	126 at 12 hr	3.4	55	0
INITIAL TEMPERATURE OF CONCRETE—90 to 95 F										
RC90— 1	none	...	...	...	3.9	5.3	451 at 10 hr	3.4	126	0
2	*OP*	low	¼ lb	8.5	5.7	7.6	301 at 10 hr	3.6	22	0
3	none	...	...	...	4.7	6.4	362 at 12 hr	4.0	139	0
4	*AO*	high	¼ lb	9.1	7.1	9.1	294 at 12 hr	4.0	30	0
5	*AO*	high	½ lb	12.1	13.1	15.4	179 at 12 hr	3.2	0	1.0
6	*SO*	high	¼ lb	7.7	6.0	7.8	373 at 12 hr	3.6	20	0
7	*SO*	high	½ lb	11.7	12.0	14.4	147 at 12 hr	3.4	0	1.0
8	*LP*	0	3 fl oz	4.1	5.6	7.4	351 at 12 hr	3.6	80	0
9	*LP*	0	4 fl oz	5.5	6.9	8.5	236 at 12 hr	3.8	55	0

TABLE III.—*Continued.*

Mix	Admixture	Sugars in Admixture	Dosage of Admixture, per sack	Reduction^a in Water, per cent	Time, hr, to Penetration Resistance of 500 psi	Time, hr, to Penetration Resistance of 4000 psi	Compressive Strength, psi	Air Content: Air, per cent	Air Content: Air-Entraining Agent, ml per cu yd	Air Content: Air-Detraining Agent, ml per cu yd
10.....	none	...	...	...	5.2	6.8	423 at 12 hr	3.6	121	0
11.....	*RC*	high	¼ lb	9.0	7.5	9.3	262 at 12 hr	3.3	21	0
12.....	*RC*	high	½ lb	13.0	13.9	16.8	8 at 12 hr	3.4	0	0.8
13.....	*OP*	low	¼ lb	10.5	5.9	7.6	247 at 12 hr	3.4	20	0
14.....	*OP*	low	½ lb	10.5	10.0	11.7	64 at 12 hr	3.3	0	0.8
SOME EFFECTS OF ADMIXTURES WITH TYPE I CEMENT *DI*										
INITIAL TEMPERATURE OF CONCRETE—50 to 55 F										
R50— 1.....	none	...	...	...	7.2	12.6	64 at 16 hr	4.0	58	0
2.....	*SO*	high	¼ lb	8.3	10.1	13.8	29 at 16 hr	4.6	0	0
3.....	*DP*	low	¼ lb	8.3	9.2	13.0	57 at 16 hr	4.8	0	0
4.....	*OP*	low	¼ lb	9.5	8.5	12.7	57 at 16 hr	4.9	0	0
5.....	*RW*	low	6 fl oz	4.1	7.2	9.8	115 at 16 hr	3.9	0	0
9.....	none	...	...	...	8.2	12.5	32 at 12 hr	3.4	37	0
10.....	*QA*	high	⅛ lb	4.7	8.5	12.6	20 at 12 hr	3.4	0	0
11.....	*QA*	high	¼ lb	7.1	10.2	15.3	15 at 12 hr	3.8	0	2.0
12.....	*QA*	high	⅜ lb	7.9	13.2	20.4	6 at 12 hr	3.5	0	3.0
INITIAL TEMPERATURE OF CONCRETE—70 to 75										
R— 1.....	none	...	...	...	4.3	6.9	530 at 16 hr	3.6	80	0
5.....	*SO*	high	¼ lb	6.7	6.4	8.8	527 at 16 hr	3.8	0	0
4.....	*DP*	low	¼ lb	9.0	5.8	8.0	584 at 16 hr	4.6	0	0
2.....	*OP*	low	¼ lb	8.6	5.8	7.9	623 at 16 hr	3.6	0	0
3.....	*RW*	low	6 fl oz	3.5	4.4	6.2	760 at 16 hr	3.6	26	0
13.....	none	...	...	...	5.3	7.8	172 at 16 hr	3.5	55	0
14.....	*QA*	high	⅛ lb	3.5	5.4	7.7	200 at 16 hr	3.5	10	0
15.....	*QA*	high	¼ lb	7.8	6.3	8.8	192 at 16 hr	3.4	0	1.0
16.....	*QA*	high	⅜ lb	7.4	7.7	10.5	135 at 16 hr	3.5	0	2.0
INITIAL TEMPERATURE OF CONCRETE—90 to 95 F										
R90— 1.....	none	...	...	...	3.3	4.8	541 at 10 hr	3.4	88	0
2.....	*SO*	high	¼ lb	9.5	5.3	7.0	480 at 10 hr	4.0	21	0
3.....	*DP*	low	¼ lb	8.3	5.0	6.7	566 at 10 hr	4.7	0	0
4.....	*OP*	low	¼ lb	7.1	4.9	6.6	462 at 10 hr	3.7	16	0
5.....	*RW*	low	6 fl oz	3.6	3.7	5.0	595 at 10 hr	3.4	29	0
12.....	none	...	...	...	4.4	6.0	441 at 12 hr	3.0	60	0
13.....	*QA*	high	¼ lb	5.3	5.7	7.4	520 at 12 hr	3.5	0	0
14.....	*QA*	high	⅜ lb	7.9	7.9	9.5	376 at 12 hr	3.3	0	1.0
15.....	*QA*	high	½ lb	7.6	8.8	10.8	262 at 12 hr	3.8	0	2.0
SOME EFFECTS OF ADMIXTURES WITH TYPE II CEMENT *EP*										
INITIAL TEMPERATURE OF CONCRETE—50 to 55 F										
RP50— 1.....	none	...	...	...	9.4	13.4	34 at 12 hr	4.0	15	0
2.....	*RC*	high	¼ lb	6.2	14.1	18.2	6 at 12 hr	3.6	0	1.0
3.....	*OP*	low	¼ lb	5.8	10.8	16.2	19 at 12 hr	3.3	0	0.9
4.....	none	...	...	...	7.5	11.7	54 at 12 hr	4.0	89	0
5.....	*LP*	0	2 fl oz	7.7	8.5	12.1	44 at 12 hr	2.9	20	0

TABLE III.—*Concluded.*

Mix	Admixture	Sugars in Admixture	Dosage of Admixture, per sack	Reduction[a] in Water, per cent	Time, hr, to Penetration Resistance of		Compressive Strength, psi	Air Content		
					500 psi	4000 psi		Air, per cent	Air-Entraining Agent, ml per cu yd	Air-Detraining Agent, ml per cu yd
INITIAL TEMPERATURE OF CONCRETE—70 to 75 F										
RP— 1.....	none	...	...	...	5.5	7.7	401 at 16 hr	3.1	62	0
2.....	*SO*	high	¼ lb	12.0	10.3	12.8	201 at 16 hr	3.5	0	0
3.....	*DP*	low	¼ lb	9.2	8.0	10.0	487 at 16 hr	3.6	0	0
4.....	*OP*	low	¼ lb	10.0	7.8	9.8	308 at 16 hr	3.4	0	0
5.....	*RW*	low	6 fl oz	9.2	6.2	8.1	638 at 16 hr	3.6	20	0
6.....	none	...	...	...	5.4	7.5	365 at 16 hr	3.3	64	0
7.....	*HO*	low	¼ lb	10.6	8.5	10.9	333 at 16 hr	3.4	0	0
8.....	sugar	100 per cent	0.03 per cent by weight	2.0	7.2	9.1	369 at 16 hr	3.7	62	0
9.....	sugar	100 per cent	0.06 per cent by weight	4.3	10.0	12.5	193 at 16 hr	3.5	60	0
10.....	none	...	...	...	5.6	7.7	412 at 16 hr	3.2	65	0
12.....	*AD*	low	9 fl oz	11.7	9.2	11.9	351 at 16 hr	3.6	0	0
13.....	none	...	...	...	5.8	7.9	369 at 16 hr	3.6	64	0
14.....	*LP*	0	1 fl oz	3.9	6.7	8.9	419 at 16 hr	3.8	51	0
15.....	*LP*	0	2 fl oz	5.5	8.4	11.0	272 at 16 hr	3.7	42	0
16.....	*LP*	0	3 fl oz	7.5	11.3	13.7	156 at 16 hr	3.4	34	0
17.....	*LP*	0	4 fl oz	10.2	15.0	18.3	...	3.1	24	0
18.....	*RW*	low	3.5 fl oz	6.7	5.8	7.5	606 at 16 hr	3.8	39	0
24.....	none	...	...	...	6.7	9.3	139 at 12 hr	3.3	50	0
25.....	*AO*	high	¼ lb	9.1	12.3	15.8	19 at 12 hr	3.6	0	0
26.....	*SO*	high	¼ lb	8.7	11.0	14.3	39 at 12 hr	3.4	0	0
27.....	*RC*	high	¼ lb	7.5	13.5	17.4	16 at 12 hr	3.2	0	0
28.....	*OP*	low	¼ lb	7.9	10.1	12.9	59 at 12 hr	3.0	0	0
29.....	*LP*	0	3 fl oz	5.1	10.4	13.4	48 at 12 hr	3.4	50	0
INITIAL TEMPERATURE OF CONCRETE—90 to 95 F										
RP90— 1.....	none	...	...	...	4.1	5.8	398 at 10 hr	3.4	103	0
2.....	*SO*	high	¼ lb	8.5	7.2	8.8	136 at 10 hr	3.6	22	0
3.....	*DP*	low	¼ lb	7.3	6.1	7.2	272 at 10 hr	3.5	0	0
4.....	*OP*	low	¼ lb	6.5	6.6	8.0	229 at 10 hr	3.7	17	0
5.....	*RW*	low	6 fl oz	3.6	4.2	5.5	584 at 10 hr	3.0	40	0
9.....	none	...	...	...	4.9	7.0	70 at 12 hr	3.1	90	0
10.....	*RC*	high	¼ lb	6.9	8.8	11.1	79 at 12 hr	3.4	30	0
11.....	*RC*	high	½ lb	10.0	23.1	27.0	15 at 13½ hr	3.6	0	0.8
12.....	*OP*	low	¼ lb	6.9	8.1	10.0	105 at 12 hr	3.8	30	0
13.....	*OP*	low	½ lb	9.2	12.7	15.3	26 at 12 hr	3.2	0	1.0

---

[a] The plain concrete used as a basis of comparison is in all cases air-entrained concrete. The water reduction was computed after adjusting all mixes to the same slump and air content.

to 300 psi is sufficient to prevent structural failure when forms are removed. Usually, with concrete of such low strength, the greatest problem in form removal is to accomplish it without damage to surfaces, corners, edges.

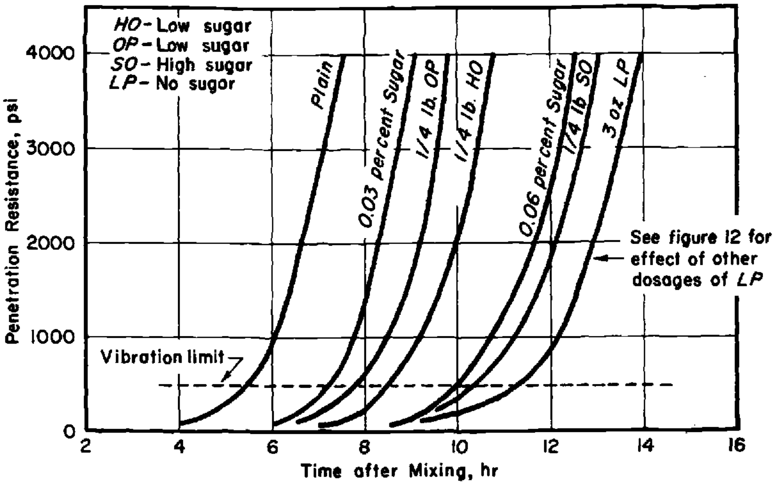

FIG. 9.—Effect of Table Sugar and Admixtures on Rate of Setting at 70 to 75 F, Cement *EP*

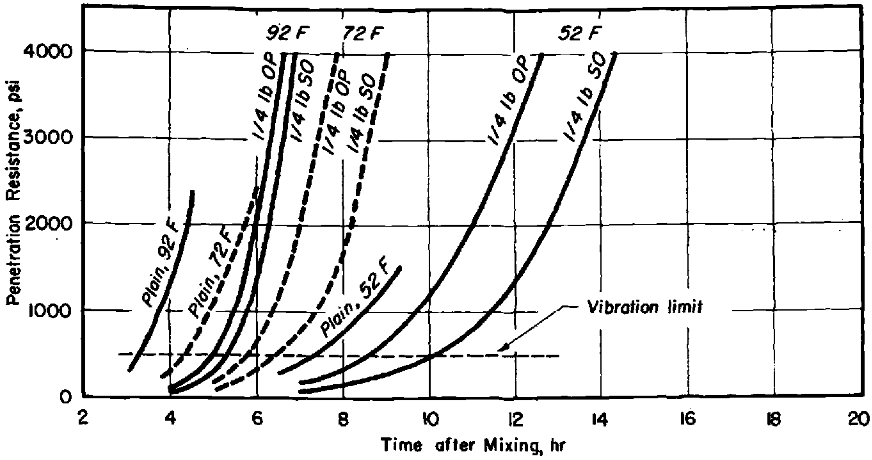

FIG. 10.—High *SO* or Low *OP* Sugar Content of Admixture Has Unimportant Effect on Time to Vibration Limit, Particularly at Higher Temperatures, Cement Type I *DI*.

When retardant admixtures are used, the question naturally arises as to its influence on strength at the time forms must be removed. For this reason 10-, 12-, or 16-hr strengths were obtained with several of the admixtures and 12-hr strengths at various initial temperatures and dosages were determined for admixture *QA* which was to be used in concrete for lining Feather River project railroad relocation tunnels Nos. 4 and 5. From the results shown in Figs. 1, 3, 4, 5, and 6, and reported in Table III, it appears evident that in most cases normal dosages of the admixtures tested do not reduce early strength significantly below that of concrete in which no admixture was used. Some lower values will be noted in Figs. 2 and 6 in cases of large dosages, even at 90 to 95 F. However, for those tested with initial temperatures of 50 to 55 F (Table III), it was evident that neither concrete with or without an admixture would be strong enough in 12 hr for form removal and that it would therefore be necessary to raise the initial concrete temperature to 70 to 75 F.

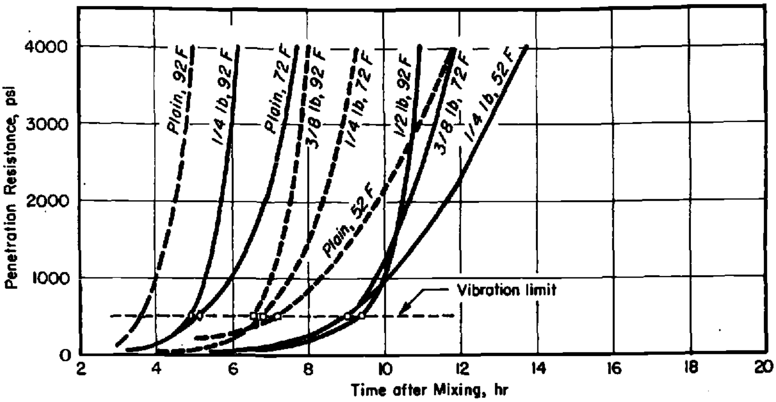

FIG. 11.—Concrete of Similar Vibration Limit at Various Temperatures Can be Made by Varying Dosages of a Retarding Admixture. Admixture *QA* Here Used with Type I Cement *DI*.

EFFECTS OF SUGAR CONTENT OF ADMIXTURES

Much contemporary consideration has been given to the sugar content of the various admixtures, to the character and possible effect of these sugars, and to means of determining their kind and amount, particularly in the lignin-based materials. This concern has been due to a somewhat prevalent idea that, presumably, sugar could be detrimental to concrete and cause troublesome and embarrassing delays in hardening of job concrete. For this reason observance of the effect of sugar has been one of the principal items noted during the testing and field experience here reported.

As a starting point, small quantities (0.03 and 0.06 per cent by weight of cement) of ordinary table sugar were used as an admixture. Figure 9 and comparison with Figs. 10, 13, 14, and 15 show that the time and rate of hardening of the sugared concrete are no different than with other retarders. Figure 7 shows strength superior to that of the plain concrete obtained at all ages tested, except at 16 hr when concrete with the higher sugar content had lower strength than concrete without sugar.

However, 1-yr strengths were below expectations for each of the four mixes. Although the mixes containing sugar were still stronger than the plain mixes at 1 yr, they showed less strength than at 90 days. Probably more than these few tests will be necessary to show whether or not this effect at later ages is significant. It should be noted on Fig. 1 that the high-sugared, lignin-based admixture *SO* showed normal strength increase from 90 days to 1 yr.

It was noted that water reduction was only about 4 per cent for the 0.03 per cent dosage and 5 per cent for the 0.06 per cent dosage. Thus pure sugar appears to be more effective as a retarder than as a water-reducing admixture.

Other tests with large dosages of sugar are reported in a Portland Cement Assn. information sheet; these large dosages become increasingly damaging to strength. However, it is of interest to note that the highest strength obtained was with a dosage of 0.15 lb per sack or about 2½ times the maximum dosage in Figs. 7 and 9, provided the test cylinders were cured in moist air and not in water.

Table I shows relative amounts of sugar compounds in the various admixtures, and Table III lists these with corresponding time between mixing and the vibration limit for normal dosages in concrete of the same initial temperature. It is regretted that precise, reliable information could not be obtained as to the type or the amount of sugar in the lignin-based admixtures used. Consequently, only the general terms "high-sugared" and "low-sugared," as used in the trade, are used in Tables I and III and elsewhere. The dividing line is probably about 10 to 12 per cent.

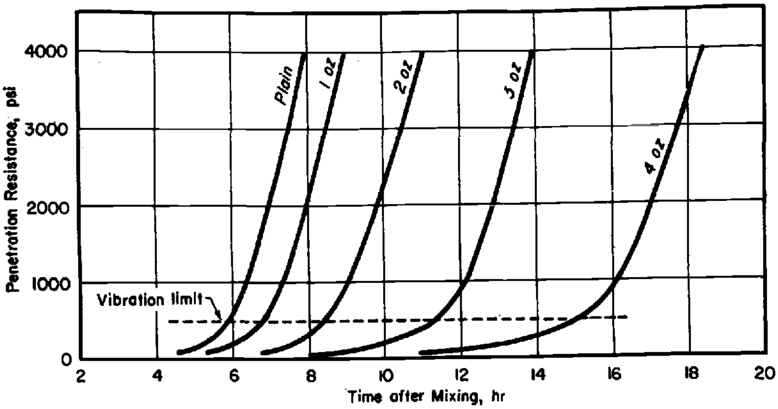

FIG. 12.—An Increasing Dosage of a Retarding Admixture Increases the Time to the Vibration Limit. Thereafter Rate of Hardening Is Similar. Admixture *LP* Here Used with Type II Cement *EP* t 70 to 75 F.

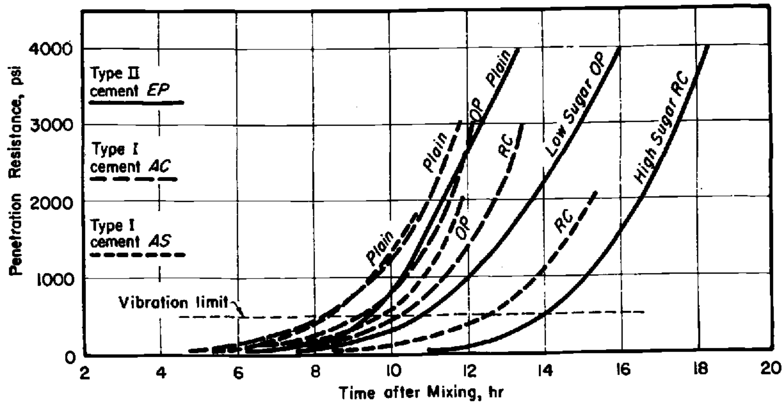

FIG. 13.—At 50 to 55 F Time to Vibration Limit May Be Affected by the Brand and Type of Cement in Combination with ¼ lb per Sack Dosages of Retarding Admixtures, Regardless of Sugar Content.

At lower temperatures it will be noted

that the *QA* and *SO* agents of comparatively high sugar content postpone the vibration limit or initial set only about 1 hr, or 10 to 15 per cent longer than such low-sugared lignin-based admixtures as *OP* and *DP*. At normal and higher temperatures, there is little practical difference between them in this respect. These relationships are also shown in Figs. 9 and 10. Similar relationships are shown in Figs. 13, 14, and 15, except for the considerable retardation when a ½-lb dosage of the high-sugared admixture *RC* is used with type II cement *EP* at a temperature of 90 to 95 F, as shown in Fig. 15.

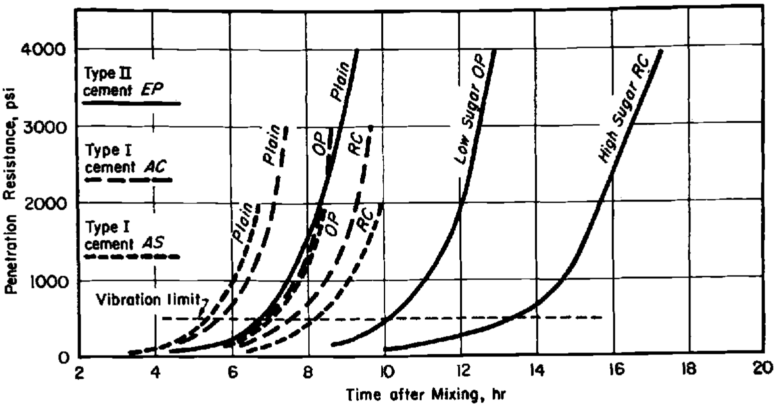

FIG. 14.—At 70 to 75 F Time to Vibration Limit May Be Affected More by the Type and Brand of Cement Than by the Sugar Content of ¼ lb per Sack Dosages of Retarding Admixtures.

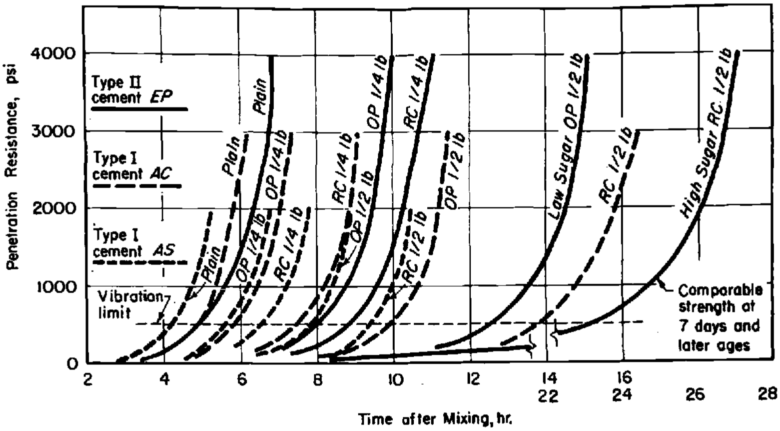

FIG. 15.—At 90 to 95 F Time to Vibration Limit May Depend as much on Type and Brand of Cement as on Sugar Content or Amount of Retarding Admixture.

In Figs. 1, 4, 5, and 6, it may be noted that the high-sugared lignin-based admixtures *SO* and *RC* most often exhibited the highest strength of the group reported.

From these and similar results in earlier laboratory tests elsewhere and from similar good results with high-sugar admixtures in field trials and in regular use, it is concluded that sugar content of itself (as is commonly measured and indicated) is not a critical factor on which approval or acceptance of a water-reducing retarder should be based. Evidently, if a product performs as desired in job concrete and no undesirable properties are imparted to the fresh or hardened concrete, there is no reason to be concerned with its hypothetical content of sugar compounds. Because there is so little evidence that these sugar compounds affect the properties of concrete in proportion to their alleged amounts, it has been suggested by some that these compounds may be in such a form in the admixtures that their action is relatively minor and that the effects of the admixtures are in fact achieved primarily by other elements than sugars, among their ingredients. Moreover, normal $\frac{1}{4}$-lb dosages of compounds containing the higher sugar contents of about 18 per cent would contribute only 0.045 lb of sugar per sack, an amount which, as sucrose, has been demonstrated to be harmless.

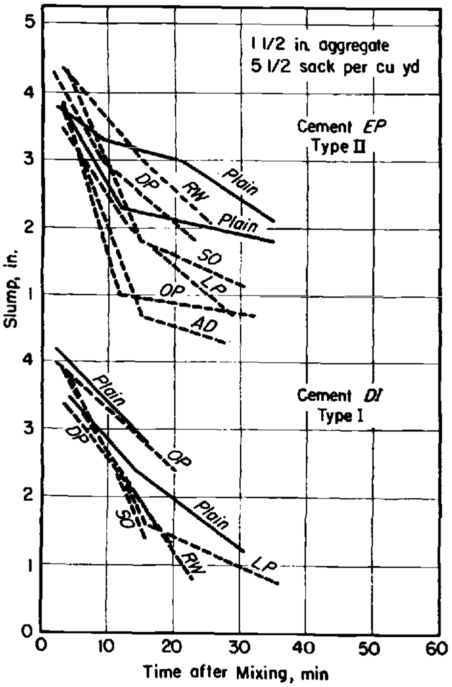

FIG. 16.—Slump Loss with 90 to 95 F Concrete and Various Retarding Admixtures.

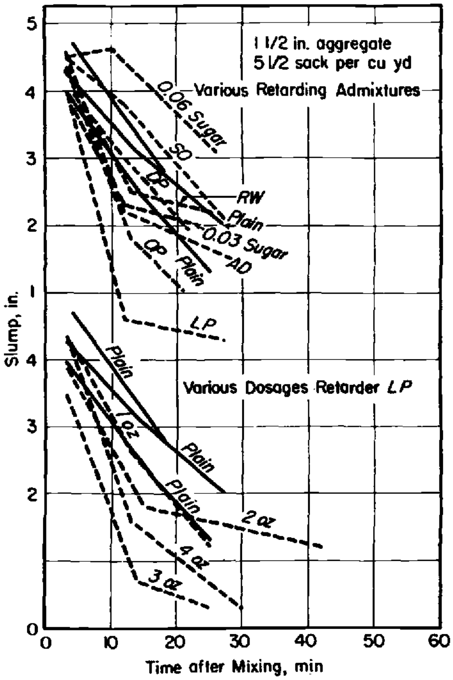

FIG. 17.—Slump Loss with 70 to 75 F Concrete Using Type II Cement *EP*.

Figure 11 illustrates how concrete at various temperatures can be made to have approximately the same vibration limit simply by changing the dosage of the retarding admixture. For instance, for a time to vibration limit as at 52 F, a dosage of $\frac{1}{4}$ lb per sack is required in 72 F concrete and a dosage of $\frac{3}{8}$ lb is required in 92 F concrete. For these data a high-sugared admixture was used. Figure 10 shows that the effects of a low- and a high-sugared admixture are about the same. Figures 12 and 15 show how an increase in dosage at the same temperature lengthens the time required to reach the vibration limit.

Figures 13, 14, and 15 show that the

retarders may have different effects with different cements. A similar variety of effects are found with other retarders and other cements. As may be seen from these figures, particularly Fig. 15, these differences may be considerable. It is therefore emphasized that proposed combinations of retarders and cements, including maximum dosages of retarders, should be tested at probable job temperatures before use is made of retarders on the job. This is particularly important where the work is such that an unexpected delay in setting would result in inconvenient or costly delays in form stripping or other subsequent construction operations.

EFFECT ON SLUMP LOSS

Presumably because most of the water-reducing admixtures were also retarders in that they increased the time required to reach the vibration limit, it has been taken for granted by many that these admixtures also reduced or postponed slump loss. Unfortunately such a helpful effect is not confirmed in many tests of slump loss (see Figs. 16, 17, and 18).

While making many of the laboratory tests reported, slump tests were made on a portion of the test batch at increasing time intervals after mixing. The concrete was not remixed except as it was reworked in filling and rodding the slump cone. After the initial slump was taken as soon as the batch was discharged, one or two other slump tests were made as other test work permitted, up to an age after mixing of 20 to 40 min. Slump was often less than 2 in. after 20 min, although most started at 3½ to 4½ in. Test batches for railroad tunnel lining started with slumps ranging from 4½ to 5½ in., with the expectation that such a slump range would represent concrete as usually placed in side wall and arch forms.

In general, in all the figures showing slump loss measurements, it will be noted that the slope of the lines representing rate of slump loss were essentially parallel, often including the line representing the plain mix without the admixture. Steeper slopes show more rapid slump loss and flatter slopes mean slower slump loss.

Figure 16 shows slump loss with a variety of retarding admixtures in concrete at initial temperatures of 90 to 95 F.

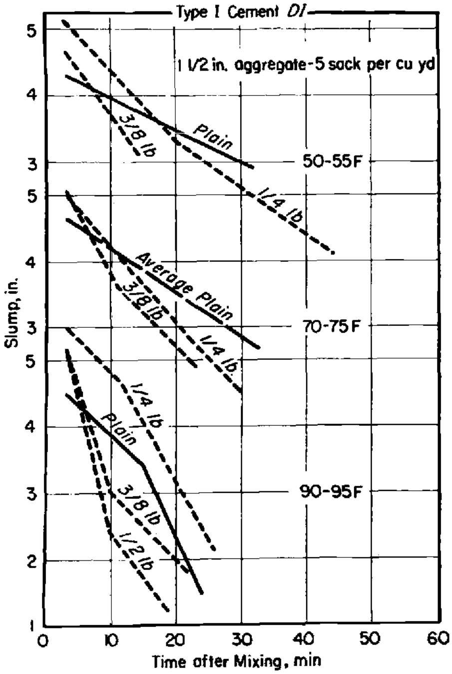

FIG. 18.—Slump Loss as Affected by Temperature and Varying Dosages of Retarder *QA*, Type I Cement *DI*.

These tests were with both type I and type II cement as shown. No marked or consistent difference in slump loss with any of the admixtures is apparent. If anything, in this case the plain mixes with type II cement have a slightly flatter slope and thus exhibit a slightly lower rate of slump loss; but this is not the case with this type II cement at the lower temperatures shown in Fig. 17.

Figure 17 shows slump loss with a

variety of retarding admixtures in concrete at initial temperatures of 70 to 75 F. All lose slump at about the same rate. Figure 17 also shows the effect on slump loss of increasing the dosage of one of the admixtures in 70 to 75 F concrete. A slight increase in slump loss may be seen. Both groups of tests were with type II cement *EP*.

Figure 18 shows the slump losses at various temperatures with admixture *QA*, the admixture that was used in tunnel-lining concrete. It will be noted that the effect of increasing temperature, although noticeable, was not marked. The similar effect of slightly increased slump loss is noticeable for the increased dosages of the admixture. These dosages are within a practical range of use for the temperature shown. These tests were with the type I cement *DI* used in the tunnel-lining concrete.

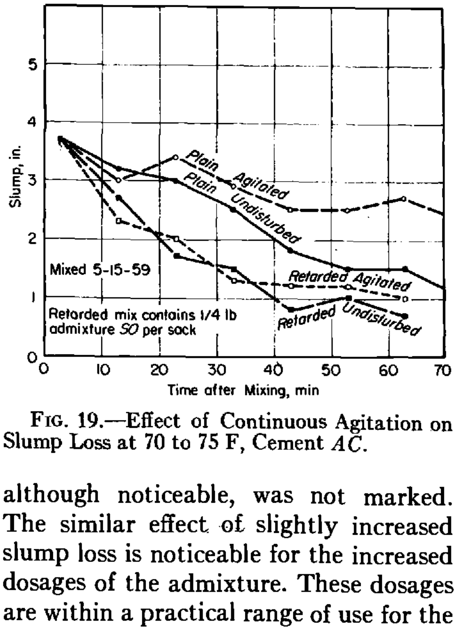

FIG. 19.—Effect of Continuous Agitation on Slump Loss at 70 to 75 F, Cement *AC*.

The rate of slump loss of plain and retarded concrete during continued agitation is shown in Fig. 19, in comparison with the slump loss in the same concretes when undisturbed. From this group of tests it appears that concrete with a retarding admixture is very little different in slump loss under continued agitation than without agitation. It will be noted that agitation appreciably reduced the slump loss of plain concrete.

It would be helpful in many central mixing situations for concrete to lose no more than 25 per cent of its slump in the first 15 or 20 min after mixing. But the fact that it obviously loses much more than this unless it is agitated becomes much less objectionable when the concrete can be made to respond readily to vibration for a considerably longer time by the addition of a suitable retarding admixture. Despite use of these admixtures, concrete must still be handled with dispatch and placed in the shortest time possible after mixing. Otherwise slump loss will be sufficient to encourage use of higher slumps initially to compensate for the loss. But with adjustment of the dosage of a retarder, the vibration limit can be set at any time desired for convenient placing of each layer of concrete to avoid cold joints, and the dosage can be further adjusted to hold this time reasonably constant for any prevailing initial temperature of the concrete. An example of this is indicated in Fig. 11 in which increasing dosages of admixture *QA* at increasing temperatures produce time rate of setting curves with about the same vibration limits in concrete tested for tunnel lining. Other such possibilities are shown in Figs. 13, 14, and 15.

No noticeable difference could be observed in the workability of concrete with and without the admixtures when the slump and air content of the concretes were the same.

EFFECT ON AIR-ENTRAINMENT

Some of the admixtures such as *LP* entrain very little air while others entrain amounts ranging up to 7 or 8 per cent in laboratory mixes at normal dosages, depending on the temperature. Higher amounts of air are entrained at the lower temperatures and with higher dosages of these admixtures. When this gratuitously entrained air is more than is desired, air detraining (defoaming) agents have been successfully employed. Where substantial percentages of entrained air are not needed to improve durability in freezing climates, minimum amounts benefiting workability and cohesion of the fresh concrete are the most that are desired in view of the unfavorable effect on strength of larger amounts. For this reason, in some cases it is preferred that no air be entrained. Actually the strength of concrete containing 5 to 6 sacks of cement per cubic yard is not significantly reduced by entrainment of 2 or 3 per cent of air, if the cement content and slump remain constant. Some of this air is lost through vibration. The benefits of a proper amount of entrained air usually outweigh whatever reduction there may be in strength, if any. Because of these benefits, some prefer to add enough air-entraining agent to entrain at least these minimum amounts of air, and more where durability is a consideration.

An indication of the air-entraining properties of some of the lignin-based admixtures can be obtained from Table III by noting the per cent of air entrained and the amount of supplemental air-entraining agent, if any. In the mixes reported in Table III, an effort was made to hold the air content up to 3.5 per cent ±0.5 per cent. Some tests reported in Table III show that those exceeding this amount can be held down to it with a proper dosage of an air-detraining agent.

It should be noted that air entrainment obtained in laboratory mixes may not be obtained in field mixes. In one case, based on laboratory tests, it was expected it might be necessary to use a defoaming agent to keep air content down to the 2.5 per cent desired only for workability and cohesion in a mix with $2\frac{1}{2}$-in. gravel. Actually it proved necessary, even at 60 F, to add a small dosage of an air-entraining agent to obtain the desired amount of air. This experience re-emphasizes the importance of verifying all aspects of performance of any admixture on the job, under job conditions, and with job materials.

EFFECT ON WATER REDUCTION

Review of the per cent reduction in water requirement attained by means of the various water-reducing admixtures reported in Table III shows that in most cases the reduction ranges from about 5 to 10 per cent. It should be remembered that this is in comparison with the water requirement of plain air-entrained concrete. The average reduction with a $\frac{1}{4}$-lb dosage of the unmodified lignosulfonates in 35 mixes was approximately 8 per cent and for a $\frac{1}{2}$-lb dosage nearly 11 per cent. Other admixtures averaged somewhat less for normal and larger dosages.

It is difficult to see a clearly consistent superiority of one water-reducing admixture over another. More often than not, decreases greater than 10 per cent are apparently the combined result with a higher than usual air content or a larger than usual dosage. Summarization of the data in Table III reveals no clear-cut influence of temperature on water reduction. Neither does it reveal any significant difference which may be attributed to the brand or type of cement except for an indication of less water reduction with one of the type I cements.

Many factors affect accurate determination of the per cent of water reduction. These include primarily not having the same slump and air content and any variables there may be in aggregates, cement, or temperature. Assuming perfect control and uniformity of test batches, it may be that differences in the amount and per cent of water reduction will be found due to different admixtures, different brands and compositions of cement, different aggregates (particularly sands), and different temperatures. Moreover, every day each job will be faced with some combination of these factors. Therefore, from a practical standpoint, the most significant water reduction is that which can be regularly obtained in the largest quantity under conditions and with materials available on the job.

One practical aspect of water reduction is the corresponding effect of making a given water content go farther. In so doing, a greater slump is provided without exceeding the water content for a lower but sometimes impractical slump. Even with no reduction in water content, strength is sometimes slightly improved as appears at 90 days in Fig. 20 for two concretes. Often a combination of some increase in slump, some reduction in water, and some increase in strength is obtained from using a water-reducing admixture.

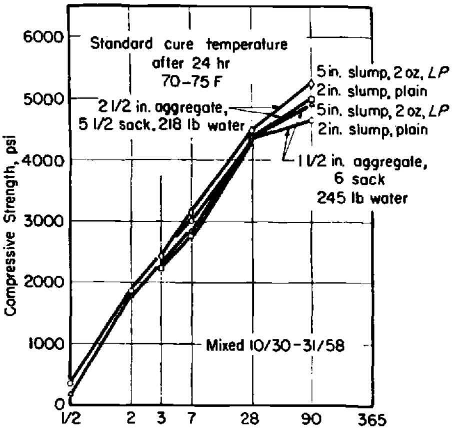

FIG. 20.—Effect of Admixture *LP* in Concrete of Similar Unit Water Content, Cement *EP*.

Another practical aspect of water reduction is the use of it to compensate for job conditions or equipment that inherently demand more water and sometimes more slump than others. One example is to offset to some degree the higher water requirement at higher temperatures. Another is to offset the higher water requirement used for higher slumps to allow for greater slump loss in concrete hauled long distances in truck mixers, particularly in warm weather. Another is to compensate for higher slumps than are sometimes desired in order that truck mixers may discharge expediently.

ACCEPTANCE TESTING AND JOB USE

When a water-reducing retarder is purchased and used on a job, its cost is appreciable, and it is important to know that expected results are being obtained regularly with the product used. Usually a product is supplied with a guaranty and deliveries are made with a certification that the material will perform in a manner to be expected from past performance of the material. A good practical approach to this is a guarantee that performance of subsequent deliveries will compare favorably with that of a substantial sample originally tested.

Where jobs have close control and concrete properties and performance of ingredients are closely observed, it is quite evident when rate of hardening, water requirement, and slump remain unchanged, as use is commenced from a new delivery, that there has been no change in the material. Laboratory test batches can also be made and comparison will establish its performance with that of the standard sample. These tests will include water requirement, time rate of setting, time to reach the vibration limit, and strength at various ages. For such tests a carefully duplicated standard mix must be used with similar fine and coarse aggregate, and cement from the same carefully sealed laboratory supply lot. Thus the admixture sample should be the only variable.

Examples of such tests, the first on

TABLE IV.—COMPARISON OF DIFFERENT LOTS OF ADMIXTURE *QA*—CEMENT *DI*.

¼ lb per sack used. Agrgegate, 1½-in. maximum size.

Mix	Sample	Specific Gravity of Admixture	pH of Admixture	Temperature of Fresh Concrete, deg Fahr	Slump, in.	Air Content, per cent		Unit Weight Fresh Concrete, lb per cu ft	Quantity per cu yd				Time, hr, to Penetration Resistance of		Compressive Strength, psi					
						Meter	Gravity		Air-Entraining Agent, ml	Air-Detraining Agent, ml	Water, lb	Cement, lb	500 psi	4000 psi	12 hr	1 day	2 day	3 day	7 day	28 day
R—17....	Control mix..............	...	...	71	4.3	3.5	4.1	153.2	55	0	263	467	5.2	7.5	192	700	1060	1320	2280	3400
18....	Laboratory *QA*............	1.224	6.6	71	4.7	3.5	4.3	154.0	0	2.0	244	466	6.3	9.1	176	752	1310	1620	2750	3880
19....	First field sample *QA*......	1.196	6.4	71	4.2	3.7	4.3	154.0	0	2.0	244	466	6.3	8.8	168	740	1320	1560	2790	3620
21....	First field sample *QA*......	1.196	6.4	70	3.6	3.2	3.2	155.2	0	2.0	254	471	6.6	9.4	226	727	1210	...	2660	3970
22....	Second field sample *QA*....	1.195	7.2	70	4.0	4.0	4.0	154.0	0	2.0	252	467	7.1	10.0	170	696	1270	...	2660	3880
23....	First field sample *QA*......	1.196	6.4	73	4.0	3.4	3.5	155.2	0	2.0	246	740	6.1	8.6	...	805	...	...	2590	3600
24....	Third field sample *QA*......	1.199	6.8	72	4.0	3.2	3.1	156.0	0	2.0	247	472	6.3	9.0	...	759	...	...	2370	3450
25....	First field sample *QA*......	1.196	6.4	70	3.8	3.4	4.1	153.6	0	2.0	255	464	6.8	9.2	...	933	...	...	2530	3880
26....	Fourth field sample *QA*....	1.205	6.1	70	2.5	2.7	2.7	156.0	0	2.2	258	471	6.1	8.6	...	1030	...	...	2780	3970

Same batch quantities used in all mixes except water. Water adjusted on mix R18, 21, 23, and 25 to give desired slump. Same water used on mixes R19, 22, 24, and 26 as with companion mix.

Fourth field sample *QA* is same product as other samples except slightly lower wood sugars.

the laboratory or standard sample, the others of field samples from subsequent deliveries, appear on Table IV. The close similarity of the resulting concrete data may be noted. This particular admixture is delivered as a 42 per cent solids solution by tank truck, 5000 gal at a time, for use in concrete for tunnel lining. The delivery is made into a 15,000-gal steel storage tank at the roadside at an elevation where the liquid will flow readily down to dispensing equipment in the batching plant. The schematic arrangement of these facilities is indicated in Fig. 21. For best results in safety from overdosage, accuracy, and uniformity, this arrangement includes:

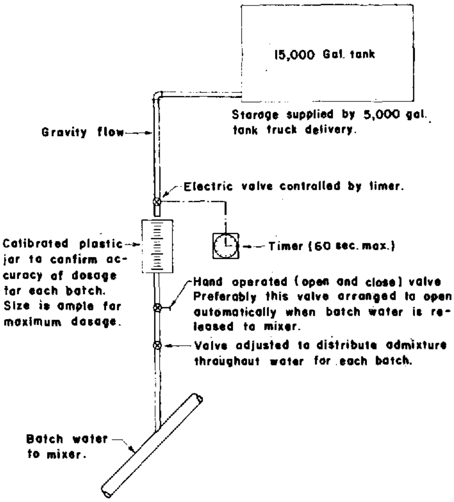

FIG. 21.—Arrangement of Dispensing Facilities for Water-Reducing Retarding Solution. Feather River Project, April 1959.

1. An accurate time-controlled valve for measurement of the correct dosage.

2. A calibrated plastic container large enough to receive each full dose and in which the correctness of each dose can be verified at a glance. This is a must for safe operation.

3. In addition to the release valve, a valve to adjust flow from the plastic container so that the agent will enter the mixer during the entire period the batched water flows.

4. A mechanical stirring device in the supply tank to prevent settling is needed with many but not all admixtures, including air-entraining agents which are best similarly dispensed.

If dispensing is accurate and reliable, there is no evidence in the laboratory testing or field experience that proper dosages of any of the admixtures discussed will under any foreseeable circumstances cause a concrete mix not to set. Accordingly it is important to insist on using dispensing equipment that is accurate, reliable, foolproof, self-checking every batch, and capable of measuring in one operation the quantity for each batch regardless of size. With dispensing facilities of this character, only beneficial results may be expected from proper use of any of the regularly marketed water-reducing and retarding admixtures of either the lignin-based or the hydroxylated carboxylic acid type.

CONCLUSIONS

From these observations we have reached and are operating on the basis of the following conclusions:

1. The brand and type of cement may influence results more than differences in the variety of water-reducing retarders investigated.

2. Concrete compressive strength in less than 24 hr may be influenced more by the temperature of the concrete than by differences in the variety of water-reducing retarders investigated.

3. The time to the vibration limit and the time rate of setting may be influenced more by the brand and possibly the type of cement than by differences in the variety of water-reducing retarders investigated.

4. There was no evidence that sugar content of lignin-based admixtures

should be a cause for concern. Properties of fresh and hardened concrete were satisfactory regardless of sugar content of admixtures used.

5. The many fine distinctions in performance often reported for the various admixtures are extremely difficult to confirm in the most careful of laboratory testing, even in an air-conditioned mixing room with materials preconditioned to constant temperature and moisture content.

6. The rate-of-slump loss is not decreased by any of the retarding admixtures.

7. The effect of water-reducing retarders on air entrainment may be different in laboratory mixes than will be found in field mixes.

8. Under most conditions, most of the available water-reducing admixtures will do a highly satisfactory job, and some with considerable economy.

9. Good performance of such admixtures, at the same cement content and initial slump, includes increased strength, lower water requirement, and set control affording more or less time before reaching the vibration limit.

10. At the same cement and air content and at the same slump, none of the admixtures appeared to impart a noticeable improvement in plasticity or workability of the concrete.

11. Only by tests with job cement and aggregates, preferably in trial runs on the job as well as in the laboratory, can performance of any admixture be properly evaluated for a particular job and purpose.

12. Acceptance tests of job deliveries can be made by comparing their performance with that obtained from repeat tests of the initial sample or an earlier delivery of acceptable material.

13. Successful results on the job cannot be assured unless dispensing equipment, which is available, is accurate and foolproof and capable of measuring in one operation the quantity for each batch regardless of size.

REFERENCES

(1) L. H. Tuthill and W. A. Cordon, "Properties and Uses of Initially Retarded Concrete," *Proceedings*, Am. Concrete Inst., Vol. 52, p. 273 (1955–1956).

(2) Raymond J. Schutz, "Setting Time of Concrete Controlled by Use of Admixtures," *Journal*, Am. Concrete Inst., No. 7, Vol. 30, Jan., 1959, p. 769.

DISCUSSION

Mr. R. B. Bailey.[1]—Our laboratory has done some work to determine the effect of various amounts of sugar on the setting time of concrete. D-mannose comprises about half of the mixture of sugars referred to as "wood sugars" found associated with lignin sulfonates. Starting with a sodium lignin sulfonate containing 12.9 per cent wood sugars, a number of samples were prepared containing increasing amounts of d-mannose to adjust the sugar content, resulting in a series of sodium lignin sulfonates containing from 12.9 to 30.3 per cent wood sugars.

The set time of a standard 5-sack concrete was measured with 0.5 lb per sack of each of these admixtures present, double our recommended amount. Results are shown in the accompanying Fig. 22. The points below 10 per cent sugar are for lots of sodium lignin sulfonate containing the percentage of sugar shown, without the addition of any d-mannose. Measurements were made with a Proctor needle according to the method of Tuthill and Cordon.[2]

Extrapolating to the 0 per cent sugar line, it seems probable that other fractions of the lignin sulfonate composition are retarding the set of the cement. It would also seem that the amount of set retardation can be predicted from the sugar content for a given lignin product and a given set of conditions.

We feel that sugars definitely contribute to the benefit to be gained from the use of admixtures but that the amount should be carefully controlled in the manufacturing process to insure uniform performance on the job.

Mr. H. K. Cook[3] (*presented in written form*).—This paper has added a great deal of valuable information on the laboratory and field use of water-reducing retarders. However, while I am sure that the authors knew what they had in mind with respect to their conclusions, I believe that there is danger of misinterpretation of their conclusions by others who may not be as fully informed. I strongly feel further clarification is necessary because some of the conclusions, if accepted without qualification, contradict industry experience and may be misleading.

I am particularly concerned with conclusions 4 and 5 that sugar content of admixtures is no cause for concern and that differences in the performance of various admixtures are extremely difficult to confirm.

The paper is vague about what is meant by low and high sugar contents. The authors indicate that over 12 per cent is high and that at least one of the admixtures included in their tests had a sugar content of 18 per cent. They state that reliable information was not

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[1] Manager, Chemical Sales, Chemical Products Division, Crown Zellerbach Corp., Camas, Wash.

[2] L. H. Tuthill and W. A. Cordon, "Properties and Uses of Initially Retarded Concrete," *Proceedings*, Am. Concrete Inst., Vol. 52, p. 273 (1955–1956).

[3] Vice-President for Engineering, The Master Builders Co., Cleveland, Ohio.

obtained on the sugar content of the lignosulfonates.

The chemistry of lignin and lignosulfonates is very complex and they may contain several types of sugar as well as other carbohydrates.

The number and identity of sugars and of non-sugar carbohydrates and reducing agents present in a given lignin material depends on the origin of that material and the processing that it has experienced. Sugars present in effluents of yeast and alcohol plants, for example, are principally pentoses, that is, sugars which are nonfermentable in those particular processes. In the unprocessed lignin material, on the other hand, the easily-fermentable hexoses predominate.

The calculated content of sugar and other carbohydrates in lignin material varies both with the analytical method applied and with the assumptions which underlie the calculation itself. Normally, the various carbohydrates are determined as a group and then calculated as the equivalent of a particular, arbitrarily-selected sugar. Variability of calculated carbohydrate content for the same lignosulfonate can exceed a factor of two. For example, the summation of individual sugars determined by paper chromatography may be less than half the total carbohydrate content of the same material indicated by application of a nonspecific reagent like anthrone and calculating the result as equivalent mannose. If a lignosulfonate contained 18 per cent of carbohydrates as determined by Fehling's method and calculated as mannose or glucose, it is believed that there would be danger of serious difficulty with the concrete in which it was used. On the other hand, it has been found through research that for some lignosulfonates, if the total carbohydrate content is reduced by processing below a certain point, the water-reducing properties of the lignosulfonates are adversely affected. While this is not potentially of as much concern as too high a carbohydrate content, the user at best is not getting his money's worth in terms of performance.

If "high sugar content" is of no concern then several large construction agencies were quite wrong in their conclusions 20 yr or so ago when several concrete structures failed to set up because of the use of lignosulfonate with uncontrolled carbohydrate content.

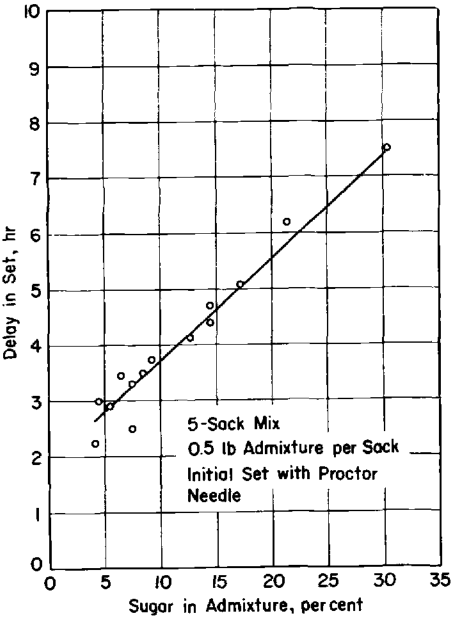

FIG. 22.—Effect of Sugar on Set Time of Concrete.

Further, a considerable amount of time and money has been invested in developing and placing in production, facilities for the control of carbohydrate content of lignin. It is obvious that this was not done without positive and sometimes spectacular and costly evidence that there was a real need for such control.

I therefore feel rather strongly that the authors, for the benefit of those not so well informed, should establish more clearly what they mean by high sugar content being of no concern.

The statement in conclusion 5 that, "The many fine distinctions in performance often reported for the various admixtures are extremely difficult to confirm . . . . " is contrary to the results obtained in hundreds of tests conducted in our Research and Engineering Laboratories and is not borne out by the data presented by the authors on either strength or rate of hardening.

Our research laboratory is concerned with the development of improved admixtures for concrete. Over the years a very considerable amount of effort has been expended in determining differences in materials as they affect the properties of concrete. If the statement by the authors is to be taken literally, we would have closed the doors to our research laboratory a long time ago. Actually, the test data presented by the authors, in our opinion at least, confirm what we have also found. Strengths of concretes containing the various admixtures in what appear to be comparable mixtures with the same cement and with comparable dosages of the admixtures differ by as much as 1000 psi at 28 and 90 days and by approximately 2000 psi with increased amounts of the admixtures. Rates of hardening, at the limit of vibration, vary by as much as 3½ hr, the high-sugar admixtures producing the longer periods of retardation.

For the type of construction in which the authors are engaged it is possible that the above differences are only considered as fine distinctions in performance. It is believed, however, that such differences would have considerable importance in many structural concrete jobs both in over-all cost and also in the time required for finishing concrete floors or in slip-form work, to cite only two examples.

It appears to be the philosophy of the authors that variations in or between admixtures can best be dealt with by varying the rate of use of the admixture. It is agreed that rate of hardening can be controlled very closely by varying the amount of retarder used. However, this variation in amount used will also affect the amount of water reduction obtained, the air content, strength, and other desired properties of the concrete. While on well-controlled projects such as those of the authors, acceptable results can be obtained, the elaborate and costly control procedures required would be impractical for the great majority of relatively small construction projects throughout the country. Even on large well-controlled projects it would appear that some sacrifice of optimum desirable properties would be bound to occur.

It is suggested that a more satisfactory approach for universal application is the well-established procedures of adequate performance specifications assuring specific uniformity so that best advantage can be taken of all of the improvements in concrete properties. For example, the greatest beneficial property of these admixtures is believed to be water reduction. Through water reduction, many of the properties of both fresh and hardened concrete are made better. Secondary consideration is given to the property of retardation inasmuch as this is not too often desired in most structural concrete. There seems to be a too prevalent belief that water reduction cannot be obtained without retardation. Such is not the case since there are a number of available water-reducing admixtures which do not produce retardation and some that even produce acceleration of set. Performance specifications would permit the user to specify the particular properties he required for his particular job or portion thereof without the necessity of varying greatly the amount of admixture required and the necessity of sacrificing one desirable property in order to obtain optimum performance with respect to another. Even when retardation is one of the more desirable properties, as it is for many of the jobs with which the authors are concerned, it is possible to obtain retarders that are uniform in composition and performance. With adequate performance specifications, acceptance tests of job deliveries of admixtures advocated by the authors could be simplified to simple and quick tests of composition such that the shipment could be released for immediate use. While acceptance tests on a performance basis may be satisfactory for relatively large shipments that can be held in storage until strength tests mature, it would not be practical for the smaller user, particularly when shipment is made in drums or bags.

The above comments apply only to acceptance of job deliveries. I am in complete agreement with the authors on the necessity of tests with job cement and aggregate as the preferred procedure in the original selection of the admixture or admixtures to be used on a specific job.

While I disagree with some of the conclusions of the authors, to the extent discussed above, I do want to commend them for a very valuable contribution to the use of admixtures. Certainly I have no fears that in capable hands such as theirs good results will be obtained through the use of water-reducing retarders. My concern is over the possible misinterpretation of their conclusions by those not so well informed and the belief that the relatively small user may feel either that he can successfully use a lignin from any source without concern over the performance he will get, or on the other hand will be scared by the complex nature of the suggested job acceptance requirements to the point that he will not attempt to obtain the benefits available through the use of admixtures.

Having worked with some of these materials daily for over 5 yr I am quite aware of the benefits to be obtained as well as the difficulties that can be encountered in the use of admixtures. The responsible manufacturers of admixtures as well as members of the cement, aggregate, and concrete industries I am sure will agree with me that the industry can be done very serious harm if the average user concludes from this paper that he need not concern himself with the sugar content of admixtures and that differences in performance between admixtures are indistinguishable.

MR. E. A. ABDUN-NUR[4] (*by letter*)—The authors have given the profession an excellent contribution, made doubly useful because they have coupled laboratory work with field experiences.

The conclusions that the early compressive strength, time-to-vibration limit, and time rate of setting may be influenced more by temperatures, brand and type of cement, and other construction factors than by differences in the brands of water-reducing retarders are in agreement with the writer's field experience. No one will deny that there are small differences between the admixtures marketed by different manufacturers, but such differences are so small in eventual effect (as compared to other variables that affect the finished product in practical applications), that these become of very minor influence in the finished concrete.

Although the authors do not present data or indicate that their work with the sugar content of the admixtures was based on the determination of sugar contents in the various admixtures by the same method of analysis, in order to make such determinations subject to

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[4] Consulting Engineer, Denver, Colo.

valid comparison, there is no doubt from experience in the field that the amount of sugar in present-day water-reducing retarders does not appear to damage or have any ill affects on the concrete in which they may be used.

Close control of the sugar content for any given make of admixture is definitely an important requirement in order to permit a realistic control of the concrete batching, but a difference of from about 8 per cent to 15 per cent (the range of admixtures on the market) in two different admixtures would not make one better or worse than the other for use, provided the properties of the mix and the mix proportions are determined using the same admixture as will be used in the field operation. The amount of sugar in the final mix is very small, even though one admixture may have twice the sugar found in the other.

The authors conclude that many fine distinctions between different admixtures are not warranted when judged by the final performance in the field. This falls in line with the two observations discussed above in that the small differences in the admixtures themselves are overshadowed by many other more important variables in the field. Fine distinctions may be necessary for competitive promotion and selling of products by the various manufacturers, but the writer is in full agreement with the authors that there is no real practical difference in the final analysis, as long as the concrete mix is adjusted to the particular admixture being used in order to provide the desired properties.

The difference found in air entrainment between laboratory mixes and field mixes using the same materials and proportions may be due to poorer mixing in field operations than in carefully mixed laboratory batches. Nearly every case of this type of inconsistency that has developed on work with which the writer has been connected was eventually traced to poorly adjusted mixers and improper mixing operations and was successfully corrected by taking proper measures. It is felt that one of the most sensitive measures of field mixer performance would be a comparison of the field air content with that obtained by some standard laboratory mixing—that is, if the latter could be standardized for the purpose of such comparison.

The importance of foolproof and accurate dispensing equipment cannot be overemphasized. The authors' suggested features for proper dispensing equipment go a long way towards meeting these objectives. Another feature is, however, needed to make such an installation really foolproof. The discharge of the calibrated plastic jar, which is in full view of the operator, should be automatic and should be tripped by the same mechanism that trips the water. If this is not done, a busy operator may occasionally forget to trip it, thus permitting a batch through without the admixture.

The authors are to be highly commended for providing the profession with a very practical down-to-earth appraisal of the field problems encountered in the use of water-reducing retarders and the effects of such problems on the finished concrete.

MESSRS. L. H. TUTHILL, R. F. ADAMS, AND J. M. HEMME (*authors' closure*).—The authors are appreciative of these discussions which have significantly supplemented the paper. Mr. Bailey's data confirms the suggestion we mentioned that other compounds than the wood sugars were also responsible for the effects of the lignin-based admixtures.

Mr. Cook's discussion is particularly helpful in emphasizing the complexity of the sugar element in the lignin-based admixtures and the consequent complexity of determining their character and amount. Probably this is a good reason why such tests are not practical for inclusion among acceptance criteria. Fortunately, as we and Mr. Abdun-Nur have pointed out, the amount of sugar is unimportant as long as it is uniform in the admixture as used, and as long as the admixture meets the requirements of the job on which it is used.

The controls Mr. Cook describes to to secure uniformity are indeed well merited, and it is certainly not our intent to diminish their importance because it is by such means that reliable materials and consistent results are obtained. Nevertheless, continuing experience suggests that the spectacular and costly evidence which Mr. Cook says inspired these controls may have been produced by some variation in the joint performance of admixture and cement when there was no change in the dosage or character of the admixture, and perhaps no change in any property of the cement as measured by standard ASTM tests that ordinarily would be considered significant.

When the admixture is a liquid dispensed from a supply of several thousand gallons in a large job storage tank, and its uniformity is further attested by substantially uniform concrete properties and strength for nearly a year, the cement is the only active ingredient in which change is possible. But it can happen. Suddenly, after months of compatible and very gratifying performance, the concrete was grossly and variably retarded in setting; not in a few batches which might indicate overdosage but in awesome continuity and quantity, despite accurate, foolproof dispensing (Fig. 21). Such a supply of liquid admixture could not have been so suddenly and variably different, and all tests indicated it was unchanged.

Probably others too have come to realize that use of a standard, well controlled product by no means affords complete assurance that some such disturbing evidence of incompatibility with job cement will not occur. We can cite other cases. Laboratory rate of hardening tests (ASTM Method C 403)[5] also show that such incompatibility is possible with more than one well-controlled lignin-based material. There is much yet to be learned about why even the admixtures which are well controlled for uniformity in production, have markedly different, and sometimes seriously abnormal, rate of hardening curves with different cements and sometimes with different mill lots of the same cement brand.

Perhaps we can make no better reply to Mr. Cook's comments on our fifth conclusion, on fine distinctions between different admixtures, than to refer to Mr. Abdun-Nur's fifth paragraph with which we fully agree.

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[5] Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles, 1958 Book of ASTM Standards, Part 4.

EFFECT OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES AS INFLUENCED BY PORTLAND CEMENT COMPOSITION

By Milos Polivka[1] and Alexander Klein[2]

Synopsis

Laboratory investigations carried out at the University of California Engineering Materials Laboratory on concretes containing the two most common types of water-reducers and retarders show that their effectiveness is greatly influenced by the composition of the portland cement.

The effects of three lignin type and of one organic acid type water reducers on properties of fresh concretes and compressive strength of concretes made with four different California portland cements is evaluated. In a second program, a second organic acid type water reducer was used in concretes made with some twenty American cements; compressive strengths of concretes containing these various cements are reported.

Also presented are data demonstrating the effect of water reducers and retarders on the early-age heat of hydration of different cements.

During early investigations with water reducers and with set retarders for use in grouts and in concretes, it was observed that the effectiveness of these admixtures was influenced by the composition of the portland cement. As a result of these findings, more comprehensive investigations were carried out to evaluate the properties of a large number of concretes containing various portland cements and the most common types of water reducers and set retarders.

Reported are the effects of cement composition on the properties of fresh concretes and on the compressive strength of hardened concretes containing water reducers and on the stiffening characteristics of concretes containing set retarders. In all, nine admixtures representing classes 2, 3, and 4 were evaluated in combination with 32 brands of portland cement produced in the United States. All cements were either type I or type II. Also reported are the effects of two class 3 water-reducing retarders on the early-age rates of hydration and setting as determined by heat of hydration and by time of set tests.

It is demonstrated that portland cement composition has a significant influence on the effectiveness of water reducers and set retarders in performing their function at both early and later ages of hardening of concrete.

Although a general relationship between the chemical composition of portland cement and effectiveness of admixtures is developed, no definite single cause of variation between cements has been established.

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[1] Associate Professor of Civil Engineering. University of California, Berkeley, Calif.

[2] Research Engineer and Lecturer in Civil Engineering, University of California. Berkeley, Calif.

MATERIALS AND TESTS

The water reducers and set retarders used are classified according to type in Table I and designated by letters *A* to *I*. They include two admixtures (*C* and *D*) of class 2, three (*E*, *H*, and *I*) of class 3, and four (*A*, *B*, *F*, and *G*) of class 4.

The 32 type I and type II portland cements were from plants widely distributed throughout the United States. Oxide analyses, total alkalies as Na_2O, and compound compositions, are shown in Table II. Altogether, 16 type I and 16 type II cements were employed.

The aggregates were natural sand and gravel, well graded to a maximum size of $\frac{3}{4}$ in.

The cement content of concretes containing water reducers was made lower than that of the corresponding control mixes, without water reducers, in order to produce comparable 28-day compressive strengths.

Although some of the water reducers caused entrainment of air, the presence of additional air in the concretes did not seem to affect the general relationship between their performance and the chemical composition of the portland cement.

For any single phase of the investigation, all concretes were of like consistency. Consistencies reported are in terms of nominal slump rather than individual values for each test. The slumps were all within $\frac{1}{4}$ in. of the nominal value. The water requirements, given in terms of water-cement ratios by weight or amount of water per cubic yard of concrete, are net values based on aggregates in a saturated, surface-dry condition.

For compression tests, the specimens were 3 by 6-in. cylinders, standard cured up to age of test. Three such specimens were employed for each test condition.

A conduction calorimeter, similar to that described by Carlson[3] operated with a water-bath temperature of 77 F, was used to determine early-age heats of hydration. Each test was carried on for at least 2 days, and in the case of the more highly retarded cement pastes, up to 4 days. The rate of heat of hydration in each test was indicated by a recorded curve, and the magnitude of the heat of hydration was determined from the area under the curve. For each test condition, time to reach maximum rate of heat of hydration was noted and is hereafter designated as "peak time." This maximum rate of heat of hydration is designated as "maximum rate."

TABLE I.—CLASSIFICATION OF WATER REDUCERS AND SET RETARDERS.

Admixture	Description	
	Class	Type
C[a] ...... *D*	2	Modifications of derivatives of lignosulfonic acids and their salts
E ...... *H* ...... *I*	3	Hydroxylated carboxylic acids and their salts
A[a] ...... *B*[a] ...... *F*[a] ...... *G*[a]	4	Modifications or derivatives of hydroxylated carboxylic acids and their salts

[a] Air-entraining type.

Setting times of cement pastes having a water-cement ratio of 0.40 by weight were determined by means of a Vicat apparatus. This relatively high water-cement ratio for a neat paste was selected *in lieu* of normal consistency in order to provide a basis for correlating setting times with rates and amounts of heat of hydration at early ages obtained by the use of the conduction calorimeter test

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[3] Roy W. Carlson, "The Vane Calorimeter," *Proceedings*, Am. Soc. Testing Mats., Vol. 34, Part II, pp. 322–328 (1934).

wherein a water-cement ratio of 0.40 is employed.

Time of initial setting was determined according to ASTM Method C 191.[4] To determine final set with the Vicat needle, the paste specimen was inverted after initial set, and subsequent penetrations were made on the bottom surface in order to avoid irregularities near the top surface resulting from bleeding. This procedure is particularly important for retarded pastes because such bleeding increases the concentration of admixture at the top surface. The technique provided reproducibility not obtainable when penetrations were made on the top surface. However, because it is believed that the determination of peak time is inherently more precise than any final

TABLE II.—CHEMICAL COMPOSITION OF PORTLAND CEMENTS.

Cement	Type[a]	Oxide Analysis, per cent								Total Alkalies as Na_2O, per cent	Compound Composition, per cent			
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O		C_3S	C_2S	C_3A	C_4AF
No. 1....	I	22.0	3.0	5.4	64.0	1.8	1.9	1.20	0.08	1.25	47	28	9	9
No. 2....	I	21.3	2.8	6.2	63.2	2.5	2.2	0.75	0.60	1.15	44	28	12	9
No. 3....	II	22.4	2.9	4.4	62.5	4.3	1.7	0.63	0.23	0.78	45	30	7	9
No. 4....		23.8	2.7	4.0	65.1	1.6	1.4	0.51	0.29	0.70	49	31	6	8
No. 5....	I	21.8	2.5	5.9	63.9	1.7	2.2	1.11	0.10	1.18	45	28	11	8
No. 6....		20.7	3.0	6.4	62.7	3.3	1.7	0.41	0.59	0.80	45	25	12	9
No. 7....		20.8	2.4	6.5	62.8	3.3	1.8	0.43	0.47	0.74	46	25	13	7
No. 8....		20.8	3.4	6.1	62.7	3.1	2.3	0.40	0.50	0.73	45	26	10	11
No. 9....		22.6	2.7	5.3	64.8	1.8	1.4	0.54	0.24	0.70	49	28	10	8
No. 10....		22.0	2.5	5.3	64.5	1.6	2.2	0.37	0.39	0.63	50	26	10	8
No. 11....		23.7	2.2	4.9	65.9	1.0	1.2	0.43	0.12	0.51	49	31	9	7
No. 12....		21.8	2.2	6.0	63.6	3.0	1.7	0.32	0.28	0.50	45	29	12	7
No. 13....		22.8	2.3	4.3	65.9	1.3	1.4	0.23	0.36	0.47	58	21	8	7
No. 14....		21.1	2.6	6.0	63.9	2.7	2.0	0.25	0.16	0.36	50	22	12	8
No. 15....	II	22.1	3.2	5.1	63.8	2.7	1.7	0.40	0.46	0.70	48	27	8	10
No. 16....		20.6	4.8	5.9	62.4	2.8	1.6	0.28	0.64	0.70	46	24	8	14
No. 17....		22.6	3.4	5.0	64.0	1.1	1.4	0.25	0.63	0.67	47	30	7	10
No. 18....		22.5	3.6	4.9	64.4	1.2	1.8	0.35	0.45	0.65	48	29	7	11
No. 19....		22.0	3.5	4.9	62.1	4.2	1.8	0.32	0.39	0.60	43	30	7	10
No. 20....	II	23.0	2.8	4.1	63.1	4.0	2.0	0.32	0.38	0.57	45	32	6	9
No. 21....		24.5	2.9	4.3	64.8	1.3	1.3	0.42	0.22	0.56	42	39	6	9
No. 22....		23.0	3.2	4.6	64.3	1.3	1.8	0.24	0.46	0.54	46	31	7	10
No. 23....		22.2	3.0	4.4	62.1	4.1	1.7	0.28	0.39	0.54	45	30	7	9
No. 24....		22.5	4.4	5.1	63.8	0.6	1.7	0.26	0.29	0.45	43	32	8	14
No. 25....		23.7	3.0	4.5	64.5	1.3	1.6	0.29	0.16	0.40	43	36	7	9
No. 26....	I	22.0	2.5	4.6	63.5	4.0	2.0	0.41	0.22	0.56	52	23	8	8
No. 27....	II	24.3	2.8	4.3	66.4	0.8	1.2	0.35	0.24	0.51	45	36	7	9
No. 28....	I	24.0	2.8	2.7	66.8	0.7	1.7	0.05	0.15	0.15	60	23	2	8
No. 29....	I	20.4	7.7	1.9	63.1	2.8	2.1	0.43	0.66	0.87	42	27	17	6
No. 30....	II	21.6	3.1	4.8	62.1	4.0	1.9	0.45	0.19	0.58	46	27	7	10
No. 31....	I	22.8	2.6	4.2	65.7	1.1	1.9	0.46	0.15	0.56	56	23	7	8
No. 32....	II	23.5	4.2	3.9	63.1	1.6	1.8	0.33	0.15	0.43	41	36	3	13

[a] Meeting ASTM chemical requirements for the type shown.[5]

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[4] Standard Method of Test for Time of Setting of Hydraulic Cement by Vicat Needle (C 191 – 58), 1958 Book of ASTM Standards, Part 4, p. 188.

set determination, peak time is used in place of time of final set in the analysis of the test results.

EFFECT OF CEMENT COMPOSITION ON PROPERTIES OF CONCRETES CONTAINING WATER REDUCERS

Class 4 Water Reducer with Representative California Cements:

This investigation was designed to evaluate the effect of the cement composition of four representative California cements on the performance of water reducer *A* (class 4), which was of the air-entraining type. Determined were properties of fresh concretes and their compressive strengths at ages 3, 7, and 28 days. The amount of water reducer employed was 0.175 lb per sack of cement. Of the four portland cements employed, two were ASTM type I and two were ASTM type II.[5] The control concretes had a nominal cement content of 5¼ sack per cu yd, and concretes containing water reducer *A* had a nominal cement content of 4¾ sack per cu yd. The results of these tests are shown in Table III, arranged in order of decreasing alkali content of the cements. The total alkali content expressed in terms of Na_2O was high (1.25 and 1.15 per cent) in two of the cements and moderate (0.78 and 0.70 per cent) in the other two cements. The two high-alkali cements (cements Nos. 1 and 2) were of normal type I composition; their C_3A contents were 9 and 12 per cent, respectively.

TABLE III.—EFFECT OF WATER REDUCER *A* ON COMPRESSIVE STRENGTH OF CONCRETES CONTAINING REPRESENTATIVE CALIFORNIA CEMENTS.

Portland Cement							Water Reducer	Water-Cement Ratio, by weight	Cement Content, sack per cu yd	Compressive Strength (3 by 6-in. cylinders; standard curing)					
	Type	Composition, per cent								3 days		7 days		28 days	
		C_3S	C_2S	C_3A	C_4AF	Alkali as Na_2O				psi	per cent	psi	per cent	psi	per cent
No. 1......	I	47	28	9	9	1.25	none	0.53	5¼	1490	100	2420	100	3860	100
							A	0.49	4¾	1840	123	2540	105	3710	96
No. 2......	I	44	28	12	9	1.15	none	0.54	5¼	1940	100	2980	100	4560	100
							A	0.48	4¾	2450	126	3240	112	4410	97
No. 3......	II	45	30	7	9	0.78	none	0.54	5¼	1520	100	2440	100	3990	100
							A	0.48	4¾	2190	144	2990	123	4280	107
No. 4......	II	49	31	6	8	0.70	none	0.54	5¼	1560	100	2540	100	4340	100
							A	0.47	4¾	2550	164	3590	141	4810	111

NOTE.—Gravel aggregate, maximum size ¾ in.; nominal slump 3 in.; nominal air content of plain mixes 2 per cent, of mixes containing admixture 5½ per cent; amount of water reducer *A* 0.175 lb per sack of cement.

The use of admixture *A* reduced the water-cement ratio of the concrete containing cement 1 by only 0.04, of concretes containing cements Nos. 2 and 3 by 0.06, and of concrete containing cement 4 by 0.07. The relative magnitudes of the strength values indicate that the effect of the water-reducer on compressive strength cannot be explained by the reductions in water-cement ratios alone but must also be a function of cement composition. This water-reducer's effec-

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[5] Standard Specifications for Portland Cement (C 150 – 56), 1958 Book of ASTM Standards, Part 4, p. 1.

TABLE IV.—EFFECT OF WATER REDUCER *B* ON COMPRESSIVE STRENGTH OF CONCRETES CONTAINING DIFFERENT BRANDS OF TYPE I AND TYPE II CEMENTS.

Portland Cement							Water Reducer	Water-Cement Ratio, by weight	Compressive Strength (3 by 6-in. cylinders, standard curing)					
	Type	Composition, per cent							3 days		7 days		28 days	
		C_3S	C_2S	C_3A	C_4AF	Alkali as Na_2O			psi	per cent	psi	per cent	psi	per cent
No. 5	I	45	28	11	8	1.18	none	0.53	1750	100	2690	100	3860	100
							B	0.51	2020	115	2740	102	3870	100
No. 6		45	25	12	9	0.80	none	0.54	1660	100	2730	100	4020	100
							B	0.50	2210	133	2920	107	4120	102
No. 7		46	25	13	7	0.74	none	0.55	1900	100	3020	100	4620	100
							B	0.52	2360	124	3070	102	4410	96
No. 8		45	26	10	11	0.73	none	0.55	1960	100	3060	100	4560	100
							B	0.51	2220	113	3070	100	4510	99
No. 9		49	28	10	8	0.70	none	0.54	1660	100	2760	100	4040	100
							B	0.50	2000	121	2770	100	3880	96
No. 10....		50	26	10	8	0.63	none	0.57	1720	100	2680	100	4380	100
							B	0.49	2680	156	3800	142	5040	115
No. 11....		49	31	9	7	0.51	none	0.54	1690	100	2700	100	4310	100
							B	0.51	2310	137	3050	113	4260	99
No. 12....		45	29	12	7	0.50	none	0.56	1660	100	2700	100	4480	100
							B	0.51	2180	131	3030	112	4570	102
No. 13....		58	21	8	7	0.47	none	0.54	2240	100	3520	100	4870	100
							B	0.50	2720	121	3580	102	4790	98
No. 14....		50	22	12	8	0.36	none	0.57	1670	100	2600	100	3910	300
							B	0.54	2130	128	2930	113	4200	107
No. 15....	II	48	27	8	10	0.70	none	0.55	1900	100	3340	100	4890	100
							B	0.52	2560	129	3600	108	5200	106
No. 16....		46	24	8	14	0.70	none	0.51	1640	100	3080	100	4800	100
							B	0.48	2080	127	3430	111	4940	103
No. 17....		47	30	7	10	0.67	none	0.53	1950	100	3050	100	4660	100
							B	0.49	2520	129	3410	112	4770	102
No. 18....		48	29	7	11	0.65	none	0.53	2110	100	3270	100	5160	100
							B	0.50	2670	127	3720	114	5330	103
No. 19....		43	30	7	10	0.60	none	0.54	1630	100	2510	100	4260	100
							B	0.50	2040	125	2890	115	4360	102
No. 20....		45	32	6	9	0.57	none	0.56	1420	100	2310	100	3570	100
							B	0.50	1950	138	3150	136	4440	124
No. 21....		42	39	6	9	0.56	none	0.53	1250	100	2240	100	4000	100
							B	0.49	2090	167	3010	134	4600	115
No. 22....		46	31	7	10	0.54	none	0.54	1890	100	2890	100	4620	100
							B	0.50	2360	125	3090	107	4840	105
No. 23....		45	30	7	9	0.54	none	0.54	1340	100	2340	100	3740	100
							B	0.50	1940	145	3110	133	4560	122
No. 24....		43	32	8	14	0.45	none	0.53	1380	100	2240	100	4490	100
							B	0.50	1830	133	2800	125	5000	111
No. 25....		43	36	7	9	0.40	none	0.56	1070	100	1740	100	3060	100
							B	0.51	1800	168	2760	158	4310	141

NOTE.—Cement content of concretes without admixture 5⅓ sack per cu yd, with admixture 5 sack per cu yd; gravel aggregate, maximum size ¾ in.; nominal slump 3 in.; nominal air content of plain mixes 2 per cent, of mixes containing water reducer 5½ per cent; dosage of admixture *B* 0.20 lb per sack of cement.

tiveness in improving compressive strength appears to be related to the alkali and C_3A contents of these cements. The admixture is more efficient in improving the compressive strengths of concretes containing the cements of moderate alkali content (cements Nos. 3 and 4) than of those containing the high-alkali cements (cements Nos. 1 and 2). Admixture *A* increased the 3-day compressive strength of the concrete containing cement No. 4 by 64 per cent but the concrete containing high-alkali cement 1 by only 23 per cent. In general, however, these marked differences tend to decrease with age.

Class 4 Water Reducer with Twenty-One Type I and Type II American Cements:

Results obtained with the four California cements prompted the investigation of the effectiveness of a class 4 air-entraining type water reducer (admixture *B*) in concretes containing 21 American cements produced outside of California. Ten of these cements were of type I and eleven of type II composition. Again, properties of fresh concretes and compressive strengths at ages 3, 7, and 28 days were determined. The cement content for the control mixes was 5⅓ sack per cu yd, and for the concretes containing admixture *B* in the amount of 0.20 lb per sack of cement was 5 sack per cu yd. Results of this series of tests are summarized in Table IV, arranged in the order of decreasing alkali content of the cements, with the two types (I and II) grouped separately.

The alkali content of the type I cements ranged from 1.18 per cent (cement No. 5) to 0.36 per cent (cement No. 14) and of the type II cements from 0.70 per cent (cement No. 15) to 0.40 per cent (cement No. 25). The C_3A content of the type I cements ranged from 8 to 13 per cent and of the type II cements from 6 to 8 per cent.

For the concretes containing two type I cements, the use of the admixture reduced the water-cement ratio by 0.02 (cement No. 5) to 0.08 (cement No. 10). The water-cement ratios for the other eight concretes containing type I cements were reduced in amounts varying between 0.03 and 0.05.

The data for the type I cements (Table IV) reveal no fixed relationship between the alkali content of the cement and the efficiency of the admixture in improving compressive strength, although on the average the admixture was more effective with the cements of lower alkali content, as shown in Table V which gives the average values of compressive strengths of concretes containing the first 5 cements (Nos. 5 to 9) which are of higher alkali content (0.70 to 1.18 per cent) and of the remaining 5 cements (Nos. 10 to 14) of lower alkali content (0.36 to 0.63 per cent).

A similar comparison of the compressive strengths of the concretes containing type II cements (Table IV) reveals that again on the average the admixture was more effective with the cements of lower alkali content. The average compressive strength values for the 5 cements (Nos. 15 to 19) of higher alkali content (0.60 to 0.70 per cent) and of the 6 cements (Nos. 20 to 25) of lower alkali content (0.40 to 0.57 per cent) are given in Table VI.

A comparison of the values given in the preceding two tabulations shows that on the average for both type I and type II cements the percentage increase in compressive strength of concretes containing water reducer *B* was greater for the lower alkali cements than for those of the higher alkali content. It may also be noted that on the average the admixture was more effective with the type II cements. The average compressive strengths of concretes containing the ten different brands of type I cement

TABLE V.

Type of Cement	Water Reducer	Cement Content, sack per cu yd	Compressive Strength					
			3 days		7 days		28 days	
			psi	per cent	psi	per cent	psi	per cent
			AVERAGE FOR 5 CEMENTS					
Type I higher alkali (0.70 to 1.18 per cent)	none	5⅓	1790	100	2850	100	4220	100
	B	5	2160	121	2910	102	4160	99
Type I lower alkali (0.36 to 0.63 per cent)	none	5⅓	1800	100	2840	100	4390	100
	B	5	2400	133	3280	116	4570	104

TABLE VI.

Type of Cement	Water Reducer	Cement Content, sack per cu yd	Compressive Strength					
			3 days		7 days		28 days	
			psi	per cent	psi	per cent	psi	per cent
			AVERAGE FOR 5 CEMENTS					
Type II higher alkali (0.60 to 0.70 per cent)	none	5⅓	1850	100	3050	100	4750	100
	B	5	2370	128	3410	112	4920	104
			AVERAGE FOR 6 CEMENTS					
Type II lower alkali (0.40 to 0.57 per cent)	none	5⅓	1390	100	2290	100	3910	100
	B	5	2000	144	2990	131	4630	118

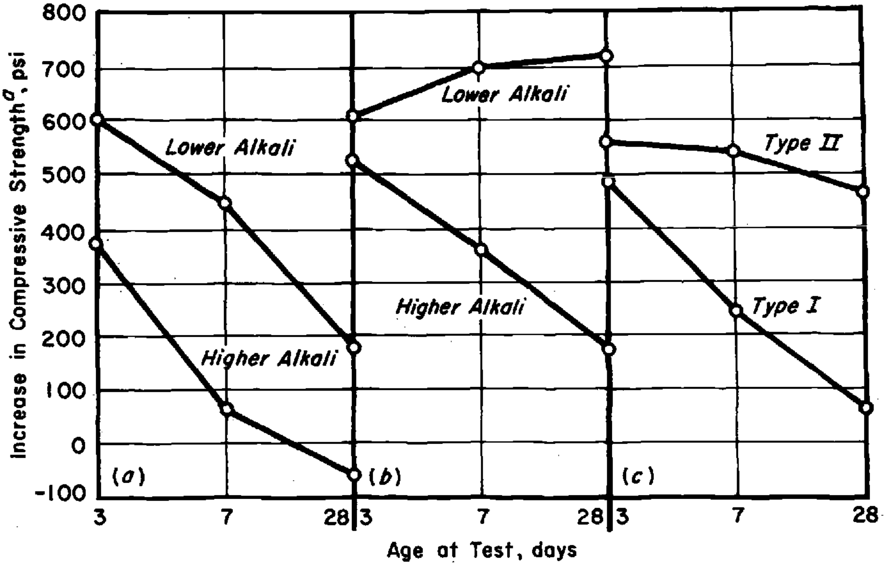
TABLE VII.

Type of Cement	Water Reducer	Cement Content, sack per cu yd	Compressive Strength					
			3 days		7 days		28 days	
			psi	per cent	psi	per cent	psi	per cent
			AVERAGE FOR 10 CEMENTS					
Type I	none	5⅓	1790	100	2850	100	4310	100
	B	5	2280	127	3100	109	4370	101
			AVERAGE FOR 11 CEMENTS					
Type II	none	5⅓	1600	100	2640	100	4300	100
	B	5	2170	136	3180	121	4760	111

and those containing the eleven different brands of type II cement are shown in Table VII.

The average values shown above indicate that the admixture when used in concretes containing type II cements produced an increase in compressive strengths that was on the average about 10 per cent greater than that observed for concretes containing type I cements

Data in Table VII show that the percentage improvement in compressive strength decreases with age of concretes. However, when this improvement is expressed in terms of the increase of compressive strength in psi as shown in Fig. 1, it affords a very interesting comparison. For the type I cements (Fig. 1 (*a*)) on the average the increase in compressive strength of treated concretes (containing admixture *B*) becomes smaller with age of test for both the higher and the lower alkali groups. For example, the average compressive strengths of treated concretes containing the low-alkali type I cements were greater by 600 psi at 3 days, 440 psi at 7 days, and only 180 psi at 28 days, than those of the corresponding plain concretes. A similar trend can be observed for treated concretes con-



(*a*) Type I
lower alkali (0.36 to 0.63 per cent) average for 5 cements
higher alkali (0.70 to 1.18 per cent) average for 5 cements

(*b*) Type II
lower alkali (0.40 to 0.57 per cent) average for 5 cements
higher alkali (0.60 to 0.70 per cent) average for 6 cements

(*c*) Types I and II
type I
average for 10 cements
type II
average for 11 cements

FIG. 1.—Effect of Alkali Content on Increase in Compressive Strength of Concretes Containing Water Reducer *B*.

[a] Difference in compressive strength between admix concretes (admixture *B* 0.20 lb per sack) and corresponding plain concretes. Cement content 5⅓ sack per cu yd for plain concrete; 5 sack per cu yd for admix concrete.

TABLE VIII.—EFFECT OF DIFFERENT WATER REDUCERS ON COMPRESSIVE STRENGTH OF CONCRETES CONTAINING THREE CALIFORNIA CEMENTS.

Portland Cement						Water Reducer	Water Content		Compressive Strength (3 by 6-in. cylinders; standard curing)							
	Composition, per cent								1 day		7 days		28 days		1 yr	
	C_3S	C_2S	C_3A	C_4AF	Alkali as Na_2O		lb per cu yd	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent
No. 26....	52	23	8	8	0.56	none	317	100	200	100	1380	100	2530	100	4580	100
						C	266	84	330	165	1580	115	2960	117	4650	101
						D	281	89	325	162	1380	100	2620	103	4540	99
						E	297	94	330	165	1400	101	2610	103	4370	95
						F	267	84	315	157	1390	101	2680	106	4400	96
						G	271	85	315	157	1460	106	2550	101	4380	96
No. 27....	45	36	7	9	0.51	none	321	100	440	100	1800	100	3650	100	5230	100
						C	268	83	715	162	2530	140	4220	116	5290	99
						D	295	92	495	112	1960	109	3650	100	4880	93
						E	295	92	470	107	2020	112	3820	105	4800	92
						F	271	84	505	115	2140	119	3710	102	4660	89
						G	277	86	530	120	2000	111	3790	104	4750	94
No. 28....	60	23	2	8	0.15	none	305	100	425	100	1490	100	2380	100	4280	100
						C	252	83	550	129	2050	137	3390	142	5130	120
						D	275	90	440	103	1630	109	2620	110	4710	110
						E	279	92	475	112	1530	103	2670	112	4490	105
						F	258	85	460	108	1760	118	3110	131	4880	114
						G	256	84	425	100	1730	116	2950	124	4960	116

NOTE.—Cement content of concretes without admixture 5¼ sack per cu yd, with admixture 4½ sack per cu yd; gravel aggregate, maximum size ¾ in.; nominal slump 3½ in.; admixtures *C*, *F*, and *G* entrained 3 per cent additional air; dosage per sack of cement of admixture *C* 0.25 lb, *D* 6 fluid oz, and of admixtures *E*, *F*, and *G* 0.20 lb.

TABLE IX.

Cement	Water Reducer	Water Content, per cent	Cement Content, sack per cu yd	Compressive Strength, per cent			
				1 day	7 days	28 days	1 yr
No. 26........	none	100	5¼	100	100	100	100
	Average for *C* to *G*	87	4½	162	105	106	98
No. 27........	none	100	5¼	100	100	100	100
	Average for *C* to *G*	87	4½	122	118	105	94
No. 28.......	none	100	5¼	100	100	100	100
	Average for *C* to *G*	87	4½	111	117	124	113

taining the higher alkali type II cements (Fig. 1 (*b*)). Treated concretes containing the low-alkali type II cements, however (Fig. 1 (*b*)), exhibited a somewhat greater increase in compressive strength with age of test, namely, 610 psi at 3 days, 700 psi at 7 days, and 720 psi at 28 days. Figure 1 (*c*) shows the average increase in compressive strength of concretes containing the ten brands of type I cement and of concretes containing the eleven brands of type II cement. On the average the strength increase of concretes containing the type II cements is nearly the same at the three ages of test, whereas it decreases rapidly with age for the concretes containing the type I cements.

Other than the relations noted above for C_3A and alkalies, there appears to be no other significant relationship between composition of cement and performance of admixture.

Different Classes of Water Reducers with California Cements:

This series of tests was designed to show the effect of cement composition upon properties of concretes made with several different types of water reducers. Evaluated were 5 water reducers with each of three California portland cements. In Table VIII are shown the compound compositions of the cements, the water requirements of the concretes, and the compressive strengths at ages 1, 7, and 28 days and 1 yr. The plain concretes had a nominal cement content of 5¼ sack per cu yd, and the concretes containing water reducers had a nominal cement content of 4½ sack per cu yd. Data of Table VIII are arranged in order of decreasing alkali content and decreasing C_3A content of the portland cements. Of the water reducers employed, two were of class 2 (*C* and *D*), one of class 3 (*E*), and two of class 4 (*F* and *G*). Water reducers *C*, *F*, and *G* were of the air-entraining type, increasing the nominal air contents of the concretes by 3 per cent.

For purposes of comparison of the effect of brand of cement on the performance of these water reducers, the average water contents and compressive strengths for all of the 5 admixtures with a given portland cement are shown in Table IX. The values given are expressed as a percentage of the corresponding control mixes whose values are taken as 100 per cent.

On the average, the admixtures allowed the water contents of the concretes to be reduced by the same amount (13 per cent) for each of the three cements. The admixtures were most effective in increasing the compressive strengths of concretes containing cement No. 28 which was of a very low alkali content (0.15 per cent) and low C_3A content (2 per cent). With this cement the percentage increase in compressive strength was greater at age 7 days than at age 1 day and was also greater at age 28 days than at age 7 days. Although the percentage increase in compressive strength was lower at age 1 yr (13 per cent) as compared with that at age 28 days (24 per cent), the average strength increase in psi was actually larger at age 1 yr (750 psi at 1 yr, 570 psi at 28 days).

It may be noted from Table VIII that the 1-day compressive strength of the untreated concrete containing cement No. 26 was only 200 psi and that of concretes containing cement No. 27 was 440 psi. It has been noted in other investigations that at early ages the lower the strengths of the untreated concretes the more efficient is the water reducer in increasing the compressive strength percentagewise.

A study of Tables VIII and IX reveals that although the cement composition has a definite effect on the behavior of the admixtures, there is little difference between the relative effectiveness of the individual brands of admixtures with the various cements. Although the use of water reducer *C* resulted in substantially greater strengths percentagewise at early ages as compared with corresponding strengths of concretes containing water reducer *G*, the difference was small at age 1 yr.

Considering the water contents of the concretes containing the five admixtures (Table VIII), it will be observed that the individual admixtures reduced the water content by about the same amount irrespective of brand of cement. It therefore appears that the effectiveness of these water reducers in improving the compressive strengths of concretes containing various brands of cement depends not only on the water reduction which they allow but also on the characteristics of the portland cement.

TABLE X.—SETTING TIMES AND HEAT GENERATION OF CEMENT PASTES CONTAINING CLASS 3 RETARDERS.

Portland Cement						Set Retarder		Initial Set (Vicat), hr	Peak Time,[a] hr	Heat of Hydration				
	Composition, per cent					Type	Amount, fluid oz per sack			Peak Rate, cal per g per hr	Total Amount, cal per g, up to age			
	C_3S	C_2S	C_3A	C_4AF	Alkali as Na_2O						1 day	2 days	3 days	4 days
No. 29...	42	27	17	6	0.87	none	...	7	11	3.64	44	56	...	...
						H	4	9	13	3.51	36	54	...	...
							5	9	13	2.57	30	54	...	...
						I	4	12	16	2.87	30	49	...	...
							5	17	20	2.70	23	47	...	...
No. 30...	46	27	7	10	0.58	none	...	6	9	2.27	35	45	...	...
						H	4	14	19	3.03	28	43	...	...
							5	19	22	3.26	23	43	...	...
						I	4	24	30	2.21	10	40	...	...
							5	38	51	2.00	3	12	34	45
No. 31...	56	23	7	8	0.56	none	...	7	9	2.63	37	49	...	...
						H	4	14	20	2.68	27	44	...	...
							5	17	22	2.66	26	45	...	...
						I	4	25	32	2.50	5	44	...	...
							5	49	64	2.23	0	0	31	41
No. 32...	41	36	3	13	0.43	none	...	8	11	2.47	35	43	...	...
						H	4	18	24	2.90	7	41	...	...
							5	25	30	2.75	5	36	...	...
						I	4	30	36	2.39	3	35	...	...
							5	61	79	1.64	0	1	7	33

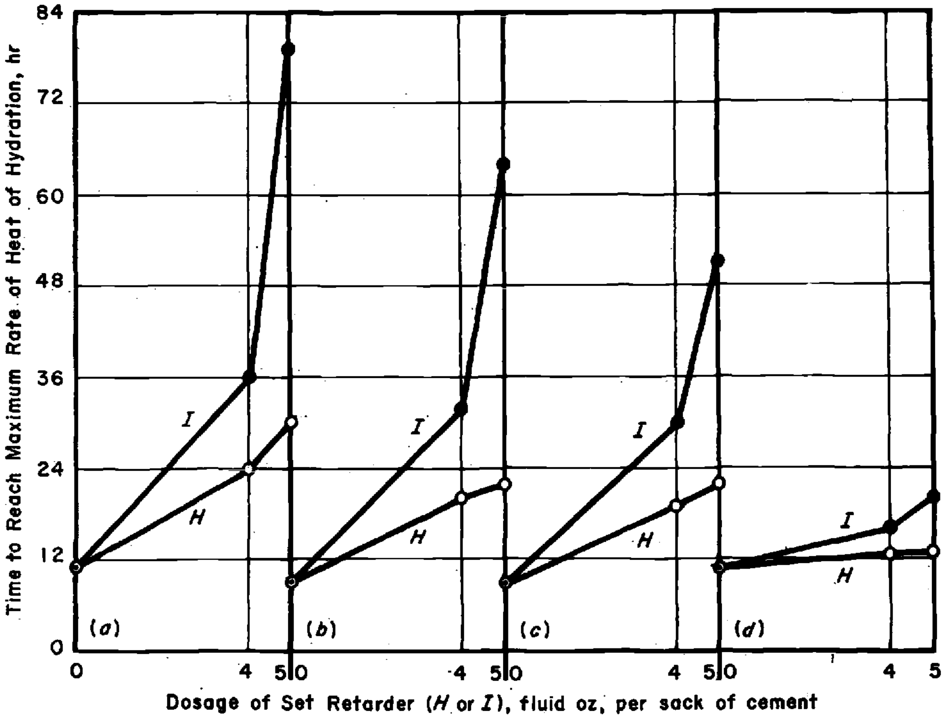
[a] Time to reach maximum rate of heat of hydration.

NOTE.—Water-cement ratio of cement pastes 0.40 by weight; heat of hydration determined in conduction calorimeter using a water-bath temperature of 77 F.

STIFFENING CHARACTERISTICS OF PASTES CONTAINING SET RETARDERS

A limited investigation was conducted to determine the effect of cement composition on setting times of cement pastes of 0.40 water-cement ratio and on heat of hydration of corresponding cement pastes also of 0.40 water-cement ratio by weight. Included were 4 cements and 2 class 3 set retarders used in amounts of 4 and of 5 fluid oz per sack of cement.

The results obtained indicate the existence of a relationship between the setting times of a paste and the stiffening characteristics of a concrete mortar containing the same cement, both with or without admixture. Using these limited data, an attempt is made to define this relationship.



(a) Cement No. 32
3 per cent C_3A
0.43 per cent alkalies

(b) Cement No. 31
7 per cent C_3A
0.56 per cent alkalies

(c) Cement No. 30
7 per cent C_3A
0.58 per cent alkalies

(d) Cement No. 29
17 per cent C_3A
0.87 per cent alkalies

FIG. 2.—Effect of Composition of Cement and Type and Amount of Set Retarder to Reach Maximum Rate of Heat of Hydration.

Setting Times:

Time of initial set and "peak time" (age, in hours, at which rate of heat of hydration is a maximum) for the several conditions are shown in Table X in which the cements are again arranged in order of decreasing alkali content (calculated as Na_2O) which ranged from 0.87 for cement No. 29 to 0.43 for cement No. 32. It is apparent that the two admixtures were more effective in retarding setting times of cement pastes containing low-alkali, low-C_3A cements (cements Nos. 31 and 32) than of those containing cements of higher alkali and C_3A content (cements Nos. 29 and 30). Cement No. 29, which had a very high C_3A content (17 per cent), was least affected by the admixtures used in these tests. The effect of alkali and C_3A content on peak time is demonstrated in Fig. 2. For a 5-oz dosage of retarder *I*, the peak time for the low-alkali, low-C_3A cement (cement No. 32) was 79 hr, whereas the peak time for the high-alkali, high-C_3A cement (cement No. 29) was only 20 hr. It may also be noted that retardation induced by set retarder *I* increases exponentially with dosage. This demonstrates clearly the danger of accidental overdosage with some retarders when used with certain cements. The data of Table X show similar trends for initial set.

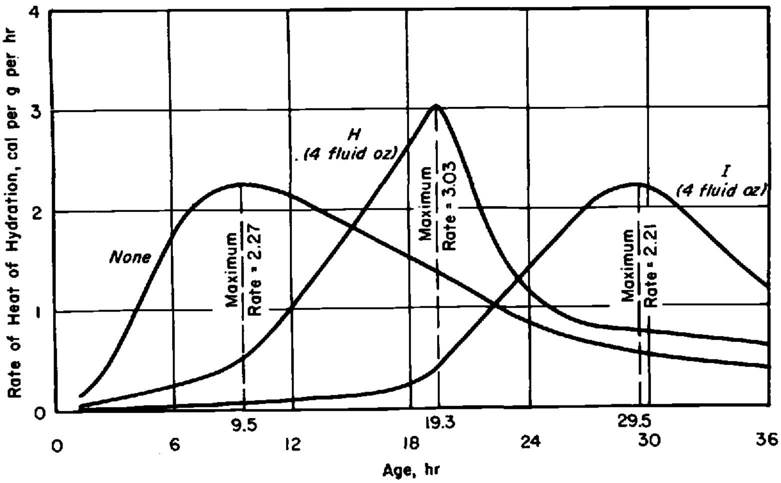


FIG. 3.—Effect of Set Retarders *H* and *I* on the Rate of Heat of Hydration of Cement No. 30.

Heat of Hydration:

Heat of hydration data obtained from calorimeter curves are summarized in Table X. The calorimeter tests were carried on for at least two days for all conditions, and for four days for tests with cements Nos. 30, 31, and 32 with set retarder *I* in the amount of 5 oz per sack of cement. As an example of heat of hydration, there are shown in Fig. 3 rate curves up to age 36 hr for untreated cement No. 30 and for the same cement with set retarders *H* and *I* at a dosage of 4 oz per sack.

The data of Table X demonstrate that these set retarders are more effective in delaying the heat of hydration of low-C_3A cements. For example, for cement No. 29 up to age 1 day for paste containing set retarder *H* in the amount of 5 oz per sack, the total heat of hydration was reduced by 32 per cent. For cement No. 32, the corresponding reduction was 86 per cent. Much greater reductions were observed for set retarder *I*, especially for cements of low C_3A content. With these cements (Nos. 30, 31, and 32), the 5-oz dosage of set retarder *I* resulted in total heats of hydration up to 4 days about the same as the heats obtained up to 2 days with the 5-oz dosage of set retarder *H*. It should not be inferred, however, that the use of set retarders results in lower ultimate heats of hydration.

Correlation Between Time of Set of Cement Pastes and Rate of Stiffening of Concrete Mortars:

For correlation studies with time-of-set results, rate of stiffening at 70 F of corresponding concrete mortars by the Proctor-needle penetration method de-

TABLE XI.—CORRELATION BETWEEN TIME OF SET OF CEMENT PASTES AND RATE OF STIFFENING OF CONCRETE MORTARS AT 70 F.

Portland Cement	Composition, per cent					Retarder		Time to Reach[a] 500 and 4000 psi Resistance to Proctor Needle, hr		Reaction[b] Velocity Constant K, $(\times 10^{-3})$	Resistance[c] to Vicat Needle Penetration at Initial Set S', psi
	C_3S	C_2S	C_3A	C_4AF	Alkali as Na_2O	Type	Amount, fluid oz per sack	T_{500}	T_{4000}		
No. 29....	42	27	17	6	0.87	none	...	6.5	9.4	2.35	440
						H	4	8.1	10.8	2.77	420
							5	9.0	12.0	2.77	420
						I	4	9.4	13.0	2.57	540
							5	11.0	14.2	2.98	630
No. 30....	46	27	7	10	0.58	none	...	7.0	10.8	2.09	610
						H	4	8.0	10.9	2.65	510
							5	9.4	12.0	3.06	640
						I	4	9.5	12.5	2.85	490
							5	11.2	15.5	2.56	550
No. 31....	56	23	7	8	0.56	none	...	6.1	8.6	2.47	610
						H	4	8.6	11.1	2.98	400
							5	10.0	13.1	2.89	510
						I	4	9.9	13.6	2.66	570
							5	12.2	16.9	2.54	580
No. 32....	41	36	3	13	0.43	none	...	6.5	10.6	1.90	690
						H	4	8.6	10.9	3.11	450
							5	9.6	11.9	3.28	540
						I	4	9.9	13.8	2.53	700
							5	12.9	18.0	2.53	570

[a] Mortars for Proctor penetration tests wet-screened from 5 sack per cu yd concrete mixes (¾-in. maximum size aggregate) on No. 4 riddle screen.

[b] K computed from: $K = -4.6 \times 10^{-3} \log_{10} \left(1 - \frac{T_{500}}{T_{4000}}\right)$, Eq 2.

[c] S' computed from: $K = K' = -\frac{2.3}{S'} \log_{10} \left(1 - \frac{T_{IS}}{T_{PT}}\right)$, Eq 3. Average $S' = 543$ psi, its coefficient of variation = 16.5 per cent.

scribed by Tuthill[6] was determined for cements Nos. 29, 30, 31, and 32 in combination with the class 3 set retarders *H* and *I* in dosages of 4 and 5 oz per sack of cement. The results are summarized in Table XI.

It was observed that in general a plot of the logarithm of resistance to penetration *versus* time after mixing yields a straight line as shown in Fig. 4. Stiffening may therefore be described by an equation of the form

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[6] Lewis H. Tuthill and William A. Cordon, "Properties and Uses of Initially Retarded Concrete," *Journal*, Am. Concrete Inst., Vol. 27, No. 8, *Proceedings*, Vol. 52, pp. 273–286 (1955).

$$T_S = T_{4000}(1 - e^{-KS})$$

or,

$$K = \frac{2.3}{S} \log_{10}\left(1 - \frac{T_S}{T_{4000}}\right) \quad \ldots\ldots(1)$$

where:

T_S = the time required to reach a resistance to penetration of S,

T_{4000} = the time required to reach a resistance to penetration of 4000 psi, and

K = a reaction-velocity constant.

If T_S is chosen as the time to reach 500 psi to correspond with the "vibration limit" as defined by Tuthill,[6] Eq 1 becomes:

$$K = -4.6 \times 10^{-3} \log_{10}\left(1 - \frac{T_{500}}{T_{4000}}\right) \quad \ldots(2)$$

Values of K, calculated from Eq 2 using values of T_{500} and T_{4000} taken from Proctor-needle penetration curves, are shown in Table XI.

Since Vicat penetration of a paste is physically similar to Proctor penetration of a mortar, an equation of the form of Eq 1 may be expected to describe resistance to Vicat penetration as a function of time, and a new reaction-velocity constant K' may be calculated as

$$K' = \frac{-2.3}{S'} \log_{10}\left(1 - \frac{T_{IS}}{T_{PT}}\right) \quad \ldots(3)$$

where:

T_{IS} = time of initial set,

T_{PT} = peak time (time to reach maximum rate of heat of hydration), and

S' = resistance to Vicat penetration at initial set.

Assuming that the reaction-velocity constants for corresponding mortars and cement pastes of 0.40 water-cement ratio are the same, Eq 3 may be solved for S' using values of $K' = K$ determined from Proctor-penetration data. Values of S' for the several conditions are given in Table XI.

It will be observed that these values of S' are all in the neighborhood of 500 psi. The average value of S' for the 20 tests

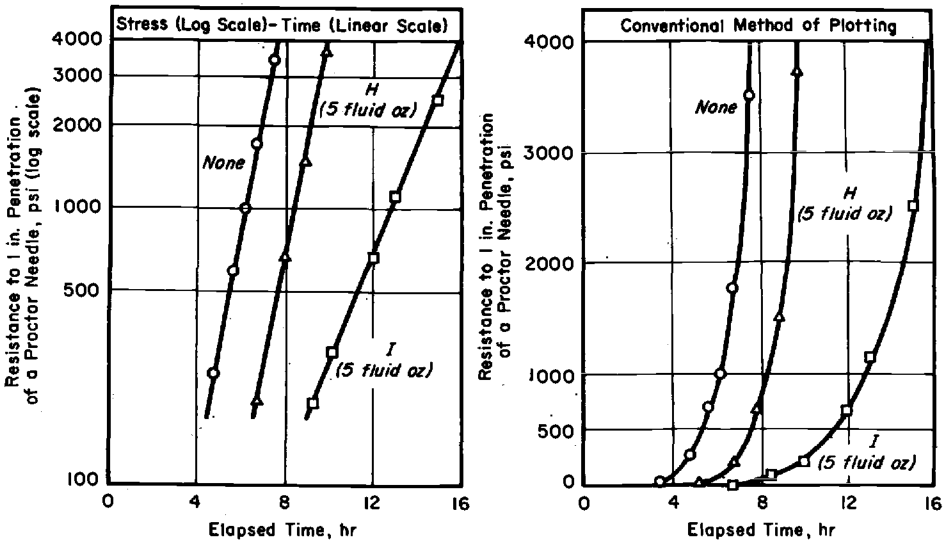

FIG. 4.—Typical Rate-of-Stiffening Curves for Concrete Mortars Containing Cement No. 32 and Set Retarders H and I.

(Table XI) is 543 psi, and its coefficient of variation is 16.5 per cent. It therefore seems possible that data for initial set and peak time of pastes of 0.40 water-cement ratio may be used interchangeably with Proctor-penetration data for studying the effect of admixtures on rate of stiffening. It would, of course, be desirable to use pastes of the same water-cement ratio as that used in corresponding concretes, since the difference in water-cement ratios will probably have some effect on the values of S'. However, there is presently no reliable method for preventing bleeding of pastes of such high water-cement ratio during tests for time of initial set and for heat of hydration without influencing the chemical reactions taking place. Because of the simplicity and economy of working with cement pastes rather than mortars from concretes, this method appears to hold promise for determining the effect of admixtures on rate of stiffening or setting.

CONCLUDING STATEMENT

Based on results of tests here reported and on other supporting data, it appears that:

1. The effect of a water reducer on compressive strength of a concrete cannot be explained by only the reduction in water-cement ratio. The brand of cement, through its chemical composition, has a large influence on the effectiveness of a given water reducer.

2. Water reducers seem to improve more the compressive strengths of concretes containing cements of low alkali content than of concretes containing cements of high alkali content. Best performances of water reducers were observed in concretes containing cements whose alkali content expressed in terms of Na_2O was below 0.60.

3. Water reducers are on the average more effective with type II cements than with the type I cements, probably because of the generally lower alkali and C_3A contents of type II cements.

4. If a water reducer exhibits poor performance with a given cement, it may be expected that other water reducers also will show similarly poor performance.

5. Generally, the largest percentage improvement in the compressive strength of a concrete through the use of a water reducer is obtained at an early age, and this percentage decreases with time.

6. The effectiveness of set retarders in controlling the stiffening characteristics of concretes and the setting times and early-age heat of hydration of pastes is influenced by the composition of the cement employed and by the composition of the set retarder. It appears that set retarders are more effective with cements of low alkali and low C_3A content.

7. In view of the large variation in composition among different brands of cement and in view of the evident dependence of the behavior of water reducers and set retarders on cement composition, the current practice of employing fixed dosages as recommended by the manufacturer can result in marked differences in results achieved. With some retarding admixtures in combination with a low-alkali, low-C_3A cement, the usual dosage may result in undesirably high retardation.

8. Water reducers used in amounts appropriate to the composition of a given cement will usually allow a reduction in cement content of 5 to 15 per cent without loss in compressive strength. Any admixture should be evaluated with the materials and mixes to be used on the job to determine optimum dosage.

STP266-EB/Jun.1960

FIELD EXPERIENCE USING WATER-REDUCERS IN READY-MIXED CONCRETE

E. L. Howard,[1] K. K. Griffiths,[1] and W. E. Moulton[1]

Synopsis

This paper covers the use of water-reducing admixtures in the design and production of ready-mixed concrete. Specification requirements are evaluated against actual on-job problems. Disadvantages in control of uniformity and some advantages that accrue in summertime use are outlined. Producers who use more than one brand of cement are in some difficulty, and data illustrating this fact are presented. Some dangers inherent in reducing cement content are highlighted with test data of on-job sampled specimens.

The use of water-reducing admixtures has changed the normal operations pattern of the ready-mixed concrete producer. Three areas of his operations are affected by the use of these admixtures: (1) the specifications and their interpretation directly affect the cost and quality of the concrete; (2) the batching of admixtures into the concrete is rarely an accurate procedure, yet accuracy is of the utmost importance; (3) the delivery of concrete treated with water-reducing admixtures, when properly controlled, will ensure better concrete on the job.

Specifications

A sentence common to concrete specifications is "The concrete admixture shall be brand *A* or brand *B* or equal." Usually the admixture *A* is a water-reducing agent and the alternate *B* is calcium chloride in solution. Salesmen's claims being what they are, the specification writer may believe an "equal" is any item labelled "concrete admixture." Two of every five specifications which come through our office have this phrase "brand *A*, brand *B*, or equal." The final choice of the admixture will be made by the contractor or concrete producer and may be dictated by cost alone. This specification, obviously, does not ensure any particular desired quality in the concrete.

Manufacturers of water-reducing admixtures properly claim increased workability of the concrete with the use of their admixture. Put another way, the desired slump may be maintained while the water content is reduced. If the water is reduced, cement may also be reduced with no loss of compressive strength. This planned reduction of cement in a concrete design is sometimes beneficial and economical.

The manufacturers of water-reducing admixtures usually recommend 15 to 20 per cent water and cement reduction. The authors' field experience dictates caution in using these recommended values. With some cements and aggregates, 5 per cent reduction of water is all that can be made when the water-

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[1] Chief Testing Engineer, Assistant Testing Engineer, District Testing Engineer, respectively, Pacific Cement and Aggregates, Inc., San Francisco, Calif.

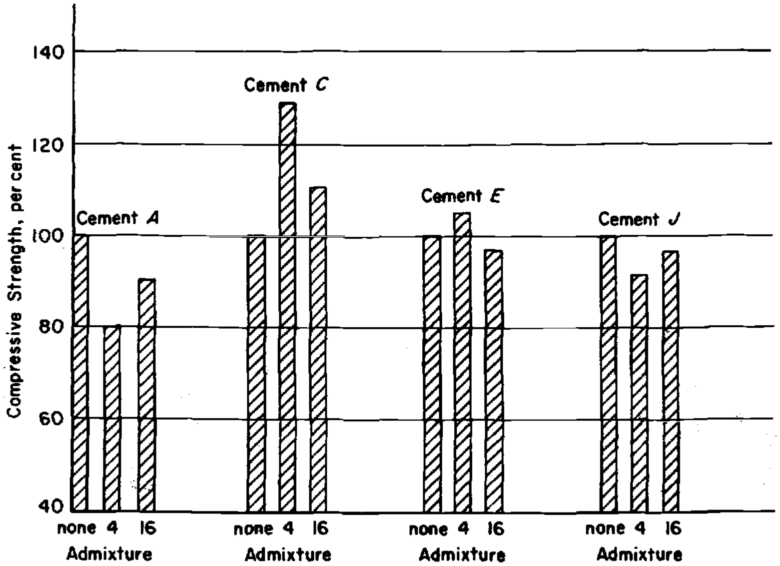

FIG. 1.—Comparative Strengths of Concrete Using Each of Four Brands of Cement.

6½ gal water per sack, ¾ maximum aggregate, 4- to 5-in. slump, water-reducing admixtures 4 and 16 are lignosulfonic acid type.

reducing admixtures are used, if the original concrete workability is maintained.

The authors' experience is with ten aggregate deposits and six portland cements in Northern California. Using available water-reducing admixtures with these possible aggregate-cement combinations in concrete, slumps are increased 2 to 5 in. The per cent of water reduction to maintain original slump is 5 to 15 per cent.

A local agency is writing specifications based on the standard recommendation of manufacturers of water-reducing admixtures. Further, it requires that 15 to 20 per cent cement savings be shown in its favor. A 15 to 20 per cent water reduction being impossible with some materials, the specified saving of cement is accomplished by overdesigning an untreated concrete mix by about ½ sack of cement. From the hypothetical design a cement saving of about 1 sack of cement per cubic yard of concrete can be shown. In a 6-sack mix the saving is nearly 17 per cent on paper and satisfies the specification agency. The "real" cement saving is less than 9 per cent.

TABLE I.—TYPICAL CHEMICAL ANALYSES OF TYPE I CEMENTS AVAILABLE IN NORTHERN CALIFORNIA.

Cement	*A*	*C*	*E*	*J*
SiO_2	21.26	24.06	23.38	21.34
Fe_2O_3	2.69	2.93	2.50	2.96
Al_2O_3	6.03	2.81	3.98	5.76
CaO	62.80	65.70	64.80	64.10
MgO	2.44	0.95	1.73	1.81
SO_3	2.21	1.95	1.78	2.10
Loss	1.12	0.90	1.02	1.26
Insoluble	0.14	0.16	0.19	0.27
K_2O	0.76	0.12	0.21	0.54
Na_2O	0.57	0.09	0.28	0.35
Total as Na_2O	1.07	0.16	0.42	0.71
C_3S	43	56	51	50
C_2S	28	27	29	24
C_3A	11.4	2.5	6.3	10.3
C_4AF	8.2	8.9	7.6	9.0
$CaSO_4$	3.8	3.3	3.0	3.6

It is not a safe practice to specify a percentage reduction of cement with the use of an admixture unless the cement-admixture compatibility is known. Each cement yields results peculiar to itself.

Figure 1 illustrates the wide variance in compressive strength changes when water-reducing admixtures are used. With water-cement ratios and slumps held constant, cements *A*, *E*, and *J* show a decrease in strength when the water-reducing admixtures are used. Cement *C* shows increases in strength under these conditions.

FIG. 2.—Admixture Dispenser Showing the Calibrated Sight Glass.

Table I shows the chemical analyses of the four cements. Beyond the scope of this paper, but worthy of note, is that cements *A*, *E*, and *J* are the highest in alkalies and show the greater percentage of C_3A. Cement *C*, lowest in these constituents, yields the greater increases in strength when used with water-reducing agents.

The ready-mixed concrete producer must know the compatibility of his aggregates and cements to water-reducing admixtures to safely sell concrete on strength specifications. He cannot always depend on the specification writer and admixture manufacturer's recommendations if he has to guarantee the quality of the concrete.

BATCHING

Accurate batching of water-reducing admixtures is most important. Short measures of water-reducing admixtures will result in lower slumps in the concrete. If water is added to the truck mixer at the jobsite to increase the slump the strengths of concrete are lowered. Overbatching of some water-reducing admixtures lengthens the setting time of the concrete and may prevent the hardening of the concrete. Excessive air entrainment and high slumps in concrete are also possible results of overbatching water-reducing admixtures.

The concrete mix proportions approved for a job become the batch plant operator's responsibility to weigh and measure into the mixer. The batch plant used as an example of this problem produces ready-mixed concrete for downtown San Francisco and is typical of many other ready mixed concrete plants. Fourteen admixtures of the type covered by this symposium are stocked to satisfy the demands of customers' specifications. The sales representative for each of these 14 admixtures states that his product will permit a reduction of water. However, at least 4 of these admixtures are not actually water-reducing as defined by this symposium.

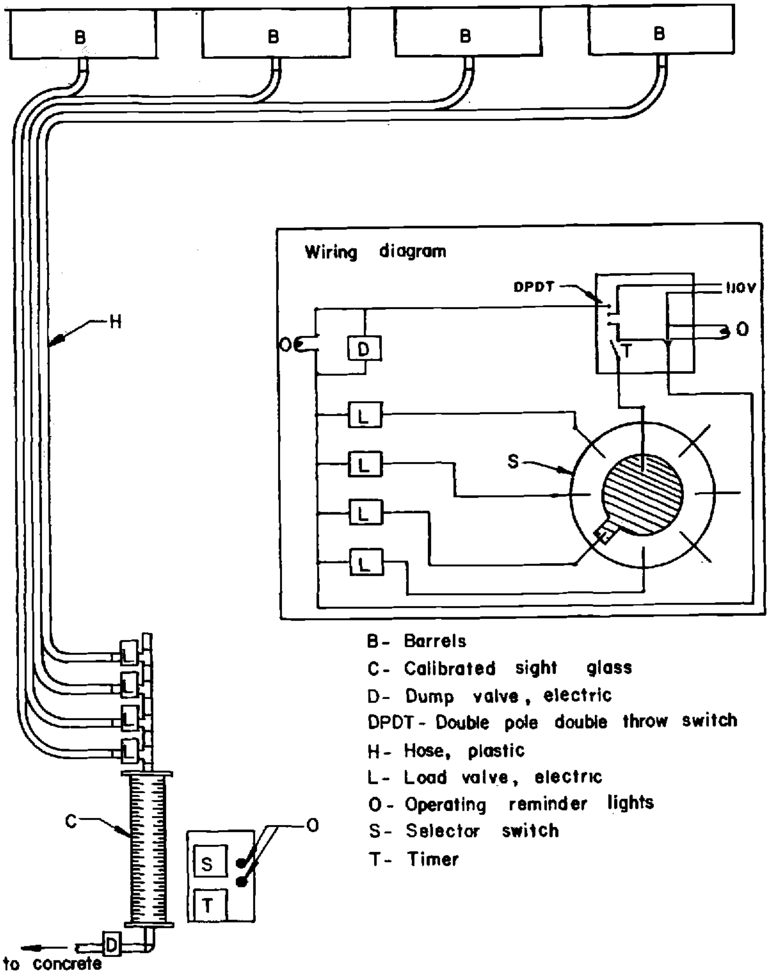

FIG. 3.—Liquid Admixture Dispensing System.

This batch plant has 4 admixture dispensers, not counting a bucket and scoop with which 10 of the admixtures are measured into the concrete. Even automatic dispensers cannot always be trusted to deliver the proper amounts of admixture to the batch. To overcome this potential trouble, it is common practice to feed the liquid admixture into the mixing water through a calibrated sight

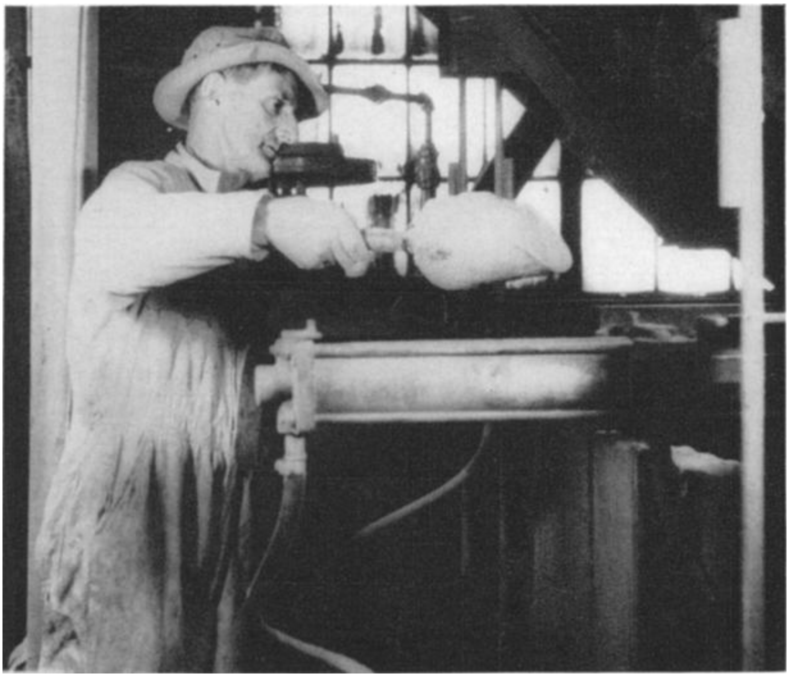

FIG. 4.—Powdered Admixture Dispensing System Showing the Scoop Method Used.

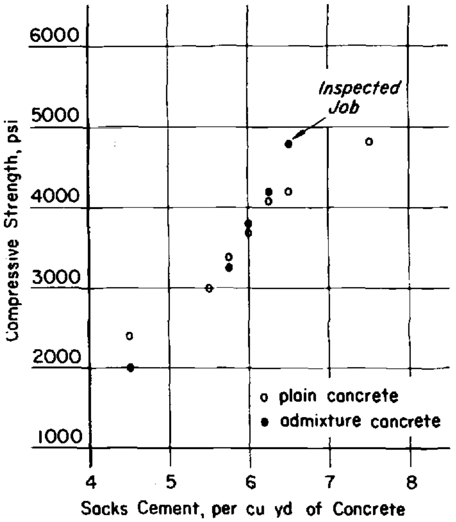

FIG. 5.—Comparative Strengths of Concrete with and Without Water-Reducing Admixes, at 4- to 5-in. estimated slump, ¾ maximum aggregate.

Each point is the average of ten tests.

glass. Such a procedure allows the operator a visual check of the amount measured by the automatic dispenser (Fig. 2). The operator selects the amount to be batched by setting the automatic timer and checks the amount actually batched visually with the sight-glass tube.

As a general practice, most liquid admixtures are roughly measured in a can or bucket because it is impractical to have a dispenser for each brand of the many admixtures used. Described in Fig. 3 is a new batching system that utilizes one dispenser unit for several admixtures. This will help remove some of the clutter and confusion common to batching liquid admixtures. Most powdered admixtures are "guesstimated" by the scoop method (Fig. 4) because the time required to weigh the comparatively small amounts each time the mixer is charged is inconvenient and costly. Packaging the proper amount of powdered admixtures in advance of concrete batching time lowers costs and insures accuracy of measuring the admixture.

ADMIXTURE-TREATED CONCRETE ON THE JOB

When concrete with the reduced water and cement, made possible by the use of an admixture, arrives on the job it has a different appearance than a regular concrete mix without the water-reducing admixture. The admixture-treated concrete has less water sheen, no mortar-aggregate separation, the "fat" does not work up to the surface as readily, and it looks "sticky" coming down the chute. The Kelly ball-slump cone relationship can be used to show this different appearance. An untreated concrete with a Kelly ball penetration of 1.75 in. may slump 3.5 in. An admixture-treated concrete with a 2-in. Kelly ball penetration may still slump 3.5 in. The Kelly ball has detected the increase in workability that is missed by the slump test.

The "eyeball test" also fails to note the difference between the actual workability in the placing and the "apparent workability" as the concrete is discharged from the truck. The concrete foreman who uses the "eyeball test" cures the "sticky mud" problem with water. If the specifications require a maximum water-cement ratio, inspection with authority is needed to maintain the water-cement ratio on the job.

INSPECTION IMPORTANT

A large portion of ready-mixed concrete goes to jobs where inspection is not provided. Concrete delivered to projects where inspection is provided is not always controlled concrete. Too many inspection agencies use men who lack the ability, the authority, or the desire to maintain the water-cement ratio specified. Concrete strength data obtained from cylinders made on typical noninspected jobs are shown in Fig. 5. Concrete made using water-reducing admixtures show no strength advantage over untreated concrete of the same cement factor. The tendency to add water after the "eyeball test" on the jobsite to concrete with water-reducing admixtures is the cause of this condition. The one high value in Fig. 5 designated as inspected concrete are tests from jobs properly inspected and controlled.

The authors believe that in addition to the good practices established for producing and handling materials, three more elements are essential for good concrete control: (1) devices to detect aggregate moisture changes; (2) Kelly ball tests to detect concrete consistency changes; and (3), and most important of all, a technician who is able to evaluate test results quickly and adjust the concrete batch weights to maintain continuously the specified water-cement ratio. Lacking these elements of control, the 15 to 20 per cent reduction of cement generally recommended by manufacturers of water-reducing admixtures is not a safe practice, if the concrete producer must guarantee the strength of the concrete.

Ready-mixed concrete delivered to summertime jobs in the hot Central Valley area of California is most difficult to control. Long hauls and standing time on the job on hot days cause the concrete to lose slump and stiffen rapidly. Water added on the job to raise the slump and improve workability increases the water-cement ratio, often beyond the maximum specified for the job. A state agency has permitted water-reducing admixtures to be added to increase the slump where these conditions exist, while not exceeding the specified water-cement ratio nor reducing the cement content.

FIG. 6.—Material for Test for Consistency of Hydraulic Cement Showing the Paper Cones Used as Molds.

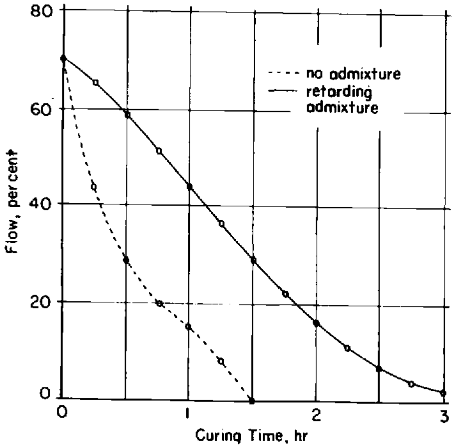

FIG. 7.—Comparative Flow of Concrete Mortar Cured at 110 F and 20 per cent Relative Humidity.

When hauling and standing times are not uniformly controlled, the best practice is to add the admixture as needed on the job.

The type of sand, brand of cement, air temperature, and length of delivery time all contribute to the stiffening problem. The authors have developed a test method that supplies enough information for estimating the amount of water and admixture needed to deliver the desired slump to the job.

TEST TO PREDICT STIFFENING RATE OF CONCRETE

From a trial batch of the proposed concrete mix the mortar portion, obtained by wet screening through the No. 4 sieve, is placed in paper cones, 4 in. in diameter at the base by 5 in. deep (Dixie cup No. 7082). A dozen of the filled cones are stored at 110 F and 20 per cent relative humidity. Flow tests are made of the mortar samples at intervals of 15 min, using equipment and procedure described in ASTM Method C 187–58,[2] Section 4 (*a*), except that a paper cone is used as a mold (Fig. 6). From these test data (Fig. 7) the rate of stiffening is determined and the need for the water-reducing admixture can be closely estimated. By this test the au-

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[2] Standard Method of Test for Normal Consistency of Hydraulic Cement (C 187 – 58), 1958 Book of ASTM Standards, Part 4, p. 174.

thors have found that a mortar with less than 20 per cent flow represents a concrete that is unworkable. The mortars shown in Fig. 7 indicate that the admixture-treated concrete will be workable for 1 hr longer than plain concrete.

HOT WEATHER CONCRETE

Some water-reducing admixtures are used to retard the set of concrete. This is held by some to be a blessing in hot weather. Finishing hot concrete (over 80 F) in slabs has been definitely improved by the retardation of set. The finishers are able to do a proper job because the admixture delays the setting time of hot concrete. Hot concrete without admixture ordinarily will set faster than the finisher can work it.

Not all concrete poured in hot weather is hot concrete. Many producers use wetted aggregates, cool cement, and cool water with resulting concrete temperature of about 70 to 75 F. The cool concrete dries out rapidly on hot dry days and often with shrinkage cracks. Retarders accentuate this problem by holding the concrete plastic and increasing the "drying out" time. Before using a retarder to prevent drying shrinkage cracks, the ready-mixed concrete producers should know the temperature of the delivered concrete. He should determine whether a crack problem is caused by loss of moisture (drying out) or by early stiffening due to accelerated hydration processes. In the first instance retarders will accentuate the drying and cracking problem.

SUMMARY

The ready-mixed concrete producer will find an increasing demand by his customer for water-reducing admixtures in concrete he produces. The concrete producer must evaluate carefully all specifications and recommendations for the use of admixtures and reserve for himself the right to reject mix proportions and admixtures he knows will not yield the quality of concrete he has guaranteed to his customer.

Savings do not accrue directly to the concrete producer from the use of water-reducing admixtures. Savings by reduction of the cement factor are passed on to the customer. The cost of applying tighter controls to all phases of his operations while producing guaranteed strength concrete containing water-reducing admixtures and the usual specified cement reduction may reduce his profits under competitive market conditions.

Accurate and convenint dispensing units and methods are available that take the guesswork out of batching admixture. Accurate measures of liquid and powdered admixtures would prevent most of the difficulties attributed to water-reducing admixtures.

Advantages do occur in delivery of concrete during hot dry weather if the water-reducing admixtures are used to control slump losses common in the summer season. Simple laboratory tests help to determine the amounts of admixture needed.

Set retarders are beneficial in preventing drying-and-shrinkage cracks under certain conditions. The user must determine whether his problem comes from accelerated hydration of the cement or from loss of moisture.

DISCUSSION

MR. WILLIAM A. CORDON[1] (*presented in written form*).—This discussion supplements the paper by Howard, Griffiths, and Moulton and discusses the use of water-reducing admixtures from the view point of the small consumer.

The placing foreman of the small builder or home owner makes the final decision regarding the water content and slump of concrete used in this type of construction. It has been estimated that 80 to 90 per cent of this type of concrete is placed at slumps ranging from 6 to 9 in. and even higher if measurements could be made. Good quality concrete may end up as poor quality concrete under such an arrangement. Concrete engineers and technical men of the industry have little or no control over such practices even though the miscellaneous uses of concrete account for a large majority of the total volume of concrete placed. Producers in general cannot assume authority to regulate slump and still sell their product. Since the concrete consumer may demand high-slump concrete, the concrete industry should make every effort to produce high-slump concrete of the highest possible quality.

Most studies of the influence of admixtures deal with increased strength and quality and the possibility of reduced cement contents. It may be more important to use admixtures to maintain desired strength and quality where concrete used by the small consumer may be of the high slump variety. This discussion has been prepared to indicate the desirability in the use of water-reducing admixtures in this type of concrete.

The accompanying Fig. 8 shows the correlation between water requirement, slump, and 28-day compressive strength for low-, medium-, and high-slump concrete with and without water-reducing admixtures. The curves in Fig. 8 represent only one combination of materials and are not presented as being typical of all concrete.

The concrete mixes containing a water-reducing admixture required an increase in water content from 302 to 320 lb per cu yd in order to increase the slump from 3 to 8 in. The same concrete without the admixture required an increase in water from 318 to 354 lb per cu yd for the same 5-in. increase in slump. This demonstrates that water reduction by means of admixtures is not uniform at different consistencies and water-cement ratios. In this case, reduction in water was $5\frac{1}{2}$ per cent at a 3-in. slump and 10 per cent at an 8-in. slump. This may explain conflicting results regarding the amount of water reduction possible with various admixtures.

The upper portion of Fig. 8 shows the influence of admixtures on the strength-producing properties of the concrete. These tests indicate the water-reducing admixture enabled the concrete to gain an extra 200 to 300 psi strength at the same water-cement ratio. At the same slump the strength advantage is much greater. For example, at an 8-in. slump the strength of concrete without the admixture is 3250 psi compared to 4100 psi with the admixture. The variation in strength for a change of slump from 3 to

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[1] Associate Professor of Civil Engineering, Engineering Experiment Station, Utah State University, Logan, Utah.

8 in. was 700 psi without the admixture and 400 psi with the admixture.

The implication is that the small consumer may be able to "have his cake and eat it too," or in this case wet up the concrete and yet maintain a respectable quality (Fig. 8).

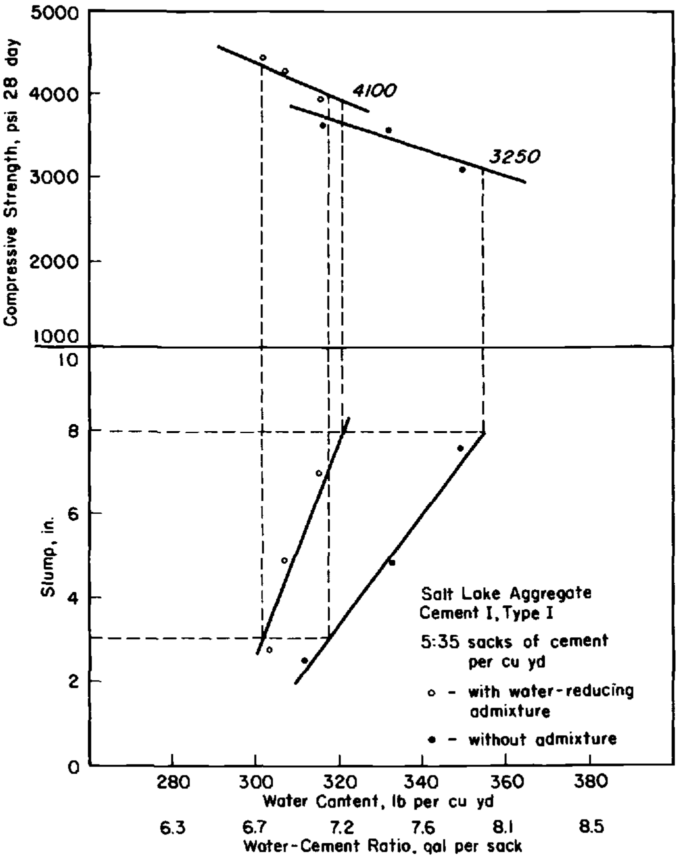

FIG. 8.—Influence of a Water-Reducing Admixture on Water Content, Slump, Water-Cement Ratio and Strength. Salt Lake Aggregate.

Familiarity with the work of the American Concrete Inst. Committee 214, "Evaluation of Strength Tests of Field Concrete," contributes to understanding why consideration of the influence of any variable on uniformity of concrete is of major importance. Consider for a moment the effect of water-reducing admixtures on the uniformity of concrete strengths.

It would normally be expected that the addition of another variable, such as an admixture to concrete, would increase variations in quality. Much has been said regarding the importance of accurate dispensing equipment. The nature of water-reducing admixtures is such that the benefit to concrete is not proportional to the quantity used. Figure 9 is a typical curve showing the viscosity of clay slurry with various amounts of a common water-reducing agent. The maximum benefit as a dispersing agent is reached with very small amounts of the admixture and may not change with increased amounts. This is exemplified by tests (Fig. 10) which indicate that double

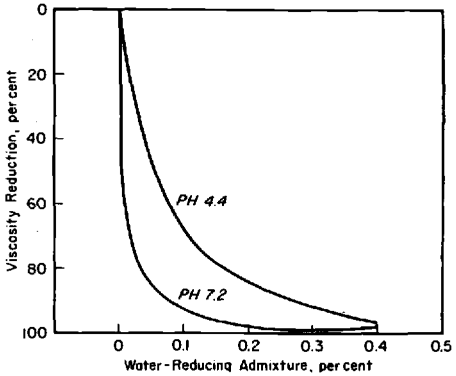

FIG. 9.—Dispersing Ability of Water-Reducing Admixtures in Clay Slurry.

the normal dosage of a water-reducing admixture does not materially change the water reduction, strength, or other properties of concrete.

One ready-mixed concrete plant made trial runs using double the normal dosage of water-reducing admixture. The only noticeable difference in the concrete other than time of set was a brownish color on the surface of slab. Test results indicate that within a reasonable range, 0.15 to 0.30 per cent by weight of cement, sulfonated-lignin water-reducing admixture may not significantly change the properties of fresh or hardened concrete.

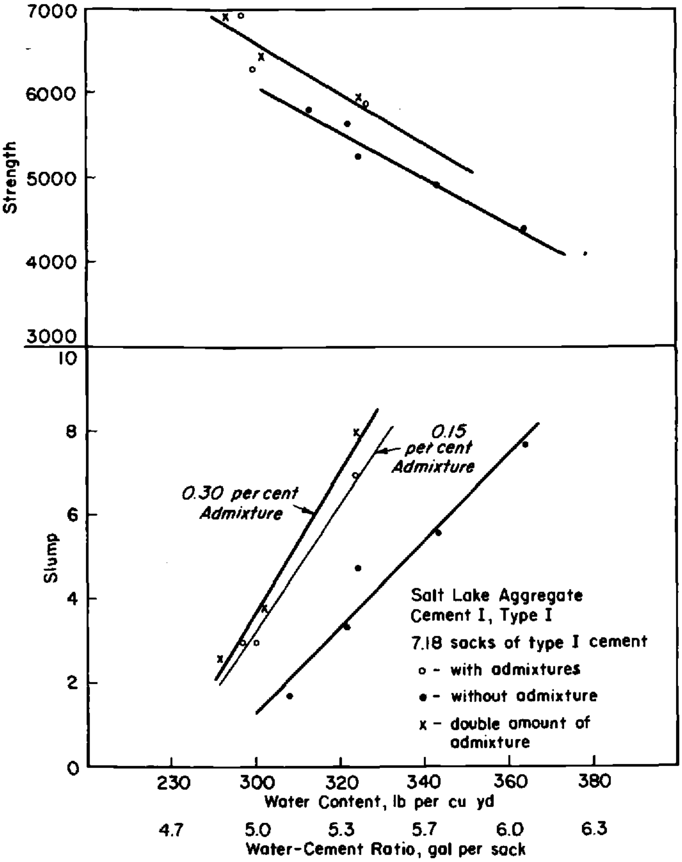

FIG. 10.—Double the Normal Quantity of Admixture Does not Materially Influence the Slump or Strength. Salt Lake Aggregate.

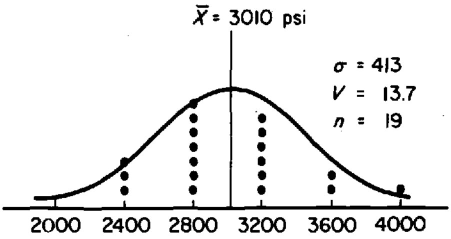

FIG. 11.—Frequency Distribution of Control Tests from a Typical Ready-Mixed Concrete Plant.

Figure 11 shows the frequency distribution of strength tests from a ready-mixed concrete plant. There is nothing unusual about these data. The coefficient of variation of 13.7 per cent is lower than generally expected and indicates a well controlled concrete operation with strict limitation on aggregate grading, moisture control, and slump with time of mixing and testing practices approved by the best construction agencies. Figure 11 may be startling, however, when we realize that these were random strength tests taken during the placing of foundations, sidewalks, driveways, curbs and gutters, and miscellaneous construction of the typical small user of ready-mixed concrete. There was absolutely no control of slump which varied from $2\frac{1}{2}$ to 9 in. depending upon the desire of the fore-

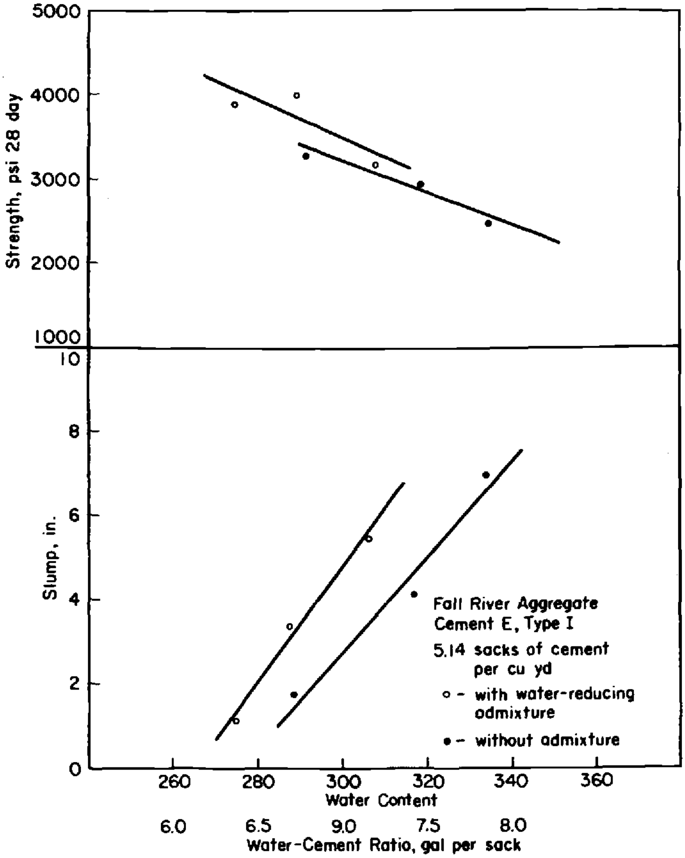

FIG. 12.—Influence of a Water-Reducing Admixture on Water-Content, Slump, Water-Cement Ratio and Strength. Fall River Aggregate.

man. The sand was pit-run and was used as it came from the pit without washing or classification, and with usual variations in grading and moisture content. Mixing time varied with the distance from the plant to the job. With this type of control we would generally expect a coefficient of variation of 25 per cent or greater. The major difference between this and the usual concrete delivered to the small consumer is that a water-reducing admixture was used throughout.

In Fig. 12, data from a different ready-mix plant is shown. Notice the slope of the lines with and without admixture. A change in slump from 3 to 8 in. without the water-reducing admixture required an increase in water-cement ratio of 1 gal, from about 7.0 to 8.0 gal, per sack of cement. With the admixture, the same variation in slump required an increase in water-cement ratio of only 0.5 gal, from 6.7 to 7.2 gal, per sack. We can assume therefore, that the concretes of Figs. 8 and 11 permitted variations in slump with less than usual variations in water requirement and water-cement ratio.

TABLE II.—LABORATORY CHECK TESTS WITH AND WITHOUT WATER-REDUCING ADMIXTURES.

Date	Job	Admixture, per cent	Slump, in.	Strength, psi
9–58....	church	none	3½	2930
		0.15	7½	3500
5–58....	home	none	2¼	2650
		0.15	7	2620
3–58....	sidewalk	none	7	1350
		0.15	7	2650
6–58....	home	none	7	1490
		0.15	7	2510

Large sums of money are properly spent in carefully controlling aggregate grading, water contents consistency, and mix proportions which in the final analysis are methods of producing a more uniform water-cement ratio. Test results would indicate that with a water-reducing admixture we have a built-in factor of safety for high water requirements which greatly reduces the variation of water-cement ratio and variations in quality.

Table II shows typical laboratory tests made with high-slump concrete from a number of ready-mixed concrete plants. The difference in strength with and without a water-reducing admixture are much more than generally expected with normal slump concrete. This again illustrates the importance of a water-reducing admixture for the high-slump concrete required by the small user.

We cannot be naive and assume that these results are typical of all concretes. Figures 12, 13, and 14 show tests results of similar investigations from other ready-mixed concrete plants using different aggregates and different cements. Although none of these series of tests duplicate Fig. 8, most show the same general trend of increased water reduction with increased slump and water-cement ratio.

Sticky Concrete:

Concrete containing water-reducing admixtures is sometimes described as being sticky. This is not only used to describe the appearance of the fresh concrete but may also apply to finishing properties.

Sticky concrete is generally associated with rich mixes. Since the water and generally the water-cement ratio are reduced with the admixtures, it is normal that these mixes appear richer. The fact that the "fat" does not work up to the surface as readily is probably due to the smaller volume of paste (reduced water) in the mix.

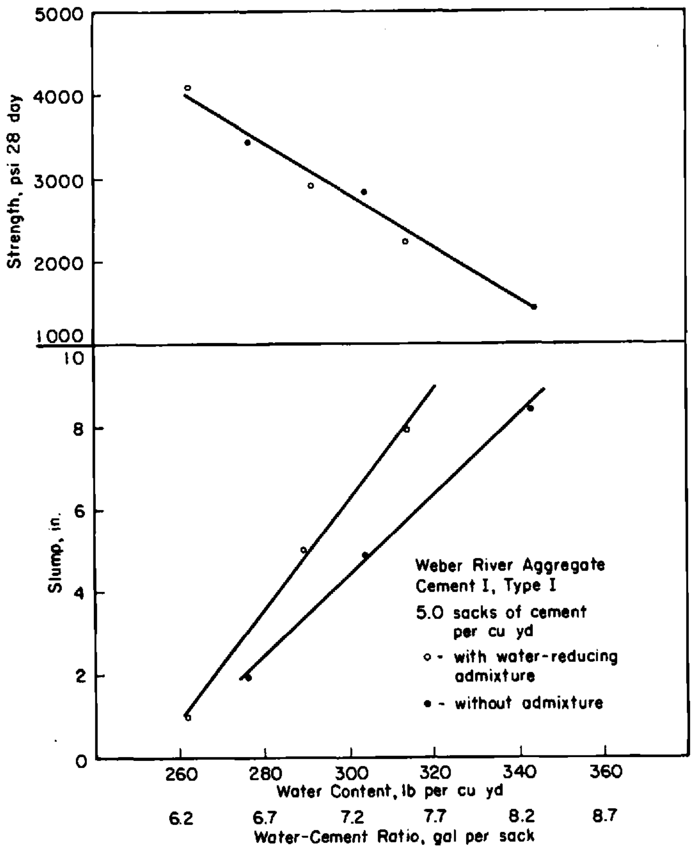

FIG. 13.—Influence of Water-Reducing Admixtures on Water-Content, Slump, Water-Cement Ratio, and Strength. Weber River Aggregate.

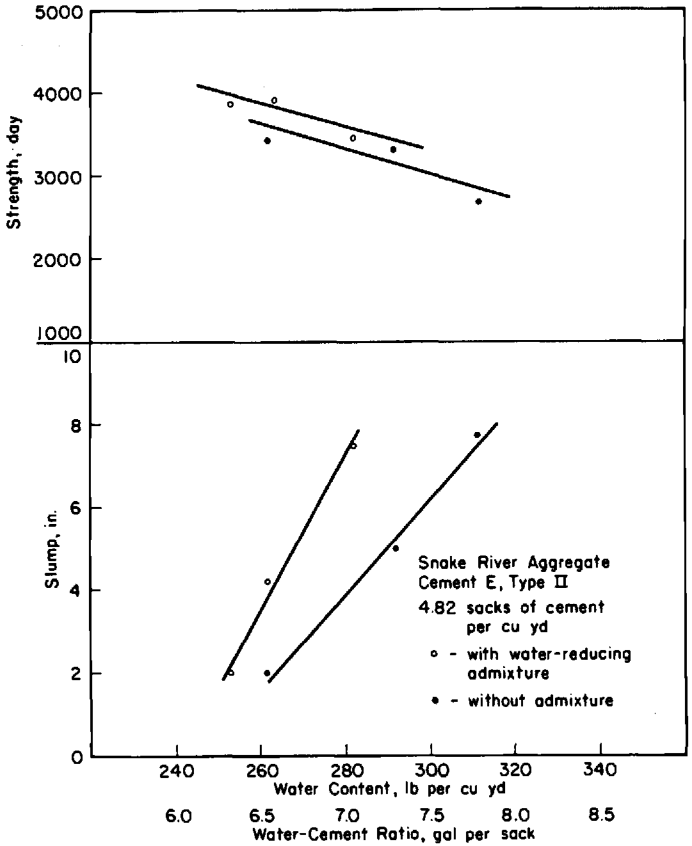

FIG. 14.—Influence of Water-Reducing Admixtures on Water-Content, Slump, Water-Cement Ratio, and Strength. Snake River Aggregate.

The "drying out" problem on concrete slabs before the concrete sets can be traced to reduced bleeding. The surface dries before the final finish is applied and the finishers complain of sticky concrete. Admixtures alone do not control bleeding, and in concrete which tends to bleed excessively the admixtures are a definite benefit to the finisher.

Considering high-slump concrete, the tendency to richer "sticky" concrete reduces segregation, excessive water gain, settlement, shrinkage, and grout leakage through the cracks. In this case sticky tendencies are highly desirable.

Slump Loss:

Reference has been made to the more rapid slump loss of concrete made with water-reducing admixtures. This may be partially explained by increased rate of absorption. Mixes containing identical proportions of cement and water indicate that the increased wetting action of water containing water-reducing admixtures increased the rate of absorption of water by cement (Fig. 15).

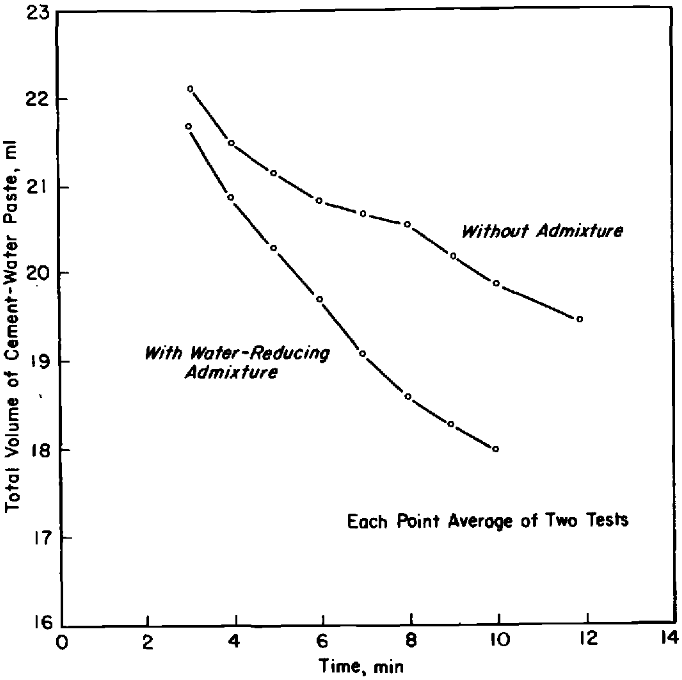

FIG. 15.—The Combination of Water and Cement (Absorption) Is More Rapid When Water-Reducing Admixtures Are Used.

More rapid combination of cement and water which may result in more complete cement hydration would be highly desirable considering the lack of curing on some structures. It has been noted in the field that small quantities of concrete that spill out of forms and dry in the sun were much stronger when water-reducing admixtures were used.

Conclusions:

1. Laboratory tests and field experience indicate that water-reducing admixtures have important possibilities in future construction with quality con-

crete. Perhaps we should think of their use as another means of improving or maintaining desired quality of high-slump concrete rather than reducing cost.

2. The cement requirement of concrete should be dictated by the requirements of the structure and the performance of the proposed concrete. Increased strength through the use of admixtures should be given no more consideration than increased strength through the use of superior aggregates and cement.

3. The use of water-reducing admixtures is particularly important to the small consumer since the danger of poor-quality concrete through the use of over-wet mixes is reduced.

4. Field and laboratory experience leads to the conclusion that the quantity of water-reducing admixture used in concrete is not critical within reasonable limits (0.15 to 0.30 per cent by weight of cement).

MR. E. A. ABDUN-NUR[2] (*by letter*).—The authors have presented a most interesting and thought-provoking commentary on problems and trials in the use of water-reducing admixture in ready-mixed concrete operations. Part of these problems can be laid at the doorsteps of the engineers and architects who specify and are responsible for accepting concrete.

For example, in specifications a specific trade name of an admixture with an added "or equal" phrase to ostensibly open it up to competition causes much trouble and, as pointed out in the paper, does not achieve what is intended to do. It is open to many objections, among which is the fact that it gives a psychological advantage to the named admixture and does not *really* open the field to equal competition. Secondly, as the authors point out, the final choice is not made in most cases by the engineer but by the contractor or producer. Such phrases and approaches to the problem have no place in a properly designed specification—they are in reality an admission of laziness on the part of the specification writer. If the engineer would decide what properties and limitations he wants in his concrete and require these in the specifications, the producer could develop these properties in his ready-mixed concrete operation in the manner most economical for his particular plants and conditions. If one producer knows more about concrete than his competitor, it gives him a chance to make a little more profit. This is the basis of the highly successful competitive economic system in this country. As long as the engineer gets the properties he wants under the limitations he has imposed in his specifications, it should not be his concern how the producer obtains these. Because a ready-mixed concrete operation is a continuing endeavor, the plant technician can, over a period of time, develop some very successful procedures to meet specifications of this type at minimum cost.

It is begging the question to force a ready-mixed concrete operator to over-design his mix in order to show an unrealistic reduction due to the use of an admixture. It would be much more in line with proper engineering to be realistic at the beginning and require what is reasonable.

Is it possible for a plant to furnish controlled concrete when it has to batch 14 different admixtures? When the chips are down, one of class 1 or 3 admixtures, together with an air-entraining agent and an appropriate accelerator will permit a good technician to obtain any property in the final mix that any of the 14 admixtures can possibly provide. This can be done at a lower cost and with much less confusion and, what is most important, it will permit him to develop enough experience with this one admixture, so that he will know exactly what he can do with

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[2] Consulting Engineer, Denver, Colo.

it under varying circumstances. Obviously, this is impossible to achieve with 14 products. In addition, in such a varied ready-mixed concrete operation, it is well-nigh impossible to make sure that each of the 14 admixtures gets in the right concrete mix at the right time, in the proper amount. Under such circumstances, with the best effort on the part of the ready-mixed concrete operator, some one on the placing end is deluding himself that he is getting what he is supposed to get.

The problem of getting around the difficulty of accurately dispensing powdered admixture is to make solutions of standard concentrations, and batch these.

The three essential elements for good concrete control mentioned by the authors are very easily realized nowadays:

1. There are on the market aggregate moisture indicators that are reliable, and that work electronically, so that they can keep up with the fastest batching.
2. It is no problem to check consistency changes, as the equipment is available, simple to use, and takes very little time.
3. Technicians who are skillful in what they are doing can be developed through proper training.

The writer's experience has been that the weak link in the chain of events is not in any of these elements. It is rather in getting management to insist that these elements are maintained and that concrete will not be accepted which does not meet the requirements of the job. Management must be made to realize that improperly controlled concrete will cost more in the long run, in increased maintenance and reduced life of the facility.

The simple rate of stiffening test described by the authors is intriguing, and it would be most interesting to get some correlations between it and the Proctor penetration resistance needle test, for which there are already extensive data available.

The authors are to be commended for placing before the profession some of the problems encountered in their operations, at least some of which are the responsibility of the engineers, and which they can correct with little effort and thus insure that their clients receive better concrete.

Mr. Cordon has brought out some most interesting, basic, and worthwhile ideas regarding the use of admixtures. The main thesis he advances is that as long as the small concrete contractor is going to place wet concrete of high slump, irrespective of what anyone says about it, then it is up to the producer to improve the quality of this sloppy concrete by adding an admixture. This sounds like a very practical and realistic idea. However, such an addition will raise the price of concrete to the contractor. If the contractor were inclined to pay more for his concrete, he could achieve essentially equal improvement by adding cement or by stiffening the mix and expending more labor. The cost of improving his concrete by each of the three methods may be different, and therefore one may be cheaper than the others. That will depend on circumstances and cannot be predicted until all the factors in the case are known. But as long as the contractor does not have any specification to meet, why would he increase his cost, no matter how small, to improve the quality?

A contractor will improve the quality of his concrete *only* if he can do so with increased profit. The best method to achieve this is to require him to meet specifications, the provisions of which have been set up realistically with this end in mind—that is, specifications with a sliding scale that contains a profit incentive keyed to quality.

In referring to Fig. 11 of his discussion, Mr. Cordon concludes that the difference between the 13.7 coefficient of variation obtained from the data and a coefficient of about 25 per cent, which would normally be expected from operations such as he describes, is due primarily to the use of an admixture. It is further stated that there was absolutely no control of the slump. Under the circumstances, is the coefficient of variation obtained from the analysis of such data of any significance? Statistical treatment is valid and provides results that have meaning only when the data are obtained from one universe and when they are obtained from controlled conditions. In this case, are the data from one universe only, and therefore capable of providing coefficients that are valid, or are they just an assembly of data thrown together from a number of universes—therefore with no significant central statistical trends?

Mr. Cordon's conclusion that the quantity of water-reducing agent is not critical within reasonable limits is of important significance. The writer agrees with this conclusion as long as the same proportion is maintained from batch to batch in any given mix that is being controlled. However, in deciding on the mix proportions in the first place, in order to arrive at concrete with certain properties, it is true that the amount of admixture is not critical.

MR. F. W. DRURY, JR.[3] (*by letter*).—San Gabriel Ready Mixt operates six ready-mixed concrete plants and two rock plants in Southern California. In one year, this firm delivers more than 250,000 cu yd of concrete, approximately 175,000 cu yd of the total being delivered to small contractors and home owners and the remainder consisting of specification work in which laboratory mix designs are required. We would estimate that at least 50 per cent of our ready-mixed concrete production contains an admixture. By far the most commonly used admixture is a water-reducing agent.

In general, our experience with water-reducing agents has been excellent, although we agree with the authors that water reductions achieved in the field very seldom approach the figures quoted by admixture manufacturers. Our experience indicates that when class 1 and 2 admixtures are used, we may anticipate from 7 to 13 per cent water reduction for equivalent consistency and that when class 3 and 4 admixtures are used, we may anticipate 3 to 8 per cent reduction in water for equivalent consistency. In either case we are assuming no purposeful air entrainment. With respect to the class 1 and 2 admixtures, we agree with Mr. Cordon in finding that concrete that is poured excessively wet containing water-reducing admixtures has certain self-protective features in that there appears to be a breakover point, resulting in the concrete going from a 5-in. slump to a 9-in. slump, with the addition of not more than 1 to 2 gal additional water per yd. Our problems in using water-reducing admixtures in nonspecification work occur when extremely lean mixes are employed, as we have found that in such mixes. water-reducing admixtures are never a satisfactory substitute for cement paste where considerations of finishability and workability are of prime importance. At higher cement factors, we agree that some water-reducing admixtures tend to increase the stickiness of concrete, but in our opinion this is a function of air entrainment rather than effects of admixtures as such. In our area, air-entrained concrete is rarely used and concrete finishers are not familiar with the finishing characteristics of concrete containing from 4 to 6 per cent air and generally complain that such concrete is rubbery and sticky.

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[3] General Sales Manager, San Gabriel Ready Mixt, Pasadena, Calif.

We appreciate the authors' problem in dealing with a variety of admixtures both from the standpoint of predicting performance and from the standpoint of stocking and accurately dispensing more than a few materials. We suggest that the ready-mixed concrete companies consider stocking relatively few well-known materials, and insist that when other admixtures are to be used, the contractor purchase and furnish such materials to the ready-mixed concrete plant, and that an appropriate service charge be made to cover the extra expense of accurately dispensing these materials. We have found it necessary in many cases to discourage the use of certain products in order to overcome the problem of stocking a variety of products. In any case, however, we insist that our personnel at the ready-mix plants be aware of the danger of improperly adding admixtures. We furnish them with adequate equipment to insure that when admixtures for which no dispensers are available are used, 3 per cent accuracy in measurement is maintained.

Our prime complaint in the use of admixtures is that specification writers are not aware of the performance characteristics of various materials and that on many occasions they will specify water-reducing retarders for concrete being placed under low-temperature conditions. When the concrete fails to set until the next day, the producer invariably gets the blame.

We believe that many of the technological improvements in concrete of the future will be achieved through the use of admixtures, and as a matter of policy we encourage their use. Because we have no control over the fifth ingredient of concrete—"workmanship"—we feel a strong obligation toward educating the contractor in the technology of concrete. To achieve this, we have established and operate monthly a course on "Quality Control of Ready-Mixed Concrete," a full two hours of which are devoted to discussion of the pros and cons of admixtures in general. The present and anticipated future competition among the admixture producers will result in competitive prices which will permit water-reducing admixtures to be used in all concrete and which will, in our opinion, produce superior concrete at lower cost.

MESSRS. E. L. HOWARD, K. K. GRIFFITHS, AND W. E. MOULTON (*authors' closure*).—We are appreciative of the fine contributions to the practical problems of admixture use made by Messrs. Cordon, Abdun-Nur, and Drury. We are gratified to note that they have recognized in their field experience problems similar to those we have discussed. We certainly agree with Mr. Abdun-Nur that the answer to control lies with management in the ready-mixed concrete industry and their support in supplying well-trained men and facilities to accomplish the work.

STP266-EB/Jun.1960

DETECTION OF LIGNOSULFONATE RETARDER IN CEMENT SUSPENSIONS AND PASTES*

By E. G. Swenson[1] and T. Thorvaldson[2]

Synopsis

The problem of detecting the presence of the lignosulfonate type of retarder or plasticizer in hardened cement paste is investigated by a spectrophotometric method based on ultraviolet absorbance measurements of aqueous extracts. The interaction of hydrating portland cement and lignosulfonate salt, whether in water suspension or in hardened paste, results in the disappearance of the characteristic 280 mμ maximum of the original lignosulfonate and the appearance of two new maxima at wavelengths of 245 and 350 mμ. This change is attributed to alkaline hydrolysis, with the formation of vanillin. The experimental results are discussed in relation to the qualitative and quantitative aspects of the method in detecting lignosulfonates in portland-cement products.

A lignosulfonate salt is the basic ingredient in certain commercial admixtures for concrete which are used primarily as plasticizers and retarders (**1**,**2**,**3**).[3, 4] Despite their extensive use for many years, little or no published information is available on the nature of the interaction between lignosulfonate and cement, on the response of different cements, particularly to overdosage, or on methods of determining the presence or absence of such admixtures in concrete.

Field problems frequently require analysis of concrete to determine the nature or quantities of original ingredients. At best, such analyses are approximate, owing to the nature of cement and aggregate, but they are nonetheless of practical importance. Detection of the presence of certain admixtures may also present difficulties.

In an investigation of a field problem carried out by the authors, it became necessary to determine the presence or absence of a lignosulfonate retarder in a faulty concrete, and this led to the experimental work described in this paper. Following preliminary studies which indicated that direct tests for lignosulfonate were apparently doomed to failure, a possible method was explored which is based on spectrophotometric determination of absorbance curves in the ultraviolet for water-soluble products of interaction between lignosulfonate and hydrating cement.

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* This paper is a contribution from the Division of Building Research of the National Research Council of Canada and is published with the approval of the Director of the Division.

[1] Formerly, Research Officer, Division of Building Research, National Research Council of Canada, Ottawa, Ont. (Canada), now Director of Research, Miron and Frères Ltd., Montreal, P. Q.

[2] Dean Emeritus of Graduate Studies, University of Saskatchewan, Saskatoon, Sask.

[3] The boldface numbers in parentheses refer to the list of references appended to this paper.

[4] E. W. Scripture, U. S. Patents Nos. 2,081,642 (1937); 2,127,451 (1938); 2,169,980 (1939); and 2,229,311 (1941).

Preliminary Observations

Lignosulfonate salts are lignin derivatives from waste sulfite liquors of the wood pulp industry. They are normally obtained by neutralization of the lignosulfonic acids, are variable in composition, and contain impurities. The lignosulfonate salt is considered to be a colloidal electrolyte which ionizes in solution to give metallic cations (usually calcium or magnesium) and lignosulfonate anions, the latter being positively absorbed by the cement particles in aqueous medium. It has been postulated that this phenomenon accounts for the dispersing effect which such substances apparently have on cement particle (3).

The detection and quantitative determination of a lignosulfonate salt in set cement paste and concrete presents difficulties. Although it was found by the authors that the usual qualitative test for lignin (chlorination with subsequent addition of sodium sulfite (4)) gave a distinctly positive result when 0.1 mg of a commercial lignosulfonate product was present, negative results were obtained with aqueous extracts of set cement pastes to which a larger quantity of the soluble lignin salt had been added. This suggested that the radical of the lignosulfonate molecule or ion responsible for the production of the color in this test was modified or destroyed in portland cement - water systems.

It was also found that mixtures of portland cement and the same lignosulfonate salt, when shaken with water, developed alkalinity much more slowly than similarly treated mixtures of cement and water. This may be due to adsorption of the lignosulfonate anion or molecule on the surface of the cement particle. Attempts to recover the lignosulfonate salt from hardened cement pastes by extraction with various solvents were not successful.

Zeisler's method for methoxyl determination (5) presented difficulties when applied to cement pastes containing a small amount of lignosulfonate. Authoritative advice indicated that modification of the conventional procedure which would be required to test such combinations was likely to produce questionable results. It is possible, however, that this method may be adapted to such determinations.

Ultraviolet spectroscopy has been used for some time in studies on the structure of lignin and its derivatives (6,7) but no published results appear to be available on the use of this method for detecting lignosulfonates in portland-cement products. For dilute aqueous solutions of two lignosulfonates used commercially as plasticizers and retarders for concrete, two maxima are found in the absorbance curve, one at a wavelength of about 205 mμ, the other at about 280 mμ (absorbance is the negative logarithm of p/P_o, the ratio of the radiant energy of the transmitted light to that of the incident light). For detection of "lignin substances" this method appears to be extremely sensitive (8).

The sample of commercial calcium lignosulfonate retarder used in most of the spectrophotometric tests was subjected to paste and mortar tests to ensure that its influence on setting and hardening accorded with claims made for such admixtures. Dosages varying from $\frac{1}{20}$ to 10 times the prescribed or normal dosage were used. Results showed that this lignosulfonate product was typical of this class of dispersing and retarding agent.

Materials and Methods

The main test sample of lignosulfonate was a commercial preparation derived from sulfite liquor and used very considerably as a plasticizer and retarder in concrete. A second commercial admixture containing lignosulfonate as a basic ingredient, and used very widely in practice, was found to give essentially similar absorbance curves in the ultraviolet region covered in the following experiments. Several samples of type I cement from five different plants were used.

The lignosulfonate salt dissolved or became colloidally suspended in water with no residue left. The cement pastes were made as thin "pats" on Lucite or bakelite plates. After curing for 1 day they were partly broken and stored in beakers in a desiccator over water. They were ground to powder just prior to aqueous extraction for analysis.

The reaction vessels, used for shaking the cement with the lignosulfate solution, and the extraction vessels, in which the powdered pastes were shaken with water, were made of different materials in order to eliminate any possible influence of the container on absorbance values. Some were steel, lined with pure silver or gold foil and sealed with a suitable cap and clamp; others were polyethylene bottles with caps of the same material. Results of many experiments showed that no significant difference in absorbance values could be detected when using any of these materials. Mechanical shaking was used to keep the cement particles dispersed.

The aqueous extracts were clarified by high-speed centrifuging before absorbance measurements were made. This method gave more consistent results than filtering. When extracts were "cloudy" they were centrifuged again, but standing for 1 day permitted settlement of such suspensions.

The dosage of lignosulfonate used in most of the experiments was approximately that recommended for this material, 0.125 per cent of the weight of the cement. This is designated as a "normal" dose, N, and higher doses are designated as multiples of N.

Two Beckmann spectrophotometers were used, with hydrogen lamps and paired silica glass cells. The DU instrument was hand-operated; the DK1 was an automatic recording instrument. With the first unit the absorbance of the test solution was measured against redistilled water, and the blank for the particular cement used was determined separately. With the automatic unit, the measurements were made directly against a blank which consisted of a similarly treated sample of cement, the absorbance of the blank being automatically deducted from the absorbance of the test sample.

The absorbance of the blank cement-water suspension and of the extract from the blank cement-water pastes was very low in the region of 240 to 400 mμ and gave a smooth curve over this range (bottom curve of Fig. 2). Since the results obtained in these studies on cement-water-lignosulfonate systems had a high dependence on time of contact, the blank values were not always deducted from the test values.

Absorbance curves for saturated solutions of lime, gypsum, and mixtures of both were very similar to those for cement blanks, being of about the same order.

ULTRAVIOLET ABSORBANCE STUDIES

Dilute Solutions of Lignosulfonate:

Figure 1 gives typical absorbance curves for two very dilute aqueous solutions of the lignosulfonate retarder (0.002 and 0.004 per cent). They show a very steeply sloping shoulder in the 220 to 240 mμ region, a minimum at 260 mμ, and a characteristic maximum at 280 mμ. Beer's law is applicable both on the basis of relative total absorbance and on the basis of the relative difference (280 maximum minus 260 minimum). While there was a definite maximum in absorbance at about 205 mμ, readings at wavelengths below 215 mμ were not consistent and were considered unreliable since the ce-

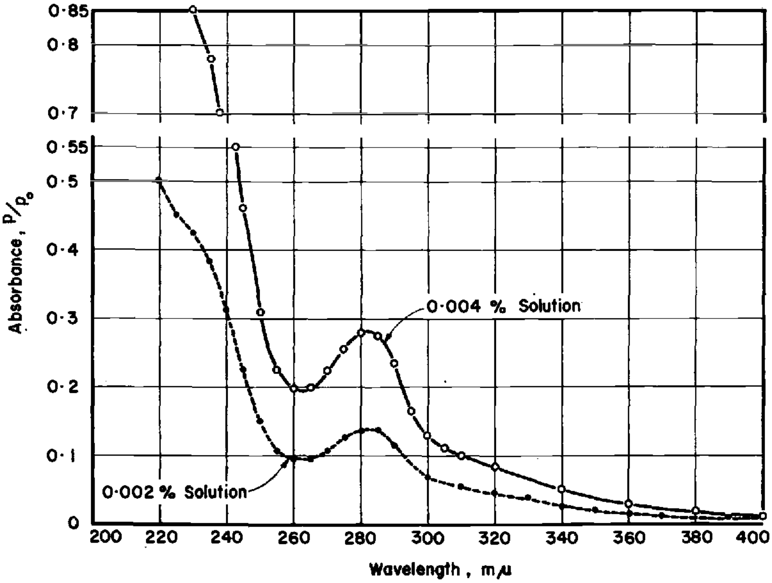


FIG. 1.—Ultraviolet Absorbance of Dilute Aqueous Solutions of a Commercial Lignosulfonate Product.

ment blank also showed high absorbance in this region.

The absorbance curves of dilute solutions of the lignosulfonate remained essentially unchanged on standing at 23 C for up to $3\frac{1}{2}$ months in glass bottles. For example, the absorbance values of the 260 mμ minimum and 280 mμ maximum

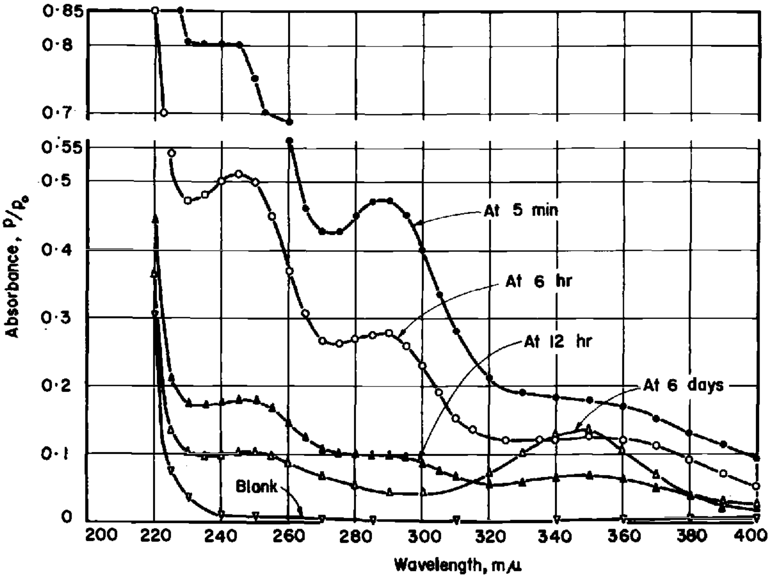


FIG. 2.—Change in Absorbance of Lignosulfonate Solution with Increasing Time of Contact with Portland Cement.

for a 0.005 per cent solution were, respectively, 0.33 and 0.41 after 2 days' standing, and 0.32 and 0.39 after 3 months' standing. For a 0.018 per cent solution, the corresponding values were 0.91 and 1.26 at 1 day's standing and 0.97 and 1.27 at 3½ months' standing. The same was true for solutions stored in polyethylene bottles.

No significant changes occurred in the absorbance curves when the solutions were shaken in glass, polyethylene, or metal tubes for long periods of time. Partial neutralization of a dilute solution with HCl, boiling, or a combination of the two, did not alter significantly the absorbance values at the 260 mμ minimum or the 280 mμ maximum. Aeration of the solution appeared to lower the absorbance values slightly, especially at the shorter wavelengths. This may have been due to the difficulty of equalizing the pressure of water vapor in the air stream and the vapor pressure of the solution. The readings at 0 C were slightly lower than those at 25 C (order of 0.01 for wavelengths between 230 and 290 mμ and of 0.005 for longer wavelengths). None of these altered the position of the minimum at about 260 mμ or the maximum at about 280 mμ.

Suspensions of Cement in Lignosulfonate Solutions:

Figure 2 gives absorbance curves for suspensions of 10 of type I cement in 50 ml of 0.025 per cent lignosulfonate solution. This represents a "normal" dosage of retarder (0.125 per cent of the cement by weight), but also represents an extreme condition where a large excess of the liquid phase is present. The time of shaking was varied from 5 min to 6 days, and measurements of absorbance were made immediately after centrifuging. The curve for a pure lignosulfonate solution of 0.025 per cent concentration (not shown) is in accord with Beer's law when compared with the curves in Fig. 1.

It is observed that the 5-min contact between the lignosulfonate solution and the cement has materially changed the character of the absorbance curve from that of the pure lignosulfonate solutions (compare with Fig. 1). Calculation by Beer's law indicates that over 90 per cent of the radical or group responsible for the increase in absorbance at the maximum of 280 mμ has disappeared from the liquid phase. Such a rapid change would explain the failure of the sodium sulfite color test referred to earlier.

It is also observed that, with increasing time of contact between the cement and the lignosulfonate, the characteristic maximum of the latter at 280 mμ has shifted slightly to a higher wavelength of about 290 mμ and is finally replaced by a minimum, or "trough," at this point. The shift of the 280 mμ maximum to about 290 mμ has been observed for lignin products when strong alkali is present (7). At the same time the "shoulder," which began to develop at 230 to 245 mμ on 5-min contact has further developed into a new minimum at about 230 mμ and a new maximum at about 245 mμ. In this region, however, the over-all absorbance shows a rapid decrease with time of contact. Concurrent with these changes was the development of a new maximum, at about 350 mμ, which increased with time of contact up to 6 days.

Not shown in Fig. 2 are corresponding curves for 24 hr and 12 days of shaking. The 24-hr curve fits in with the other curves, as expected, but the 12-day curve (the lower dotted curve in Fig. 3) shows an over-all absorbance slightly lower than the 6-day curve, even at the new 245 and 350 mμ maxima. This "recession" in the absorbance curves for cement-lignosulfonate-water systems, after long contact with excess liquid phase, was also found for paste extracts (see next section).

Similar experiments were carried out using four times the "normal" dose of lignosulfonate, that is, 10 g of type I cement shaken with 50 ml of 0.100 per cent lignosulfonate solution. The absorbance curves were similar to those obtained with the normal dose samples, but the time for the reaction to run to completion was longer. At 9 days' shaking, the 260 mμ minimum and the 280 mμ maximum had completely disappeared, with a new minimum absorbance of 0.15 at about 300 mμ. The maxima at 245 mμ and 350 mμ gave absorbance values of 0.40 and 0.44 respectively, as compared with 0.10 and 0.13 for the 6-day run of the normal dose sample (Fig. 2). At longer shaking times with the 4N samples, these maxima increased and then subsided as for the N samples.

It would appear from these and other experiments that the radical of the lignosulfonate that is responsible for the characteristic maximum at 280 mμ is modified by the presence of the hydrating cement so as to destroy its absorption of light of that wavelength. Concurrently, two new maxima of light absorption gradually appear, one at about 245 mμ, the other at about 350 mμ. It is possible that the maximum of absorption for lignosulfonate observed at about 205 to 210 mμ also undergoes change, but the only experimental evidence available indicates increased absorbance in this region during the growth of the maxima at 245 and 350 mμ. The addition of solid CaO to a dilute solution of calcium lignosulfonate produced short-term changes in the absorbance curve similar to those produced by the addition of cement.

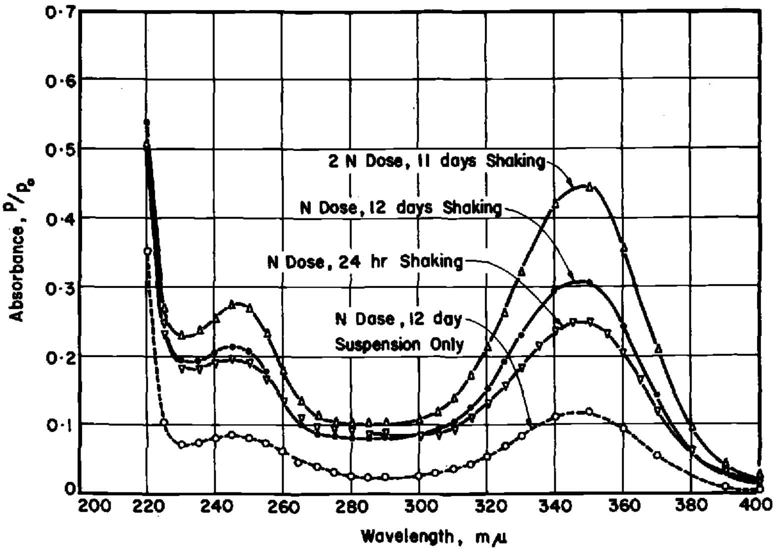


FIG. 3.—Absorbance Curves for Aqueous Extracts from Aged Cement Pastes Containing Lignosulfonate Retarder.

NOTE.—4 month old pastes; 12.5-g powdered samples; extraction with 47.5 ml water; N, normal dose (0.125 per cent) lignosulfonate; dotted curve, 12-day old suspension.

Water Extracts from Hardened Cement Pastes:

In the experiments discussed in the preceding section, an excess of the aqueous phase was always present during the interaction of cement and lignosulfonate. This would represent one extreme or limiting condition not normally present in concrete except in the first hour or two in the plastic state. A large number of experiments were carried out on aqueous extracts of hardened cement pastes which would represent the other limiting condition where the liquid phase would be limited mainly to adsorbed films on solid surfaces during most of the period of "interaction."

Figure 3 shows typical absorbance curves for aqueous extracts from 4-month-old cement pastes with "normal," *N*, and twice normal, 2*N*, doses of lignosulfonate retarder. The amount of extracting liquid used was such that concentrations of dissolved materials would be comparable with the solutions used in the preceding section. These results were obtained on the DU hand-operated instrument, with distilled water as a blank.

These curves are strikingly similar to the 12-day dotted curve for the cement-lignosulfonate-water suspension in Fig. 3 and to the curves in Fig. 2. The maxima at 245 and 350 mμ are increased with longer shaking times up to about 11 or 12 days but tend to recede slightly for longer shaking times (as with the suspensions). The 2*N* curve has a higher maximum than the *N* curves, but the differences are not proportional to original concentrations of the lignosulfonate. From these and other experiments, it appears to be quite definite that there is a considerably greater build-up of the molecules or radicals responsible for the maxima at 245 and 350 mμ in the paste than in the cement-solution suspension. It is conceivable that normal curing of paste made with a limited amount of mixing water (as for normal consistency requirements) provides a condition more conducive to degradation of the original lignosulfonate and to the stability of the new product or products.

At younger ages of paste, results were obtained similar to those for the cement-lignosulfonate solution suspensions, but again with a greater build-up of the new maxima at 245 and 350 mμ. Table I gives absorbance values from cement-lignosulfonate pastes after curing periods varying from 6 to 67 days. These were obtained with the KG-1 automatic instrument and with the blank deducted. Original samples were made up separately. The maxima show a general tendency to increase with time of curing up to 67 days. Comparison with Fig. 3 (with a different cement) would indicate, however, that no appreciable additional build-up of the peaks can be expected. The minimum or "trough" at about 290 mμ shows only a slight increase in absorbance with increasing curing time. The minimum at 225 to 230 mμ shows a fluctuation which is not unexpected in view of its nearness to the high absorbance range for the blank.

TABLE I.—ABSORBANCE OF AQUEOUS EXTRACTS FROM PASTES CONTAINING LIGNOSULFONATE, AFTER VARYING INTERACTION PERIODS.

M cement; "Normal" dosage of lignosulfonate

Interaction Conditions		Absorbance, p/P_o, at maxima and minima			
Paste Curing, days	Shaking Time, days	Minimum 225 to 230 mμ	Maximum 245 mμ	Minimum 270 to 300 mμ	Maximum 350 mμ
6.......	2	0.13	0.15	0.05	0.22
9.......	11	0.18	0.21	0.07	0.33
22.......	11	0.12	0.20	0.06	0.35
67.......	11	0.20	0.28	0.10	0.48

At still younger ages of paste, with only 1 or 2 days' shaking time, absorbance curves were obtained on the extracts which resembled closely that shown for the 6-hr suspension in Fig. 2. The characteristic 260 mμ minimum and the 280 mμ maximum for the original lignosulfonate were still prominent; the

245 mμ maximum had only begun to develop at a relatively high absorbance in the short wavelength region, and the 350 mμ maximum had developed only to a small extent.

Further experiments with varying curing periods, in the order of 2 days, and with varying shaking periods, for 1 to 6 days, produced absorbance curves showing the gradual disappearance of the original lignosulfonate and the gradual build-up of the new product of interaction. These also showed that the build-up of the new product was favored by the paste condition as compared with the shaking of anhydrous cement with excess water. The rate of disappearance of the original sulfonate appeared, however, to be slower for the pastes than for the suspensions at very short periods of contact.

TABLE II.—ABSORBANCE OF AQUEOUS EXTRACTS FROM PASTES INVOLVING 3 CEMENTS, 2 LIGNOSULFONATE CONCENTRATIONS, AND 2 AGES OF PASTE.

Period of extraction by shaking with water, 10 to 11 days

Cement Type I	Lignosulfonate Dosage	Age of Paste, days	Absorbance, p/P_0, at maxima and minima			
			Minimum 225 to 230 mμ	Maximum 245 mμ	Minimum 270 to 300 mμ	Maximum 350 mμ
B.....	*N*	22	0.07	0.18	0.05	0.39
		67	0.21	0.31	0.09	0.56
	3*N*	22	0.46	0.65	0.23	1.06
		67	0.54	0.73	0.25	1.16
M.....	*N*	22	0.12	0.20	0.06	0.35
		67	0.20	0.28	0.10	0.48
	3*N*	22	0.39	0.55	0.18	0.88
		67	0.48	0.66	0.21	1.16
P.....	*N*	22	0.16	0.21	0.06	0.29
		67	0.17	0.23	0.06	0.37
	3*N*	22	....	0.57	0.18	0.86
		67	0.46	0.63	0.19	1.10

In Table II, absorbance maxima and minima are recorded for extracts from normal, *N*, and thrice-normal, 3*N*, dose cement pastes made with three different type I cements and taken at two paste ages, 22 days and 67 days. The cements are from three different plants, and the only significant difference in composition is the low alkali content of the *P* cement as compared with the high alkali contents of cements *M* and *B*. All shaking times were 11 days, and all readings were made in the KG-1 automatic unit with the blanks deducted. All samples are separate preparations.

It may be seen that over-all absorbance has increased with the longer curing period, with higher maxima at 245 and 350 mμ. The increase in these peaks going from *N* to 3*N* dosages is not uniform for the three cements and is not proportional to the original lignosulfonate concentrations. The "trough" at about 270 to 300 mμ, which was quite flat for the *N* samples, showed with the larger dosage a definite rise at about 290 mμ to the higher wavelengths, suggesting residual amounts of unaltered lignosulfonate in the extract. For 9*N* samples (not recorded), inconsistencies were even greater and unchanged lignosulfonate higher, with a definite hump at 280 mμ. It appears that only a limited amount of lignosulfonate will react with a given amount of cement under these conditions of test. It might be added that microscopic evidence for unaltered lignosulfonate was found in aged pastes originally of high lignosulfonate content.

The stability of these products in solution after extraction appears to be high. In Table III are given the values for minima and maxima in the absorbance curves for an *N*-dose paste for progressively longer periods of standing of the extract (up to 13 days). No significant change occurred. The paste had been cured for 6 days at 100 per cent relative humidity, followed by 2 days of shaking.

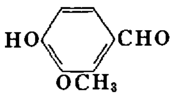
Table IV shows that the speed and times of centrifuging within the ranges used had no appreciable effect on absorbance values.

Identity of the Reaction Product Giving Absorbance Maxima at Wavelengths 245 and 350 mμ:

J. M. Pepper, Professor of Organic Chemistry at the University of Saskatchewan, drew the attention of the authors to the similarity between the absorbance curves obtained above for the aqueous phase of cement-lignosulfonate-water systems and those for high pH aqueous solutions of vanillin. J. M. Pepper and his assistant, M. Siddiqueullah, then kindly made chromatographic analyses of three of our aqueous extracts which showed the very prominent typical absorbance maxima. One was produced by the interaction of lignosulfonate solution with type I cement (4*N*) for 6 months in a gold-lined steel tube; the second was an extract of a powdered cement-lignosulfonate paste (2*N*, cured over water for 6 months, then extracted for 6 months in a silver-lined tube); the third was obtained by shaking a type I cement from another plant with a lignosulfonate solution, *N*, for 24 hr in a Pyrex bottle and allowing the mixture to stand at 25 C for 2 months.

The liquids were acidified with HCl and extracted continuously for 24 hr with ether. The ether extracts were dried over anhydrous magnesium sulfate, then concentrated to small volume. All the extracts gave strongly positive tests for both the phenolic hydroxyl group and the carbonyl group.

The extracts were chromatographed on a Whatman No. 1 filter paper for 16 hr, using the developer petroleum ether: *n*-butyl ether: water (6:1:1, organic phase). Concurrently, authentic samples of vanillin and syringaldehyde were chromatographed. Only a trace of syringaldehyde was present, but the position and density of the spots confirmed the presence of considerable amounts of vanillin in each sample of extract. Vanillin is an aromatic aldehyde of the formula



and is a degradation product of lignin.

TABLE III.—EFFECT OF TIME OF STANDING OF AQUEOUS CEMENT PASTE-LIGNOSULFONATE EXTRACTS ON ABSORBANCE VALUES.

Lignosulfonate dosage = *N* cement *M*
6 day moist-cured paste plus 2 days aqueous extraction.

Age of Extract at Time of Measurement	Absorbance, p/P_o, at maxima and minima			
	Minimum 225 to 230 mμ	Maximum 245 mμ	Minimum Approximately 290 mμ	Maximum 350 mμ
1 hr.	0.13	0.15	0.05	0.22
2 days	0.14	0.16	0.05	0.22
8 days	0.13	0.15	0.06	0.23
13 days	0.14	0.16	0.05	0.23

TABLE IV.—INFLUENCE OF SPEED AND TIME OF CENTRIFUGING ON ABSORBANCE VALUES OF AN EXTRACT.

Cement *M* lignosulfonate dosage = *N*
9 days moist-cured paste plus 11 days extraction time.

Speed of Centrifuging, rpm	Time of Centrifuging, min	Absorbance, p/P_o, at maxima and minima			
		Minimum 225 to 230 mμ	Maximum 245 mμ	Minimum 270 to 300 mμ	Maximum 350 mμ
9450	20	0.16	0.21	0.07	0.33
14750	20	0.18	0.22	0.07	0.33
14750	40	0.17	0.21	0.07	0.33
15850	20	0.16	0.19	0.07	0.33

It might be noted that a solution of pure vanillin at pH 10.75 has been found to be very stable at room temperature (9). The observation of a slight drop in the absorbance of the two maxima, noted above for aged mixtures, was therefore probably due to reaction with other products in the mixture or to a decrease in the pH of the solutions.

The possibility that degradation products other than vanillin, such as aldehyde derivatives of lignin, might produce similar maxima at 245 and 350 mμ is not excluded (7).

SUMMARY AND CONCLUSIONS

Interaction between a calcium lignosulfonate salt and hydrating cement in an aqueous medium is very rapid, as shown by ultraviolet absorbance measurements in the range of 220 to 400 mμ. This interaction is evidenced by the rapid disappearance of the characteristic 280 mμ maximum of the original lignosulfonate, followed by a new absorption system with maxima at about 245 and 350 mμ. An alteration or degradation of the original lignosulfonate structure apparently occurs, the product of which possesses at least some degree of solubility in aqueous media of high pH (or containing calcium hydroxide).

The change in absorbance at these maxima with change in ratio of original lignosulfonate to cement do not show a direct proportionality, although the absorbance at the maxima is roughly proportioned at a given time to the original quantity of lignosulfonate. At greater ages there is some tendency to regression of the absorbance at the maxima.

Experimental evidence indicates a high stability of the product responsible for the absorbance maximum at 350 mμ and that its formation and stability are favored by a limited aqueous phase such as obtained in a hardened cement paste under ideal curing conditions. This peak can therefore be used as a reliable indication of a lignosulfonate admixture in hardened portland-cement paste. The possibility that organic admixtures or adulterants might interfere with this determination was not investigated. The probability of any such material exhibiting a peak at this particular wavelength was considered very slight.

The two absorbance maxima which develop at wavelengths of about 245 and 350 mμ appear to be due to the alkaline form of vanillin resulting from alkaline hydrolysis of lignosulfonate.

Reproducibility of absorbance curves, under the conditions of test described, appears to be good. Absorbance values for the interaction product as well as for the original lignosulfonate were not affected significantly by certain deliberate variations in conditions of test.

In the present study, concentrations of lignosulfonate solutions and dosages in pastes covered only a range consistent with its use as an admixture in concrete. Experiments were also limited to a short wavelength range. It is possible that significant changes may occur at other wavelengths.

Despite these limitations and the possibilities of other methods, the experimental studies described provide a basis for a spectrophotometric method for determining qualitatively the presence of a lignosulfonate admixture in hardened portland-cement pastes. It is suggested that this method should prove equally effective for hardened mortars and concretes. Considerable further study would be required, however, to determine the influence of aggregate materials, organic adulterants, carbonation, and other factors.

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DISCUSSION

MR. W. G. HIME.[1]—The authors are to be congratulated on their excellent work in the very difficult field of organic analysis. My comments are made in the hope that they will be helpful in future work designed to give detailed procedures for the determination of organic admixtures in concrete.

The authors' statement concerning the improbability of other organic admixtures or adulterants exhibiting a peak at the ultraviolet wavelength of vanillin may be misleading. According to Fig. 3, vanillin absorbs appreciably in the 240 to 260 mμ range and in the 335 to 365 mμ range. These ranges represent 25 per cent of the ultraviolet region.

Nearly all aromatic organic compounds and several aliphatic compounds possessing conjugated double bonds absorb in the ultraviolet region. In fact, most organic compounds, except for some of low molecular weight, absorb to some extent. It would not appear to be unlikely that many of these several thousand compounds, each absorbing over up to 25 per cent of the ultraviolet region, could interfere in the lignosulfonate (as its hydrolysis product, vanillin) determination.

It would appear that a quantitative determination must be preceded by a qualitative test. This may be by spectrophotometric means or perhaps as a colorimetric spot test. The authors describe a color test for lignin, but it is not applicable to the vanillin resulting from the alkaline hydrolysis of the lignin. A specific color test for vanillin would be of great value.

MR. E. G. SWENSON (*author's closure*).—Mr. Hime's comments on the paper are very useful, particularly in focussing attention on the limitations of analytical methods generally.

The limitations of the method described in the paper were early recognized by the authors. In suggesting the improbability that organic adulterants or admixtures would interfere with this method, the authors had in mind the improbability that the type of interfering substances mentioned by Mr. Hime would be found in mortars or concretes.

Analysts are well aware that even well-established methods will fail if certain interfering substances are present.

In the opinion of this author, the possibility of substances being present in mortar or concrete which would interfere with this method is very remote.

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[1] Supervisor, Analytical Chemistry Laboratories, Portland Cement Assn., Chicago, Ill.

INTRODUCTION TO PRODUCERS' PAPERS ON WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES FOR CONCRETE

By M. E. Prior[1] and A. B. Adams[1]

Synopsis

Water-reducing admixtures and set-retarding admixtures are defined and the functional difference between them explained. The products of the four producers are divided into four chemical classifications, (1) lignosulfonic acids and their salts; (2) modifications and derivatives of lignosulfonic acids and their salts; (3) hydroxylated carboxylic acids and their salts; (4) modifications and derivatives of hydroxylated carboxylic acids and their salts. The four papers of the producers' group are concerned only with products falling within this classification.

A brief explanation of the function and mechanism of the actions of such admixtures in portland-cement concrete is suggested and discussed as it applies to this series of papers

The final section of this paper points out the significance of the design and quality control exercised by the producers to insure the functional performance of these admixtures. Particular emphasis is placed on this portion of the paper because of its importance to the consumer.

This is the first of four papers prepared for the Symposium on the Effect of Water-Reducing Admixtures and Set-Retarding Admixtures on Properties of Concrete representing the coordinated contribution of four producers of nationally and internationally used water-reducing admixtures and set-retarding admixtures for concrete.

The water-reducing admixtures and set-retarding admixtures furnished by these producers fall into four general classifications by chemical type. Admixtures of some of these four chemical types have been furnished for the past 25 years, and it is estimated that these admixtures have been used for the purposes stated in more than 200 million cubic yards of concrete in the United States during this period of time. They have been used extensively in Europe and Asia, as well as in North and South America. The acceptance and use of such admixtures has grown continuously since their introduction a quarter of a century ago, and it is further estimated these admixtures are being used at a rate to produce 25 million cubic yards of admixtured concrete annually in the United States alone.

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[1] Technical Service Manager and Research Manager, respectively, Construction Chemicals, Dewey and Almy Chemical Division, W. R. Grace & Co., Cambridge, Mass.

Further indication of current interest is found in the fact that ASTM Committee C-9 and certain public agencies are presently actively engaged in drafting methods of test and specifications governing the purchases and performance requirements of water-reducing admixtures and set-retarding admixtures for concrete. The first of the ASTM methods of test for such admixtures was issued in 1957 and revised in 1959 as ASTM Method C 403, Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles.[2] These methods of test and specifications will supplement those already in existence and in use by other public agencies and numerous private engineering firms.

Although there are some differences in the chemical nature and chemical composition of the water-reducing admixtures and set-retarding admixtures supplied by the four producers participating in this symposium, and although there may be some difference in the effect that these admixtures have on some of the qualities of plastic and hardened concrete, the fundamental influences on water requirement and retardation are basically the same. Further, since these admixtures have been used generally for like purposes in the same and in all classes of concrete, it appeared that the purposes of this symposium could be better served and unnecessary duplication avoided, by the presentation on the part of the participating producers of a series of coordinated papers concerning the influence and effect of water-reducing admixtures and set-retarding admixtures on the properties of plastic and hardened concrete. Such a series of papers must necessarily entail a description of the chemical nature, mechanism of action, specifications for the quality control and use of such admixtures, and most importantly, a detailed account of the engineering experience in the use of such admixtures during the 25 years of their application. This presentation would not be complete without an expression of the interest and activity of producer companies in research on chemical admixtures and in research designed to enhance the engineering properties of concrete to the end that concrete may continue to maintain and even advance the prominent position that it holds among materials of construction. To this end, the subject matter has been divided into the series of papers here presented. Thus, in these four papers, the participating producers have attempted to present a summation of the results of their cumulative research, laboratory, and engineering experience in this field. It is hoped that this joint presentation of the producers may contribute to the understanding of the functional benefits of water-reducing admixtures and of set-retarding admixtures in concrete.

In this paper, water-reducing admixtures and set-retarding admixtures are defined and the functional difference between them explained. The internationally used admixtures of these types are classified into the four chemical classifications under which they will be discussed in this group of papers. The behavior and the mechanism of action of such admixtures in portland cement concrete is discussed; and finally, emphasis is placed on the significance to the consumer of the chemical design and quality control exercised by the producers to insure the functional performance of these admixtures.

DEFINITION OF TERMS

Water-reducing admixtures are materials generally consisting of certain organic compounds or mixtures which,

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[2] Tentative Method (C 403 - 57 T), 1958 Book of ASTM Standards, Part 4, p. 712.

when added to portland cement concrete, markedly increase the fluidity, other than that effected through air entrainment of the concrete as measured by the slump cone or similar device. When such admixtures are used to produce concrete of slump equal to that of plain or plain air-entrained concrete of the same design, a significant reduction in water content is thereby made possible, thus enhancing the desirable properties of both the fresh and hardened concrete. Water-reducing admixtures are normally designed to have a negligible effect on the setting properties of concrete, but they may be modified for special purposes to produce either an accelerating or retarding effect on the concrete when desired.

Set-retarding admixtures are admixtures designed to delay in a controlled manner initial and final set beyond the normal setting time for the plain or plain air-entrained concrete and thereafter to have no effect upon the rate of strength development, or other properties of the concrete. Generally, and as considered in this symposium, set-retarding admixtures also reduce the water content of concrete and thus combine the functional benefits of water reduction with initial retardation.

CHEMICAL CLASSIFICATION

A review of the technical and patent literature shows that a great many substances have been considered as water-reducing or set-retarding admixtures for concrete. Many of these substances were suggested for certain specific applications. Some had undesirable effects upon other properties of the plastic or hardened concrete, and few have attained technical or commercial significance. It is generally recognized that present-day usage of water-reducing admixtures and initial-retarding admixtures in concrete had a beginning in the disclosures by Tucker,[3] Scripture,[4] and Winkler[5] of the effect of small quantities of organic compounds on the fluidity of portland cement pastes and concrete mixtures. These investigators showed that the addition of small quantities, on the order of 0.02 to 0.50 per cent based on the weight of the cement, of certain chemical substances profoundly affected the fluidity of the paste such that a significant reduction in the water-cement ratio could be made to produce concrete mixtures of a slump equal to that of the untreated concrete. Thus, in accordance with Abrams' **(1)**[6] finding, concrete of greater strength would result. Subsequent investigations have shown that strengths greater than those anticipated by the water-cement ratio law are usually obtained.

In the continuing research which these disclosures stimulated, the chemical substances originally suggested have been substantially improved for these purposes by modification of the processes by which those substances are refined from their source or manufactured. Modifications and derivatives of these substances have enhanced their functional properties, and other substances having these same properties in concrete mixtures, or which have a synergistic effect upon the dispersing activity of the basic substance, have been discovered.

The nationally and internationally used water-reducing admixtures and set-retarding admixtures may be classified in the following categories:

1. Lignosulfonic acids and their salts.
2. Modifications and derivatives of lignosulfonic acids and their salts.
3. Hydroxylated carboxylic acids and their salts.

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[3] G. R. Tucker, U. S. Patent No. 2,141,569 (1938).

[4] E. W. Scripture, U. S. Patent No. 2,169,980 (1939).

[5] K. Winkler, U. S. Patent No. 2,174,051 (1939).

[6] The boldface numbers in parentheses refer to the list of references appended to this paper.

4. Modifications and derivatives of hydroxylated carboxylic acids and their salts.

For the purposes of these papers, categories 2 and 4 are considered to include mixtures of functional materials with other substances added for specific effects.

Some few materials offered as water-reducing or set-retarding admixtures may fall into another or miscellaneous category. It is not the intent or purpose of these papers to discuss this category.

FUNCTION AND MECHANISMS

The principal active component of the water-reducing and set-retarding admixtures considered in the classifications given above are surface active agents; that is, they are substances which because of their chemical configuration or due to the influence of substituent groups therein are concentrated at the interface between two immiscible phases and alter the physicochemical forces acting at this interface. Such adsorption is sometimes due to the amphipathetic (2) nature of the molecule; but in the instances and with the classes of substances with which we are concerned, this adsorption is most probably a chemisorption effected by hydrogen bonding. The net effect is the same in either case.

Interfacial tension is always present at the interface between any two completely immiscible phases. It arises from a dissymetry among forces acting upon the molecules or atoms at or near the surface. A disperse system in which there is a measurable interfacial tension between the two or more phases present is thermodynamically unstable compared to the same system in which the dispersed particles have coalesced, that is, in which the total solid-liquid interface has been reduced.

Deflocculation, or dispersion, may be facilitated by a reduction in the interfacial tension of the system. Amphipathetic molecules may be adsorbed on the surface of the disperse phase and reduce the interfacial tension. Or such adsorption may be due to a positive attraction, or to an actual linkage, between specific polar groups in the adsorbent and in the surface active molecule. Such an adsorbed molecule, or ion, acts as a bridge making the transition from solid phase to liquid phase and the differences in the forces prevailing at the interface less abrupt.

Studies of the effect of dispersing agents upon portland cement are complicated due to the fact that in portland cement concrete—in the paste—we are dealing with suspensions of particles which are unstable physically and chemically, due to hydration which commences immediately the particles are wetted. However, it has been shown (3) from measurements of optical densities of filtrates from dilute suspensions of portland cement in water that substances such as the lignosulfonates are adsorbed by cement particles, and it can be shown experimentally, by observing under a microscope the electrophoretic migration of suspended cement particles, that through such adsorption the cement particles acquire a negative potential. Similar effects can be shown in the adsorption of hydroxylated carboxylic acids.

According to the classical concept of dispersion and the stability of disperse systems, the adsorption of an ion on the surface of a particle and the acquisition by the particle of a negative (or positive) potential creates an energy barrier causing an electrostatic repulsion between the particles which contributes to the degree and stability of dispersion. This same negative potential will orient the water dipoles around each particle and form a hydrated sheath which acts mechanically to prevent close approach between particles. Thus, there are three factors contributing to the degree of dispersion and the stability of a disperse system: (*a*) a reduction of the interfacial tension; (*b*) an increase in the electrokinetic potential; (*c*) a protective adherent sheath of water molecules.

Zhuravlev and Tikhonov (4) have studied the effect of increasing concentrations of ammonium lignosulfonate on the electrokinetic potential of cement-water systems and upon the mobility of the paste. It is their conclusion that the plasticizing action of ammonium lignosulfonate on the cement paste is due primarily to the formation of a hydrated sheath around each particle of cement.

In its normal state, portland cement is flocculated to some degree; that is, particles are held together, weakly, by forces of attraction between them. Flocculation is defined as the formation of clusters of particles which are disturbed by relatively weak mechanical forces or by a change in the physical forces at the interface between the solid and the suspending medium. It is the converse of dispersion. As stated, in portland cement concrete, in the paste, we are dealing with suspensions of particles which are unstable physically and chemically, due to hydration which commences immediately the particles are wetted. In the presence of a water-reducing admixture and at the time of initial contact with water, dispersion phenomena predominate. This does not mean that each cement particle is free to act independently of all others. But it does mean that the reduction in the forces of attraction between them permits greater mobility of the particles, that water freed from the restraining influence of a highly flocculated system is now available to lubricate the mix and provide a wetter consistency. As a result, the water content of a concrete mixture of given consistency may be substantially reduced.

The cement flocs are not dispersed by the addition of a dispersing agent, but rather the particles are held apart once the flocs have been broken up; that is, the breaking up of the flocs is accomplished by mechanical action of a mixer and then the particles are held apart by physicochemical means. The separation of the particles of cement by the dispersant results in a minimum resistance to movement of the grains which, in effect, is lubrication; and this lubricating effect results in decreased water requirement for any given consistency.

Powers has stated (5) that the attraction between cement and water is so strong that each cement grain becomes completely surrounded by water even though in dilute suspension the grains are clustered. Scripture (6) has suggested that experience with other hydrophilic solids, such as clays, would indicate that complete wetting of the surfaces of the flocculated cement is improbable. One of the effects of deflocculation or dispersion would be to expose more surface area of the cement to water and to possibly more complete hydration at earlier ages of the concrete. This, together with a more uniform distribution of the cement throughout the concrete and over the surface of the aggregate, could account for observed strength increases greater than those anticipated by Abrams' law.

OTHER INFLUENCES

It is not the purpose of this paper to discuss the means or mechanism by which such adsorption alters the course or rate of the chemical reactions which result in the hydration of portland cement. Schmid (7) has indicated that admixtures of class 3 react with the hydrates initially formed to form complex soluble salts reducing the quantity of initial hydration products and thus delaying hydration. Hansen (8) advances the theory that adsorption of ions or molecules of the lignosulfonates or hydroxylated carboxylic acids on the surface of the solid cement particles by ionic or by hydrogen bonding inhibits the initial hydration reactions.

Suffice it for the present purposes to state that such chemical substances as are being discussed in this symposium, do have a retarding influence upon the rates of these reactions. Consequently, the dispersing agent must be chemically modified or the water-reducing admixture formulated to minimize this retarding effect if retardation is not desired, and the set-retarding admixture must be designed to control this effect beneficially.

The dispersing agent may be combined with a catalyst or an accelerator to offset the retarding influence of the dispersant such that the resultant water-reducing admixture will have a negligible effect upon the rate of hardening of the concrete. Certain organic materials used in very small proportions materially increase the strength of concrete. Forbrich (9) terms such materials catalysts since, he states, in the proportions used, it is apparent that such materials cannot have a significant effect on strength by direct combination with any part of the cement but must react to promote some reaction of the cement in which the compound takes no part or at least only the part of an intermediate product. The catalyst is used in minute quantities only to overcome the initial retardation resulting from adsorption of the dispersant on the surface of the cement crystals. Accelerators, on the other hand, function in an entirely different manner. An accelerator may participate (8) in the chemical reactions which it influences; and for this reason, the system is more sensitive to the concentration of the accelerator and to changes in cement composition. This type of reaction is generally accompanied by the evolution of heat which, in turn, may speed up the rate of hydration of the cement beyond that desirable, if proportions are not carefully controlled. Accelerators are normally incorporated into water-reducing admixtures only to overcome the inherent retarding influence of the dispersant, but they may also be used under controlled conditions in sufficient concentration to exert a pronounced accelerating effect such that the setting time of the concrete is reduced. It is ordinarily preferable, where reduced setting time is desired, to consider and use the accelerator as a separate admixture for concrete. It is important that the accelerator or catalyst in the concentrations employed have no adverse effect on any of the properties of concrete, either in the plastic or hardened state, or otherwise impair its use in the design application. Hence, the chemical character and the formulation of these admixtures is a major factor in the production of materials for this purpose.

Forbrich (9) has reported that it is possible to control the early rate of heat liberation of cement in almost any desired direction by the use of suitable combinations of a dispersing agent and of an accelerator or a catalyst. He found that, in general, the combination of a dispersing agent and of an accelerator delayed the time of rapid heat evolution, increased slightly the total heat evolved up to 7 days and had no appreciable effect at 28 days and that the combination of dispersing agent, accelerator, and organic catalyst retarded heat liberation up to 3 days but had no effect thereafter. A combination of dispersing agent and organic catalyst reduced the early rate of heat liberation but increased the total heat liberated at 28 and 110 days.

Class 1 admixtures have been found[7] generally to effect a substantial retardation of temperature rise (rate of hydration), but the precise effect varies with

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[7] Private communication.

the composition of cement. On the other hand, use of an admixture typical of class 2 increases the rate of hydration so that this thermal curve lies close to that for the plain paste, thus indicating that the retarding effect can be compensated for by careful formulation.

Differential thermal analysis studies of hydrated cements at ages 7 and 28 days have indicated that water-reducing admixtures and set-retarding admixtures of class 1 and class 2 do not change significantly the identity or proportion of the hydration products ultimately formed during the hydration of portland cement.

Crepaz and Semenza have reported (10) that the presence of calcium lignosulfonate modifies the crystal development of the hydration product of tricalcium aluminate and of the ferric phase. They suggest that the action of calcium lignosulfonate is exerted chiefly on the tricalcium aluminate and the ferric phase and that the addition rate of chemical admixtures should be based on the exact knowledge of the mineralogical composition of the cement.

Each of the producer companies here represented conducts extensive research in the areas of their specific interest and according to their respective concepts of the basic needs of the industry. They recognize the need of more knowledge regarding surface-active materials, despite the fact that they function according to well-defined and established principles concerning the effects which such materials make possible. Unfortunately, most of the published research regarding the use of these substances in portland cement concrete has been empirical in nature. It should be possible with a better understanding of the physicochemical relationship of surface-active agents in portland cement and concrete to construct surface active substances and admixtures having even more precise effects. The principal manufacturers of admixtures are engaged in research of this nature. It is not timely to predict what the results may be, but we can proceed with the assured knowledge that out of similar research, although empirical, has come our present knowledge of the beneficial effect that chemical admixtures have in modern concrete technology and be confident that efforts expended in this direction will produce new and even more useful chemical admixtures for concrete.

QUALITY CONTROL

Water-reducing admixtures are designed for addition to a concrete mixture in a predetermined quantity as recommended by the manufacturer. The addition rate is based on the results of the research and engineering experience of the producer with various applications and different mix designs. Water-reducing admixtures are furnished in both dry and liquid form but generally are added to the concrete mixture in solution to afford more rapid and efficient distribution throughout the mass. As the term water-reducing implies, the primary function of this type of material is to reduce the water requirement of a concrete mix while maintaining the desired plasticity and workability. Normally there is considerably more water used in a concrete mixture than required for the complete hydration of the portland cement. This excess water is commonly referred to as water of convenience. Both water-reducing admixtures and set-retarding admixtures of types referred to in the producers' papers effect a marked reduction in this water of convenience with the result that the concrete to which admixture has been added is improved to an even greater extent than can be attributed to the familiar water-cement ratio law. The properties that are most notably benefited by this action are bleeding, segregation, compressive strength, flexural strength, permeability, volume change, abrasion resistance, and durability. These effects will be discussed in the subsequent papers of this group.

Set-retarding admixtures are sometimes referred to as water-reducing retarding admixtures for, as considered in this symposium, these combine some water reduction with initial retardation. Their primary function is to retard initially the set of concrete for a predetermined period of time. It has long been recognized that under certain conditions, concrete will set up too rapidly to be properly handled in the field. Difficult placing conditions may cause delay to such an extent that set takes place before the concrete is properly consolidated. Hot weather, low humidity, drying winds all contribute to rapid drying and fast setting which can result in cold joints between successive pours, plastic shrinkage, and poor bond to steel—to cite a few examples. The addition rate of a set-retarding admixture will vary, or it may be substituted by one of a series of set-retarding admixtures, depending upon the ambient temperature and specific job requirements. With higher temperatures, higher addition rates are employed in order to maintain the concrete in a plastic state for the desired period of time. While dispersing agents will normally have a retarding influence on the rate of hydration of portland cement, it is essential that this property be regulated in such a manner that the setting time of the concrete can be controlled in a manner and to the extent desired. The influence of some dispersing agents on the rate of hydration of portland cement may vary considerably with normal variation in the composition of the cement.

It is essential that admixtures be specifically designed for the intended purposes. Responsible producers recognizing the importance of quality control, maintain physical and chemical laboratory facilities where these materials are subjected to exacting chemical and performance specifications, from raw materials through processing to finished product to insure that the designed characteristics are maintained.

The use of water-reducing and set-retarding admixtures is based on fundamental principles of concrete design. Admixtures, like other ingredients of concrete, must be used in strict accordance with the design criteria of the mix. Relatively small quantities of these admixtures are added to the concrete and therefore, percentagewise, variations in addition rates may markedly change the properties of the concrete even as variations in cement content, water, or aggregate. The major manufacturers and distributors of admixtures have pioneered the development of dispensing equipment for proper proportioning the admixtures to concrete. The growing demand for automatic batching equipment, coupled with the recognition that admixtures have become an integral part of high-quality concrete, has resulted in batch plant manufacturers incorporating dispensing equipment in their latest construction. Similar types of equipment are also available for use on paving mixers and in product plants.

The producers of admixtures have attempted to recognize the needs of the concrete engineer and, through close liaison between the field and the research laboratory, are constantly striving to improve the application of these products to meet the increasing technological advances in the field of concrete. Knowledge of these requirements is based on the combined experience in the use of these admixtures in over 200,000,000 cu yd of concrete, plus a basic knowledge of the beneficial types of additions and admixtures in cement and concrete. This background enables these producers to evaluate the need of the design engineer, as well as the supplier.

SUMMARY

Water-reducing admixtures and set-retarding admixtures are surface-active chemicals specifically designed to perform their separate functions in portland cement concrete. Water-reducing admixtures are normally designed to have a neglibible effect upon the setting time of concrete, but they may be designed for specific purposes to have an accelerating or a retarding effect upon the setting time of concrete. Set-retarding admixtures, as considered in this symposium, have water-reducing characteristics.

The available water-reducing admixtures and set-retarding admixtures are divided into four general classifications by chemical type.

Although the study of the physicochemical effects that such admixtures have on portland cement is complicated by the inherent instability of the cement-water system, the surface active components of these admixtures appear to act in accordance with established physicochemical principles. Normally flocculated cement is broken up by mechanical action of the mixer, and then the particles are held apart by physicochemical means. Water freed from the restraining influence of the flocculated system becomes available to lubricate the mix. As a result, the water content of a concrete mixture of given consistency may be substantially reduced. Adsorption of these surface-active materials on the surfaces of the cement minerals does not appear to change the proportion or the identity of the hydration products formed; but such adsorption, unless compensated by incorporation into the admixture of an accelerator or of a catalyst, may have a retarding effect upon the rates of the reactions. The use of water-reducing admixtures and set-retarding admixtures in concrete contemplates the attainment of significant beneficial effects discussed in the other papers of this series.

The chemical substances selected for these purposes and the admixtures into which they are converted are subjected to exacting chemical requirements and performance qualities prior to their use. The use of the commercial, nationally and internationally available, water-reducing admixtures and set-retarding admixtures is supported by the research and technical personnel and facilities of the producer companies. The extensive research engaged in by the producer companies anticipates continued enhancement of the engineering qualities of concrete through chemical admixtures.

Acknowledgments:

This paper is one of a coordinated series of four papers prepared by representatives of four producers of water-reducing admixtures and set-retarding admixtures for concrete. The authors wish to acknowledge with appreciation their colleagues of the producer group who cooperated in furnishing information applicable to this paper; this information supplemented that available in the Dewey and Almy Chemical Division, W. R. Grace & Co., files.

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EFFECT OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES ON THE PROPERTIES OF PLASTIC CONCRETE

By C. A. Vollick[1]

Synopsis

Commonly used water reducers and set retarders are divided into four basic categories. The effect of materials from each of these classes on water reduction, set retardation, air entrainment, bleeding, workability and unit weight of plastic concrete is discussed.

Data are presented to show the effect of normal dosage and over-dosage of the admixtures at various temperatures. Influence of type and brand of cement, air entraining agents, and other admixtures on properties of plastic concrete is shown.

Application and dosage of the admixtures are given. Qualities of plastic concrete containing water reducers or set retarders that may be used to the advantage of the engineer who is seeking to solve a particular problem in the construction of a project are discussed.

Information presented in this paper is based upon field and laboratory tests and exchange of information among the producers participating in this symposium. This paper discusses the effect of water reducers and set retarders on the properties of plastic concrete. It should be recognized, however, that the properties of the plastic concrete influence properties of hardened concrete, including compressive strength, shrinkage, etc. Water-reducing admixtures discussed in this paper are compounds that derive their effect from influences other than air entrainment. Some of these products may also entrain air.

For the purpose of this symposium, nationally distributed water reducers and set retarders, as indicated in the introductory paper, are divided into four main classes:

Class 1.—Lignosulfonic acids and their salts.

Class 2.—Modifications or derivatives of lignosulfonic acids and their salts.

Class 3.—Hydroxylated carboxylic acids and their salts.

Class 4.—Modifications or derivatives of hydroxylated carboxylic acids and their salts.

The various products have been given a letter designation, which is the same in all of the producer papers.

Most water-reducing chemicals are also set retarders. The water-reducing effect of these admixtures is generally caused by one component that has retarding effects. Retarders may be modified by addition of an accelerator without losing their water-reducing effect. The resulting product, depending on formulation, may accelerate, retard, or have little effect on the rate of harden-

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[1] Chief, Engineering Laboratories. Sika Chemical Corp., Passaic, N. J.

ing of concrete. Class 1 admixtures are retarders that usually entrain small quantities of air. Class 3 admixtures are non-air-entraining retarders. Admixtures belonging to classes 2 and 4 may or may not entrain air and they may retard, accelerate, or have no effect on setting time.

Although all of these compounds are water reducers, their influence on specific properties of concrete may be quite different. In order to obtain desired results in modifying characteristics of plastic or hardened concrete, admixtures of one class or within one class, may be preferred over others, depending on type of concrete or job and temperature conditions.

TABLE I.—WATER REDUCTION OBTAINED WITH CONSTANT AIR, ONE BRAND OF CEMENT, AND DIFFERENT WATER REDUCERS OR SET RETARDERS.

Admixture	Neutralized Vinsol Resin	Product *A*, Class 1	Product *J*, Class 2	Product *H* Class 3	Product *M*, Class 4
Slump, in.	2¾	2¾	2½	3	3
Air content, per cent	4.8	4.3	4.5	4.5	4.7
Water reduction, per cent (compared with non-air-entrained concrete)	8	13	11	13	12

Effect on Plastic Concrete

Water Reduction:

Less water is required in a concrete mixture for a specified workability when a water reducer or set retarder is added. The use of these admixtures will permit reduction in the water-cement ratio if the cement content is maintained constant. The benefits derived from reduction in water-cement ratio may thus be expected to result from the use of these admixtures if all other conditions are equal. In many cases the benefits are much greater than would be expected from a simple reduction in water-cement ratio. Benefits can often be expected from their use even if the water content is not reduced.

Water reduction is desirable in any concrete mixture, provided the concrete can be properly compacted. Better concrete with increased compressive strength and less drying shrinkage may result from the use of water-reducers when the slump and air content are maintained constant. Water reduction is particularly desirable if aggregates have a high water requirement or if concrete slump must be greater than 3 in. for placing.

Recommended proportions of water reducers or set retarders will permit a reduction in mixing water of 5 to 16 per cent for a given slump. The actual water reduction is influenced by several factors, including type and brand of cement, air entraining capacity of the admixture, and richness of mix.

Water reduction can be obtained with air entrainment alone, but additional water reduction is possible when a water reducer or set retarder is added to the air-entrained concrete. Results shown in Table I were obtained with one brand of type I cement. Cement factor was 5.5 sacks per cu yd. Neutralized Vinsol resin was used as the air-entraining agent. Recommended dosages of admixtures were used and air content was adjusted where necessary by changing the proportion of air-entraining agent.

Table II demonstrates the relative effect of different air-entraining agents and water-reducing admixtures on water reduction at equivalent air content. Brand *A*, type I, cement was used with natural sand and crushed limestone coarse aggregate.

Increased water reduction is possible with air-entraining water reducers when the dosage, and consequently the air content are increased. Table III shows the water reduction and air content of concrete containing 5½ sacks per cu yd of a blend of four type I cements and various dosages of water-reducing admixtures of classes 1 and 2.

TABLE II.—RELATIVE EFFECT OF AIR-ENTRAINING AND WATER-REDUCING ADMIXTURES OF CLASSES 1 AND 2 ON WATER REDUCTION AT EQUIVALENT AIR CONTENT AND 3½ IN. OF SLUMP.

Air-Entraining Admixture		Water-Reducing Admixture			Cement Content, sack per cu yd	Water-Content, gal per cu yd	Air Content, per cent	Water Reduction, per cent
	grams per sack of cement	Product	Class	lb per sack				
None......	...	None	...	...	4.97	34.8	1.9	...
Class 3.....	0.99	None	...	...	5.02	32.2	5.0	7.5
Class 3.....	0.57	*D*	2	0.25	5.00	29.4	5.0	15.5
None......	...	*A*	1	0.25	5.02	29.7	4.5	14.7

TABLE III.—EFFECT OF DOSAGE OF WATER-REDUCING AND SET-RETARDING ADMIXTURES OF CLASSES 1 AND 2 ON WATER REDUCTION AND AIR CONTENT OF CONCRETE.

Admixture	Dosage, lb per sack	Slump, in.	Air Content, per cent	Water Reduction, per cent
A.............	0.15	3½	3.8	11.3
A.............	0.25	4½	5.0	14.2
A.............	0.35	4½	6.5	17.9
D.............	0.15	4	2.5	5.8
D.............	0.25	3½	3.3	9.9
D.............	0.35	4	3.8	12.8
E.............	0.15	3½	2.8	8.0
E.............	0.25	4	4.0	13.5
E.............	0.35	4	5.0	15.3
None...........	...	3½	2.0	...

Effect of Type and Brand of Cement:

Water reduction can be obtained with all hydraulic cements, including aluminous cement and portland blast-furnace-slag cement. Some data obtained with a variety of cements in non-air-entrained concrete using 5½ and 6 sacks of cement and recommended dosage of a class 3 retarder (product *H*) are shown in Table IV. Original water-cement ratio of these mixes varied from 0.52 to 0.54 by weight.

Different types or brands of cement may not show the same water reduction with a given water-reducing admixture or with different admixtures. A few cements may not show the anticipated water reduction when tested in concrete with recommended proportions of water reducers.

Cement *A* in Table V is an example of a cement that permitted relatively low water reduction in concrete when admixtured with product *H*, class 3; product *D*, class 2; and product *J*, class 2. For comparison, data on concrete admixtured with product *H*, class 3 and product *J*, class 2 using the same fine and coarse aggregates, but with a different cement, are shown. Nominal cement content was 5½ sacks per cu yd, in all mixes.

Scripture and Litwinowicz (1)[2] reported a series of tests with twelve cements from different sections of the country. Nine of the cements were type I portland cement, two were type III, and one was type II. Concrete mixtures containing nominal cement contents of 4½ and 6 sacks of cement per cu yd were made with each cement and the influence of a class 1 (product *C*) water-reducing admixture was determined.

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

TABLE IV.—WATER REDUCTION OBTAINED WITH ONE CLASS 3 WATER-REDUCING RETARDER (PRODUCT *H*) AND DIFFERENT CEMENTS.

Cement	Water Reduction, per cent	Cement Factor
Aluminous	5.0	5.5
Type I, brand *A*	7.7	5.5
Type I, brand *B*	5.4	5.5
Type I, brand *C*	6.4	5.5
Type I, brand *D*	5.1	6.0
Type II, brand *E*	5.1	6.0
Type II, brand *F*	6.3	6.0
Type III	4.9	6.0

TABLE V.—WATER REDUCTION INFLUENCED BY BRAND OF CEMENT.

Admixture	Cement *A*				Cement *B*		
	None	Product *H*	Product *D*	Product *J*	None	Product *H*	Product *J*
Water, gal per cu yd	35.9	34.6	34	34	33.4	30.4	29.7
Slump, in.	2.3	2.3	2.5	2.8	2.3	2.0	1.8
Entrained air, per cent	1.1	1.2	2.5	2.0	1.6	2.1	1.9
Computed cement factor, sack per cu yd	5.42	5.44	5.38	5.43	5.46	5.51	5.54
Computed water-cement ratio, gal per sack	6.62	6.36	6.32	6.26	6.12	5.52	5.36
Water reduction, per cent	...	3.6	5.4	5.4	...	9.0	11.1

Water reduction obtained with the water-reducing admixture varied from 9.2 to 18.7 per cent in the 6-sack mixes and averaged 13.7 per cent. Water reduction in the 4½-sack mixes varied from 10.8 to 19.5 per cent and averaged 16.0 per cent.

Effect of Aggregate:

Significant water reduction can be obtained in concrete using angular, rounded, lightweight, and heavyweight aggregate. Table VI shows the water reduction obtained with natural sand and gravel, expanded shale coarse and fine aggregate, and expanded blast-furnace slag coarse and fine aggregate, when a class 2 admixture (product *D*) was added to the mixtures. The same brand of type I cement was used in all of these concrete mixtures.

An air-entraining agent (AEA-1) was added to the mixtures containing expanded shale and blast-furnace slag to increase air content.

Water reduction obtained with ilmenite, natural sand and gravel, expanded shale fine and coarse aggregate, and natural sand and crushed stone coarse aggregate with a class 3 admixture (product *H*) is shown in Table VII. No air-entraining agent was added to any of these mixtures.

A few aggregates will have a different effect on water reduction and strength development ordinarily expected from the admixture concrete. Sand and gravel from source *B* in Table VIII permitted approximately 50 per cent as much water reduction as sand and gravel from source *A* when used in concrete with the same cement and recommended amounts of a class 2 admixture. In addition, the admixture concrete containing aggregates from source *B* did not produce the expected increase in compressive strength.

Effect of Cement Content:

Water-reducing admixtures have been used in concrete containing 3 to 9 sacks of cement per cu yd. Water reduction obtained with two class 2 admixtures (products *D* and *J*) when cement content was varied from 4 to 8 sacks per cu yd is shown in Table IX. Cement was a blend of types I and II. Natural sand and ¾-in. maximum size gravel were used in the mixtures.

Different admixtures may not have the same effect on water reduction with a particular cement when the cement content is increased. The data shown in Table X were obtained with one brand of type I cement and natural sand and gravel. Generally admixtures that entrain air show high water reduction with low cement contents and less water reduction as the cement content is increased. They also show higher air-entraining capacity for lean mixes than for richer mixes.

TABLE VI.—EFFECT OF AGGREGATES AND CEMENT CONTENT ON WATER REDUCTION OF A CLASS 2 ADMIXTURE (PRODUCT *D*).

Admixture	Slump, in.	Cement Content, sack per cu yd	Water-Cement Ratio, gal per sack	Air Content, per cent	Water Reduction, per cent
NATURAL SAND AND GRAVEL					
None	3½ to 4	4.45	7.31	2.6	...
D	3 to 4	3.91	7.37	4.1	11.4
None	4 to 5	5.91	5.64	2.5	...
D	3 to 4½	4.91	5.85	4.0	13.8
D	4 to 4½	5.84	5.00	3.8	12.9
EXPANDED SHALE COARSE AND FINE AGGREGATE					
None	2	4.97	6.31	8.9	...
D	2	4.34	5.93	11.4	18.0
None	2	6.00	5.35	7.8	...
D	2	5.38	4.91	9.5	17.9
None	2	6.90	4.69	8.7	...
D	2	6.37	4.29	7.6	15.2
EXPANDED BLAST-FURNACE SLAG COARSE AND FINE AGGREGATE					
None	2 to 2½	5.55	9.31	10.3	...
D	2 to 3	5.41	8.74	10.7	8.4
None	2 to 3	7.70	6.70	8.7	...
D	2½ to 3	7.13	6.11	10.7	15.6

Effect of Slump:

Water-reducing admixtures are effective in concrete with high or low slump. Table XI shows the water reduction obtained with three different admixtures in 3-in. and 6-in. slump, air-entrained concretes containing approximately 5½ sacks of type I cement per cubic yard.

Effect of Fly Ash:

Water reducers and set retarders may be used in concrete in which fly ash is used as an addition or a replacement for part of the cement. Total water reduction is influenced by the type and amount of fly ash. Results of a series of tests made with varying proportions of two fly ashes are shown in Table XII. A class 2 admixture (product *D*) was used and neutralized Vinsol resin was added to produce the air contents shown.

Retardation:

Subcommittee III-n on Methods of Testing Setting Time of Concrete of ASTM Committee C-9 on Concrete and

Concrete Aggregates has prepared a tentative method of test for time of setting of concrete mixtures by Proctor penetration resistance needles (ASTM Method C 403 T).[3] The test is performed on mortar sieved from the concrete and is intended for use in determining the effect of variables including temperature, cement, and admixtures on the setting time and hardening characteristics of concrete.

TABLE VII.—EFFECT OF AGGREGATES, BRAND OF CEMENT, AND CEMENT CONTENT ON WATER REDUCTION OF A CLASS 3 ADMIXTURE (PRODUCT *H*).

Admixture	Cement	Slump, in.	Cement Content, sack per cu yd	Water-Cement Ratio, by weight	Air Content, per cent	Water Reduction, per cent
ILMENITE FINE AND COARSE AGGREGATE						
None	type I	1.0	6.1	0.61	1.0	...
H	brand *A*	1.0	6.1	0.58	1.1	4.9
EXPANDED SHALE FINE AND COARSE AGGREGATE						
None	type I	3.0	8.0	0.49	2.0	...
H	brand *B*	3.0	8.0	0.43	2.5	12.2
NATURAL SAND AND GRAVEL AGGREGATE						
None	type I	2.8	7.5	0.41	...	...
H	brand *C*	2.5	7.5	0.39	...	4.9
H	....	2.5	6.5	0.44	...	6.9
NATURAL SAND AND GRAVEL AGGREGATE						
None	type II	3.8	5.4	0.54	2.3	...
H	brand *D*	4.3	5.4	0.49	2.9	9.3
NATURAL SAND, CRUSHED STONE AGGREGATE						
None	type I	4.5	5.5	0.63	...	...
H	brand *E*	5.0	5.0	0.62	...	10.4
None	brand *F*	3.5	6.1	0.55	1.5	...
H	....	3.0	6.0	0.52	1.9	7.0
None	brand *E*	4.3	8.0	0.42	...	...
H	....	4.0	7.0	0.43	...	10.4
None	type II	3.0	6.0	0.57	1.3	...
H	brand *G*	3.0	6.0	0.54	1.6	5.3

Retardation of the setting time of concrete is often desirable when temperature increases to avoid loss in slump and greater water demand. Retardation is beneficial when concrete must be transported or pumped long distances. Danger of cold joints in large concrete sections is reduced if a retarder is incorporated in the concrete.

Manufacturers of some class 1, class 2, and class 4 admixtures recommend that a fixed proportion of their admixture be used. Some manfacturers of class 1 and class 2 products make available several formulations so constituted that the effect of differing temperature can be

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[3] Tentative Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles (C 403 - 57 T), 1958 Book of ASTM Standards, Part 4, p. 712.

TABLE VIII.—EFFECT OF TWO AGGREGATES ON WATER REDUCTION OF A PRODUCT OF CLASS 2.

Aggregate	Source *A*		Source *B*	
	Plain	Admixture	Plain	Admixture
Specific gravity of sand	2.62	2.62	2.64	2.64
Specific gravity of gravel	2.62	2.62	2.68	2.68
Fineness modulus of sand	2.42	2.42	2.49	2.49
Dry rodded unit weight of gravel, lb per cu ft	104.5	104.5	96.7	96.7
Slump, in	4.5	3.0	4.0	3.5
Cement content, sack per cu yd	5.51	4.69	5.48	4.64
Water-cement ratio, gal per sack	6.19	5.91	6.56	6.97
Air content, per cent	1.4	4.4	2.0	4.5
Water reduction, per cent	...	18.7	...	10.0

TABLE IX.—EFFECT OF CEMENT CONTENT ON WATER REDUCTION OBTAINED WITH CLASS 2 ADMIXTURES, PRODUCTS *D* AND *J*.

Nominal Cement Content, sack per cu yd	4			5			6			7		8	
Admixture	None	*D*	*J*	None	*D*	*J*	None	*D*	*J*	None	*J*	None	*J*
Water-cement ratio, gal per sack	8.9	8.3	8.1	7.3	6.7	6.6	5.9	5.6	5.5	5.1	4.8	4.7	4.4
Slump, in	4.0	4.0	4.0	4.5	4.5	4.5	4.3	3.8	3.8	4.3	3.8	4.3	3.5
Air content, per cent	2.7	4.7	4.9	2.2	4.9	4.7	1.9	3.8	3.9	1.9	3.5	1.9	3.2
Water reduction, per cent	...	6.7	9.1	...	8.2	9.5	...	5.1	6.8	...	6.0	...	6.4

TABLE X.—EFFECT OF CEMENT CONTENT ON WATER REDUCTION.

Obtained with Class 3 Admixture, Product *H*; Class 1 Admixture, Product *A*; and Class 4 Admixture, Product *M*.

Nominal Cement Content, sack per cu yd	4½		5½		6½		7½	
	No Air Added	Air Added	No Air Added	Air Added	No Air Added	Air Added	No Air Added	Air Added
CLASS 3, PRODUCT *H* ADMIXTURE								
Slump, in	3.0	2.8	3.0	3.0	3.3	3.3	3.0	3.3
Air content, per cent	2.6	4.2	1.5	4.1	2.0	3.8	1.8	4.3
Water-cement ratio, by weight	0.65	0.60	0.57	0.50	0.45	0.41	0.40	0.39
Water reduction, per cent	5.5	12.8	5.0	11.4	5.8	13.1	9.0	10.3
CLASS 1, PRODUCT *A* ADMIXTURE								
Slump, in	3.5	3.0	3.0	2.8	3.3	...	3.3	4.0
Air content, per cent	3.3	4.0	2.4	4.0	4.1	...	3.2	4.5
Water-cement ratio, by weight	0.62	0.58	0.52	0.50	0.44	...	0.41	0.38
Water reduction, per cent	9.0	15.6	11.5	11.8	8.9	...	7.8	12.9
CLASS 4, PRODUCT *M* ADMIXTURE								
Slump, in	3.0	...	3.3	...	2.5	...	3.0	2.8
Air content, per cent	5.0	...	3.6	...	4.3	...	3.6	4.0
Water-cement ratio, by weight	0.61	...	0.53	...	0.44	...	0.42	0.40
Water reduction, per cent	11.4	...	11.3	...	8.2	...	7.4	9.0

controlled by using a different admixture for each temperature condition but at a constant proportion. Manufacturers of class 3 retarders suggest that the dosage of their retarder be increased as temperature increases in order to maintain similar setting time and a constant water-cement ratio at all temperatures. Some manufacturers of class 1 retarders also recommend that the dosage of their material be varied with temperature.

TABLE XI.—WATER REDUCTION OBTAINED WITH DIFFERENT WATER REDUCERS IN 3-IN. AND 6-IN. SLUMP CONCRETE.

Admixture	Neutralized Vinsol Resin		Class 1, Product *A*		Class 3, Product *H*		Class 4, Product *M*	
Slump, in.	6.3	2.8	6.3	2.8	6.0	3.0	6.0	3.0
Air content, per cent	5.6	4.8	5.6	4.3	5.0	4.5	4.7	4.7
Water reduction, per cent	9.1	8.0	14.7	13.0	14.0	13.0	13.4	12.0

TABLE XII.—WATER REDUCTION OBTAINED WITH A CLASS 2 ADMIXTURE (PRODUCT *D*) IN CONCRETE CONTAINING VARYING AMOUNTS OF TWO FLY ASHES.

	Fly Ash No. 1				Fly Ash No. 2		
Cement content, lb per cu yd	475	452	352	250	452	352	250
Fly ash, lb per cu yd	None	75	126	225	75	126	225
Slump, in.	4.5	5.0	4.5	5.0	4.5	4.5	4.5
Air content, per cent	4.0	4.0	4.5	4.6	4.4	4.5	3.9
Water reduction, per cent	12.6	8.7	9.9	10.2	10.6	8.6	5.1

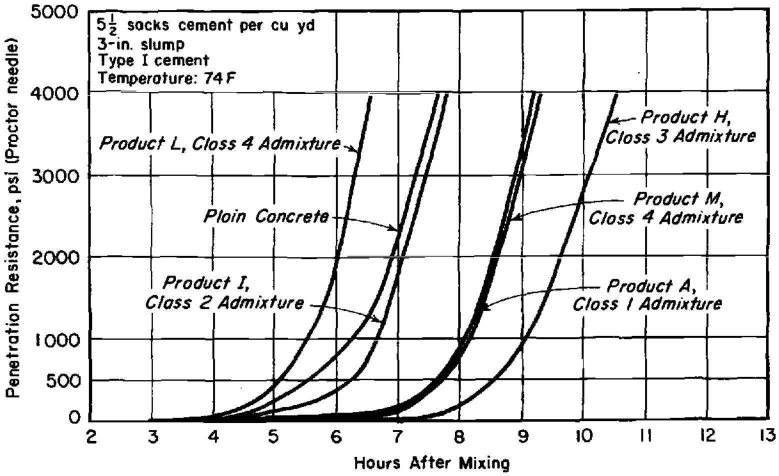

FIG. 1.—Effect of Recommended Dosage of Various Classes of Admixtures on Rate of Hardening of Concrete.

Effect of Specific Admixtures and Dosage:

Setting time is influenced differently by different admixtures. Admixtures in classes 1 and 3 normally retard. Modifications of these materials, represented by classes 2 and 4, may retard, have little effect on setting time, or may accelerate setting time. The recommended dosage for one retarder may have a different retarding effect than the recommended dosage for another material. If the dosage is doubled, greater differences may be observed.

The effect of recommended dosages of five different admixtures on rate of hardening of concrete at 74 F is shown in Fig. 1, and the effect of double dosage of the same admixtures is shown in Fig. 2. One brand of type 1 cement and aggregates from the same source meeting the requirements of ASTM Specification C 33 - 57[4] were used in all tests. Concrete mixtures were all designed for 3-in. slump. One of the admixtures used in this series (product *L*) is a class 4 accel-

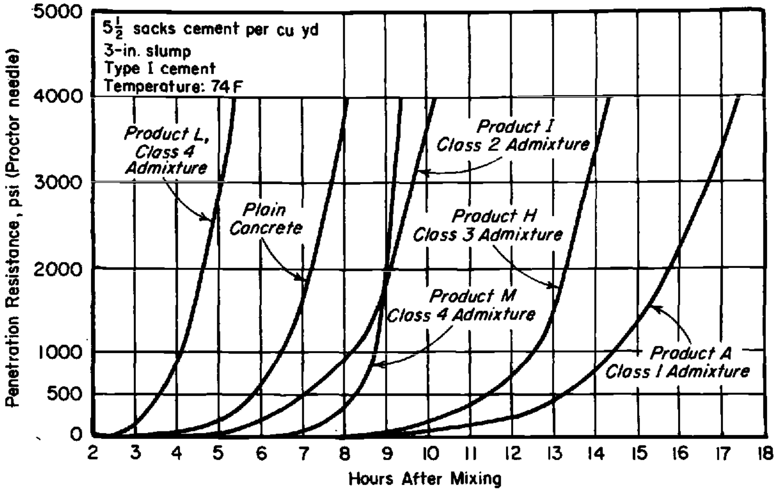

FIG. 2.—Effect of Twice Recommended Dosage of Various Classes of Admixtures on Rate of Hardening of Concrete.

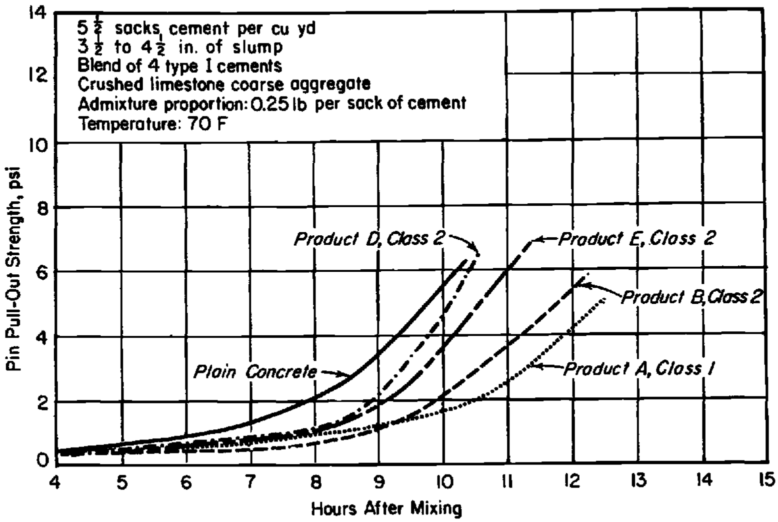

FIG. 3.—Effect of Admixtures of Classes 1 and 2 on Hardening Rate of Concrete as Measured by Bond Pull-Out Pins.

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[4] Specification for Concrete Aggregates, (C 33 - 57), 1958 Book of ASTM Standards Part 4, p. 457.

erator. The other class 4 admixture (product *M*) is a retarder.

TABLE XIII.—EFFECT OF TWO CLASS 3 RETARDERS ON HARDENING OF CONCRETE AT DIFFERENT TEMPERATURES.

Cement	Admixture	Dosage, oz per sack	60 F		80 F		95 F	
			hr	per cent	hr	per cent	hr	per cent
VIBRATION LIMIT, 500 PSI PROCTOR NEEDLE PENETRATION RESISTANCE								
Type I	none	...	8.2	100	5.8	100	4.5	100
	product *N*	3	8.4	101	5.8	100	4.9	109
		4	9.0	110	6.9	119	5.6	124
		5	11.0	134	7.7	133	6.2	138
	product *H*	3	9.9	121	7.1	122	5.2	116
		4	11.1	135	8.4	145	6.0	133
		5	13.1	160	9.3	161	7.9	176
Blend of three type I cements	none	...	7.0	100	5.2	100	4.4	100
	product *N*	3	9.3	133	6.1	117	5.2	118
		4	10.0	143	7.1	136	5.5	125
		5	11.9	170	8.1	156	6.5	148
	product *H*	3	10.6	151	7.1	136	5.7	130
		4	12.6	180	8.7	167	7.1	162
		5	15.6	222	11.2	215	9.3	211
FINAL SET, 4000 PSI PROCTOR NEEDLE PENETRATION RESISTANCE								
Type I	none	...	13.6	100	7.9	100	6.2	100
	product *N*	3	12.1	89	7.6	96	6.5	105
		4	13.1	96	8.0	101	6.8	110
		5	14.9	110	9.1	115	7.5	121
	product *H*	3	13.9	102	8.9	115	7.0	113
		4	15.0	110	10.1	128	8.0	129
		5	18.5	136	12.4	157	9.9	160
Blend of three type I cements	none	...	12.1	100	7.0	100	5.7	100
	product *N*	3	13.2	109	7.6	109	6.4	112
		4	13.7	113	8.6	123	6.9	121
		5	16.4	136	9.8	140	8.0	140
	product *H*	3	14.7	122	9.0	129	7.3	128
		4	16.3	135	10.8	154	9.0	158
		5	20.3	168	13.5	193	11.4	200

The effect of recommended dosages of three class 2 admixtures and one class 1 admixture on rate of hardening of concrete at 70 F is shown in Fig. 3. The cement used in these tests was a blend of four type I cements. Coarse aggregate was a crushed limestone, ¾-in. maximum size, and its nominal cement content was 5½ sacks per cu yd. Rate of hardening was measured by bond pull-out pins (2).

Effect of Temperature:

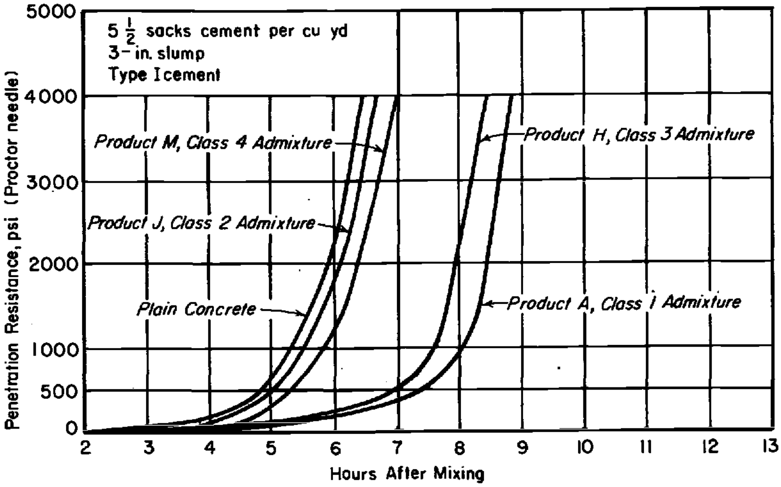

FIG. 4.—Effect of Recommended Dosage of Admixtures on Rate of Hardening of Concrete at 92 F.

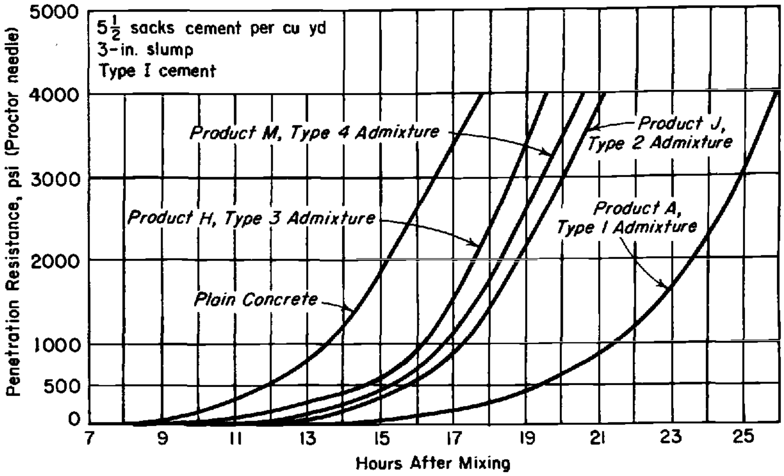

FIG. 5.—Effect of Recommended Dosage of Admixtures on Rate of Hardening of Concrete at 50 F.

Retarding admixtures will retard the set of concrete at all temperatures. Retardation at a given temperature is increased as the proportion of set-retarding admixture is increased. The retardation produced by a given dosage of a given admixture will be different at different temperatures if the retardation is expressed in hours.

Table XIII shows the percentage of retardation obtained with three proportions of two class 3 admixtures in concrete made with two different cements and tested at different temperatures. The number of hours required for admixture concrete to reach vibration limit or final set has been calculated as a percentage of the number of hours required for plain concrete to reach the same degree of hardening. When expressed in this manner, the effect of retarders is remarkably uniform.

Setting times of concrete containing recommended proportions of admixtures and maintained in a temperature-controlled room at 92 F are shown in Fig. 4; setting times at 50 F are shown in Fig. 5. The proportion of class 3 admixture used at 50 F was reduced in accordance with the manufacturer's instructions. The standard proportion of other admixtures was used. The data indicate that setting time can be controlled at any temperature by varying the amount of admixture. Water reduction and other benefits resulting from the use of admixtures can be obtained at low temperatures without undue influence on setting time if the correct proportion of admixture is used. Some manufacturers of class 1 and class 2 products make available different formulations for use at different temperatures. The rate of hardening can be then controlled by using a different admixture for each temperature but at a constant proportion.

Comparison between rate of hardening of plain concrete and four admixture concretes at 55 to 60 F and at 90 F as measured by bond pull-out pins is shown graphically in Fig. 6. Three class 2 admixtures and one class 1 admixture were used in the tests.

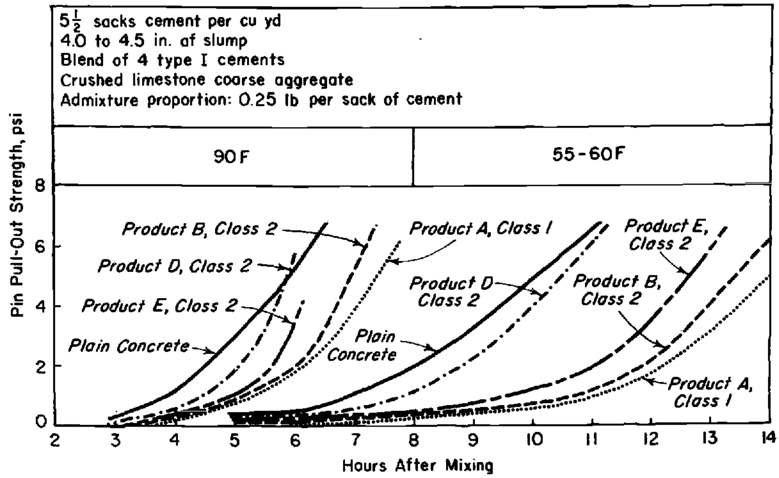

FIG. 6.—Effect of Class 1 and 2 Admixtures on Hardening Rate of Concrete at 55 to 60 F and 90 F as Measured by Pull-Out Pins.

Effect of Type and Brand of Cement:

Different types of cements and cements of the same type from different mills have different hardening characteristics. Specific retardation with a particular cement can be determined only by trial. Set retarders have been used successfully with a wide variety of cements from all parts of the world.

Rate of hardening at 76 F of four concretes made with different types of cement and standard dosage of a class 3 (product *H*) set-retarder is shown in Fig. 7. Nominal cement content was $5\frac{1}{2}$ sacks per cu yd and slump was 3 in. The vibration limit was delayed approximately the same amount with all cements, but final set was delayed more with type I and type III cements than with the slower setting cements.

Effect of Overdosage:

The dosage recommended by the manufacturer should be used unless a specific degree of retardation is desired and tests have been made to determine the correct proportion of admixture required. Overdosage may result in excessive retardation, delay removal of forms and necessitate longer curing periods.

Products sold by nationally recognized manufacturers have been tested in the laboratory and the field under a variety of conditions. These products have been refined, and harmful constituents of the raw materials have been reduced or removed. Unrefined products are variable in action. A slight overdosage of these materials may result in abnormal setting characteristics, and compressive strength may suffer. An example of results obtained with an unrefined product of class 1 is shown in Table XIV.

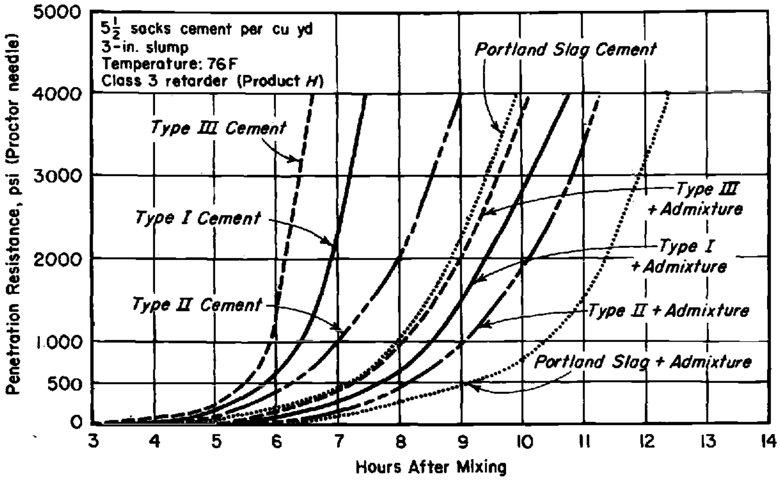

FIG. 7.—Admixtures Retard All Types of Cement.

Proven retarders will not cause permanent damage to concrete if accidentally used in excess, provided the concrete is protected from drying by fog spraying or other methods and forms are not removed until control cylinders indicate satisfactory strength has been attained.

During construction of the Kittimat Project by the Aluminum Company of Canada, Ltd., tests were made with concrete containing seven times the normal dosage of a class 3 admixture (product *H*). It is reported that the concrete did not harden for 19 days. At 28 days the compressive strength of the retarded concrete was 2190 psi and at 90 days it was 6900 psi.

An investigation of the effect of four times normal dosage of two air-entraining and two non-air-entraining retarders was made in the Joint Research Laboratory sponsored by the National Sand and Gravel Assn. and the National Ready Mixed Concrete Assn. (3). They found that four times the recommended proportions of these admixtures produced long delays in hardening. The two non-air-entraining retarders behaved much the same at four times their normal rate of usage as at normal rates except that setting and hardening were delayed longer. The air-entraining retarders produced an early stiffening which was followed by a period of inactivity of several days. At four times the recommended rate of usage, the air-entraining retarders produced lower strengths than normal cement concrete at all ages.

Air Entrainment:

Some of the basic chemicals used and some of the products marketed as water reducers or set retarders cause entrainment of air in concrete in addition to influencing water requirements or setting time of concrete, or both. Air entrainment also increases plasticity and is partly responsible for the water reduction possible with these materials. Water-reducing or set-retarding admixtures may be used in plain or air-entrained concrete. If the concrete is to be exposed to freezing and thawing and the admixture does not entrain sufficient air for frost resistance, a regular air-entraining agent must be added to secure the required air content.

Class 1 admixtures generally entrain 2 to 3 per cent air, but higher air contents are sometimes obtained. Class 3 admixtures do not ordinarily entrain air. Either class can be modified to entrain air and become class 2 or 4 admixtures, respectively. Class 2 and class 4 admixtures may or may not entrain air depending upon the modifications that were made. If the modifications do not include the addition of an air-entraining agent they will not entrain air or will only entrain limited amounts of air.

Set-retarding and water-reducing admixtures have little effect on air content of low-slump (1 to 2 in.) concrete, provided the water content is reduced to maintain the same slump in the admixture concrete. If they are added to an air-entrained concrete mixture having 3 to 6 in. of slump, the air content will usually increase unless the quantity of air-entraining agent is reduced.

TABLE XIV.—ABNORMAL SETTING AND STRENGTH REDUCTION MAY RESULT FROM USE OF UNREFINED PRODUCT OF CLASS 1.

	Plain Concrete	Unrefined Class 1 Admixture, 0.5 lb per sack	Refined Class 1 Admixture, 0.5 lb per sack
Computed cement content, lb per cu yd	517	496	520
Water-cement ratio, by weight	0.60	0.52	0.51
Slump, in.	3.0	3.3	3.5
Air content, per cent	1.6	7.4	3.3
Hours to reach vibration limit, 500 psi Proctor needle	5.5	19.5	13.0
Hours to reach final set, 4000 psi Proctor needle	7.8	23.1	17.1
Compressive strength at 28 days, psi	4265	3855	4595
Compressive strength at 90 days, psi	4900	3930	5570

The proportion of air-entraining agent can sometimes be reduced 25 to 75 per cent for the same air content and slump when a water reducer or set retarder is incorporated in the mixture. Water reducers or set retarders that normally entrain air must be used with less air entraining agent than admixtures that do not entrain air. As shown in Table XV, air content can be easily adjusted when recommended proportions of water reducers or set retarders are used. One brand of cement, Vinsol NVX, and a standard dosage of each of the four classes of water reducers and set retarders at 3-in. slump was used in the concretes.

The air content of concrete made with air-entraining cement may be more difficult to control because the air-entraining agent is interground in the cement and proportions cannot be varied. Air content of the concrete can only be controlled by adding an air-detraining agent or by substituting a regular portland cement for part of the air-entraining cement.

Some admixtures may entrain varying amounts of air with regular portland cement when the quantity of admixture is varied. Air contents obtained with 3-in. slump concrete containing 5½ sacks of one brand of type I cement per cubic yard and different water reducers or set retarders are shown in Table XVI.

TABLE XV.—AIR CONTENTS OBTAINED WITH RECOMMENDED DOSAGES OF WATER REDUCERS AND SET RETARDERS IN CONCRETE CONTAINING AN AIR-ENTRAINING AGENT.

Water Reducer or Set Retarder	None	Product *A* Class 1		Product *J*, Class 2		Product *H*, Class 3		Product *M*, Class 4	
Quantity Vinsol NVX, oz per sack cement	0.5	0.5	0.25	0.5	0.375	0.5	0.375	0.5	0.125
Slump, in.	3.0	3.0	3.0	3.0	3.0	2.75	3.5	3.0	3.25
Air content, per cent	4.8	7.4	4.4	5.7	4.7	5.9	4.4	7.8	4.9
Cement content, lb per cu yd	512	517	514	515	514	517	513	513	512

TABLE XVI.—AIR CONTENTS OF CONCRETE CONTAINING VARYING PROPORTIONS OF WATER REDUCERS OR SET RETARDERS.

Water Reducer or Set Retarder	Air Content, per cent		
	Recommended Dosage	Half Recommended Dosage	Twice Recommended Dosage
Class 1, product *A*	2.4	1.7	3.3
Class 2, product *X*	4.6	3.1	8.5
Class 2, product *J*	2.5	1.9	3.1
Class 3, product *H*	1.5	1.6	1.8
Class 4, product *M*	3.6	2.7	6.7
Class 4, product *L*	1.4	1.4	1.6

Some class 1 admixtures that have not been refined or properly engineered for use in concrete may produce abnormal air contents when used in normal proportions. One such product, which was submitted by a paper company for evaluation, produced air contents in concrete that ranged from 8 to 12 per cent when used at the normal rate of 0.25 lb per sack of cement. The product was tested with two type I, type III, and one type II cements. When the dosage was reduced to 0.1 lb per sack of cement, air content of nominal 5½-sack concrete varied from 5 to 6 per cent.

Bleeding:

Water-reducing and set retarding admixtures that entrain air will reduce bleeding and settlement of plastic concrete compared to plain concrete having the same mix proportions and slump. Bleeding can be reduced by air entrainment alone, but greater reduction in bleeding at the same air content can be obtained if the concrete contains a water-reducing admixture. Reduced bleeding in admixture concrete is attributed to the reduction in water requirement in addition to the air-entraining effects.

Table XVII shows the effect of normal dosages of four admixtures of classes 1 and 2 on bleeding of concrete containing 5½ sacks of a blend of four type I cements per cu yd. This table also shows the effect of air entrainment on bleeding. All of the admixture concretes bleed less than plain or air-entrained concrete, but bleeding is further reduced if the air content of the admixture concrete is increased by addition of an air-entraining admixture.

Water-reducing or set-retarding admixtures that do not entrain air may modify bleeding characteristics by increasing the rate and capacity to bleed clear water. Rapid bleeding reduces the total amount of water in the plastic concrete and may be partially responsible for the increased strengths obtained with concrete containing admixtures that promote bleeding.

TABLE XVII.—EFFECT OF ADMIXTURES OF CLASSES 1 AND 2 ON BLEEDING OF CONCRETE CONTAINING 5½ SACKS OF A BLEND OF FOUR TYPE 1 CEMENTS PER CU YD AND CRUSHED LIMESTONE COARSE AGGREGATE.

Water-Reducing Admixture	Air-Entraining Admixture	Slump, in.	Air Content, per cent	Sand-Aggregate Ratio	Bleeding	
					ml per sq cm of surface	per cent of total mix water
None	none	3½	1.6	0.45	0.48	14.2
None	AEA-1	4	5.3	0.42	0.30	9.7
Class 1	none	4½	4.8	0.43	0.19	6.3
Product *A*	AEA-1	4½	5.5	0.42	0.17	6.1
Class 2	none	4½	4.7	0.43	0.25	8.6
Product *B*	AEA-1	4½	5.5	0.42	0.18	6.4
Class 2	none	3½	3.0	0.43	0.30	10.2
Product *D*	AEA-1	4	5.4	0.42	0.23	7.8
Class 2	none	4	3.8	0.43	0.28	9.5
Product *E*	AEA-1	4½	5.7	0.42	0.16	5.8

TABLE XVIII.—EFFECT OF CLASS 3 ADMIXTURE ON BLEEDING OF CONCRETE CONTAINING 5½ SACKS OF TYPE 1 CEMENT PER CU YD.

Admixture	Type of Aggregate	Slump, in.	Bleeding, per cent of total mix water	Air Content, per cent	Water-Cement Ratio	Compressive Strength, psi	
						7 day	28 day
None	rounded	2	4.3	1.5	0.58	3180	4615
Class 3, product *H*	rounded	3½	5.5	1.3	0.58	3605	5240
None	angular	4	7.1	1.0	0.63	2520	4170
Class 3, product *H*	angular	3¾	8.6	1.1	0.59	3600	5100

TABLE XIX.—UNIT WEIGHT OF 3-IN. SLUMP CONCRETE CONTAINING 5½ SACKS OF TYPE 1 CEMENT, PER CU YD.

Admixture	None (Control)	Product *A*, Class 1		Product *J*, Class 2		Product *H*, Class 3		Product *M*, Class 4	
Dosage	...	*X*	½-*X*	*X*	½-*X*	*X*	½-*X*	*X*	½-*X*
Air content, per cent	1.9	2.4	1.7	2.5	1.9	1.5	1.6	3.6	2.7
Unit weight, lb per cu ft	146.6	146.6	147.5	146.2	147.6	148.4	147.6	144.8	146.1

Plastic cracking in concrete occurs when the rate of evaporation exceeds the rate at which water rises to the surface. Admixtures that increase bleeding without increasing laitance formation can be helpful in reducing surface drying during hot or windy weather.

Total bleeding in concrete containing

5½ sacks of type 1 cement and two types of coarse aggregate when a class 3 admixture (product *H*) was used is shown in Table XVIII.

Unit Weight:

Unit weight of concrete can be increased by the use of water reducers or set retarders provided air content is not increased.

The unit weight of 3-in. slump concrete containing 5½ sacks of cement per cubic yard can be increased 1 to 2 lb per cu ft if the air content is not increased. Table XIX shows the unit weight obtained with normally recommended dosage and one half normally recommended dosage of admixtures.

Compaction:

Compaction has been defined as the elimination of unintended voids containing entrapped air or water (4). It is brought about by the movement of solid particles into closer contact with each other. The ease with which concrete is compacted is determined by the mobility or flow as determined by the ability of the concrete to fill out the section and the workability, or work required for full compaction.

Water reducers and set retarders may improve workability over that of plain concrete at a given water content or water-cement ratio by decreasing the work necessary for manipulation. They may increase compaction, which is reflected in higher unit weight. Retarders increase the period over which fresh concrete can be mixed, placed, and compacted.

Flow characteristics or mobility of plastic concrete is improved when water reducers or set retarders are incorporated in the mixture. If the water content is maintained constant, slump is increased. An increase in slump may be particularly important where concrete with very low water content is used. Admixtures have increased slump 2 to 3 in. without increasing water or reducing strength when additional mobility was required for placing. In some cases the addition of an admixture will increase strength in addition to increasing slump, which may be partially caused by more thorough compaction.

Uniformity:

The water-cement paste which binds the aggregates together is the most important ingredient in a concrete mix. It has been well established that strength, permeability, and abrasion resistance of concrete are governed to a large extent by the water-cement ratio, provided all other things are equal.

In order to produce concrete of uniform quality, it is important that a uniform water-cement ratio be maintained. Uniform water-cement ratio is maintained by controlling the water content of the mixture.

Temperature variation is one of the chief factors contributing to variation in unit water content. As the temperature at which concrete is mixed and placed rises, more water is required to maintain the same slump. Tests made by Tuthill and Cordon (5) have shown that the increase in water requirement caused by increased temperature can be largely offset by effective use of a water-reducing retarder, provided the quantity of admixture is increased as the temperature increases. According to their results, plain concrete required approximately 35 lb more water per cubic yard to maintain constant slump when the temperature was increased from 40 to 100 F. Admixture concrete required only 14 lb additional water to maintain constant slump over the same temperature range. As the temperature rises, the increased proportion of retarder largely offsets the increased water demand, resulting in uniform slump, water-cement ratio and unit water content. Uniformity of the concrete quality is increased and coefficient of variation is decreased.

ADMIXTURE PROPORTIONS AND USE WITH OTHER MATERIALS

Proportions:

Water-reducing and set-retarding admixtures are usually added to a concrete mixture in an amount proportional to the cement content. Manufacturers have established proportions that produce optimum results with their product under the greatest number of conditions. The recommendation of the manufacturer should be followed unless tests indicate a different proportion would be more suitable for a particular application.

Manufacturers of most class 1, 2, and 4 admixtures specify that a fixed amount of their admixture be used regardless of temperature. One class 1 admixture is used in varying proportions depending on temperature. Some manufacturers compensate for the effects of varying temperature by furnishing different formulations which can be used at different temperatures at a constant proportion. Increasing the dosage of some of these materials may increase water reduction or set retardation but in some cases may also result in high air content. Tests should be made to determine the air entrainment obtained and the hardening characteristics.

Many of the commercial admixtures in classes 1 and 2 are powders; a few are liquids. The recommended proportion of these admixtures varies from 0.20 to 1.0 lb per sack of cement for the powders and 6 to 9 oz per sack for the liquid.

Class 3 admixtures can be in liquid or powder form. These admixtures are usually added to a concrete mixture in varying proportions depending upon air or concrete temperature in order to maintain uniform setting time. Powder admixtures are normally added in the proportion of ½ to 1 lb per sack of cement and liquid admixtures are added in the proportion of 2 to 4 oz per sack of cement, depending upon temperature. Sometimes these admixtures are used to secure extreme retardation for revibration or other purposes and then are used in much higher proportions.

Method of Addition:

Powder admixtures are usually added to the weighed aggregates. To facilitate addition to the mix soluble admixtures are sometimes dissolved in water and the resulting solution is used as part of the mixing water. Liquid admixtures may be added to the mixing water or added to the weighed aggregate. They should never be added directly to the cement.

Air-Entraining Agents:

Water-reducing and set-retarding admixtures may be used in concrete containing any of the common air-entraining agents. The exact amount of air obtained with a given proportion of air-entraining admixture and a given proportion of water-reducer or retarder should be determined by trial.

Air-entraining agents and water reducers or set retarders should not be premixed unless tests indicate that no adverse effects will occur from the combination. If the admixtures are premixed with many common air-entraining agents, coagulation or precipitation may occur. It has been demonstrated that certain alkyl aryl sulfonates can be intermixed in solutions containing calcium lignosulfonate, but neutralized extracts of wood resins should not be so intermixed.

Cements:

Water reducers and set retarders can be used with any standard portland ceent. Admixtures of all classes have also been used successfully with high-alumina cement and portland slag cement.

Performance of water-reducing and set-retarding admixtures may vary with different types of cement or with the same type of cement from different mills. Different classes of admixtures and different admixtures in the same class may produce different results with a given cement.

Few cements may not produce results as good as expected with one admixture or with several admixtures.

Aggregates:

Commercially available admixtures may be used with any type of aggregate including angular, rounded, lightweight and heavy aggregates. Results may vary with different aggregates and with different admixtures when used with the same aggregate and cement.

Pozzolans:

Field and laboratory tests have shown that water-reducers and set-retarders will reduce water and delay slump loss in structrual or mass concrete containing fly ash or other pozzolans. Total water reduction varies with the type of pozzolan and the type of concrete mixture. Usually less water reduction is obtained in concrete containing a pozzolan than in comparable concrete without pozzolan.

B. Michelis (6) reported a reduction in water content of more than 14 per cent in mass concrete containing 6-in. maximum size aggregate with a class 1 admixture when no pozzolan was used. Water reduction was 7.5 per cent when pozzolan was used.

During construction of the Tecolote Tunnel (7), a class 1 admixture was used in conjunction with a pozzolan in approximately 16,000 cu yd of concrete. Total water requirement was 9.4 per cent less in the admixture concrete than in the concrete without admixture.

Tests made with structural concrete containing different types of fly ash have shown that the total mixing water may be reduced 5 to 10 per cent when an admixture is used in the concrete.

ENGINEERING APPLICATION OF PROPERTIES OF PLASTIC CONCRETE CONTAINING WATER REDUCERS AND SET RETARDERS

Water reducers and set retarders have been successfully used for a variety of purposes in all types of concrete including precast, cast - in - place, prestressed and post-tensioned concrete. They have been used to increase workability and slump of concrete without increasing water or reducing strength where increased mobility was necessary in order to place concrete without honeycomb. They have been used in combination with other admixtures including air-entraining agents, accelerators, and pozzolans to improve the quality of concrete.

During hot weather considerable loss of slump and workability is often encountered. Judicious use of set-retarding admixtures will counteract these conditions and permit concrete to be placed at the desired slump without substantially increasing the total water in the concrete.

Occasionally it is desirable to use truck mixers to transport concrete to several small structures scattered over a wide area. Slump and workability of concrete may be increasingly reduced as the truck mixer moves from structure to structure until it finally becomes necessary to add additional water to the concrete in order to place it. Concrete containing a set-retarding admixture has been transported 35 miles in truck mixers during hot weather without appreciable loss of slump or workability (6). The use of central mixed concrete can be expanded with resultant economies if a set retarder is used.

Cold joints in deep girders and beams can be eliminated by incorporating a set-retarder in the concrete. Cracking caused by form movement can be eliminated by keeping concrete plastic until formwork has deflected under the full weight of the concrete. Monolithic construction of bridge decks and beams is made possible by the use of revibration and retardation.

SUMMARY

Water-reducing and set-retarding admixtures have an important influence on the characteristics of plastic concrete. Changes in plastic concrete resulting from proper use of these admixtures are reflected in improvement in quality of the hardened concrete.

These admixtures may be used in all classes of concrete, including precast, cast-in-place, prestressed and post-tensioned concrete. They may be used with all types of portland cement, portland slag cement and aluminous cement; they may be used with rounded aggregate, crushed aggregate, lightweight aggregate and heavy aggregate; they may be used in mortar, and in concrete containing all sizes of aggregate; they may be used in plain concrete, air-entrained concrete, and concrete containing pozzolans, calcium chloride, or other additions.

Total reduction in mixing water resulting from the use of these materials may vary from 5 to 10 per cent for the same air content. The amount of water reduction is influenced by the type and brand of cement, type of aggregate, cement content, dosage, type of admixture and other additions, including air-entraining agents and pozzolans.

Set retarders will delay slump loss and improve uniformity of concrete placed at high temperatures or hauled long distances. They can be used to prevent cold joints in deep sections placed in lifts. They can be used to prevent or reduce cracking caused by formwork deflection or plastic cracking.

Hardening characteristics and set retardation are influenced by many factors, including temperature, type of admixture, dosage, type and brand of cement and other additions.

All admixtures in a given class do not produce the same results in all types of concrete. Occasionally an admixture from one class may be preferred to other admixtures for a particular application. Unrefined products or products that have not been thoroughly engineered and tested may produce erratic results.

The type of admixture should be selected and specified by the engineer. Unless experience has been previously obtained with the admixture and other materials in the concrete, the properties of admixtured concrete and the optimum dosage for a specific application should be determined by tests prior to start of construction. Tests should be made with the cement and aggregates proposed for use on the job and under conditions similar to those antcipated. If preliminary testing is not feasible the recommendations of the manufacturer should be followed.

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THE EFFECT OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES ON THE PROPERTIES OF HARDENED CONCRETE

By D. R. MacPherson[1] and H. C. Fischer[2]

Synopsis

Concrete as an engineering material is judged, in the last analysis, by its properties in the hardened state. It is in this state that the effects of imposed load and environment are controlled by the properties of the concrete.

It is shown that specific water-reducing admixtures and set retarders permit concrete to be made with properties superior to those attainable in untreated concrete. Such enhancement of properties can usually be achieved simultaneously with economy of materials and labor.

In consideration of strength and its parameters, data are given herein to exemplify the fact that certain admixtures, when properly used, are beneficial to the resultant concrete. For example, acceleration of strength development at early ages can be accomplished even under conditions dictating the use of retarders to delay setting time. Not only can this be accomplished without adverse effects, but in some cases economies are possible while maintaining strength requirements.

With respect to weathering and environmental conditions, as affecting durability, it is shown that admixtures permit improvement of resistance to cyclic freezing and thawing and reductions in volume change and permeability.

Water-reducing admixtures and retarders have become an accepted part of the concrete industry. Opposition to anything added to concrete, other than cement, aggregates, and water, is gradually disappearing and considerable recognition is being given to the value of using other ingredients.

The future of better concrete lies in an increased understanding of concreting materials and the best manner of combining them to produce the maximum in strength and durability. An understanding and intelligent use of water-reducing admixtures and retarders complements the means for producing better concrete and, more often than not, in a more economical manner.

Properties of hardened concrete lie in the general categories of strength, durability, dimensional stability, and permeability. Strength, being more readily measured and yielding test results more easily interpreted, has been investigated to a far greater extent than other properties. As a result, durability and permeability aspects have not been studied as adequately as such important factors would warrant.

The advent and acceptance of pur-

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[1] Product Manager, Celite Division, Johns-Manville Products Corp., New York, N. Y.

[2] Research Engineer, Johns-Manville Research Center, Manville, N. J.

poseful air entrainment made the concrete industry durability-conscious to a quite unexpected degree. Water-reducing admixtures both with or without air-entrainment enhance the durability of concrete by virtue of the beneficial effects of reduced water contents. By proper mix design and in keeping with the general concepts of the water-cement ratio law, strength can be simultaneously increased.

Strength and durability are complementary and the following discussion, with exemplifying data, will show the beneficial results obtained from use of admixtures. These admixtures are divided into the four chemical classifications of (1) lignosulfonic acids and their salts; (2) modifications and derivatives of lignosulfonic acids and their salts; (3) hydroxylated carboxylic acids and their salts; (4) modifications and derivatives of hydroxylated carboxylic acids and their salts.

In the following discussions and tables of data, admixtures have been given a class number (1, 2, 3, or 4) in keeping with the previously stated classifications. Letters (*A*, *B*, *C*, etc.) have been affixed to each class number to differentiate between the individual products in any one class, *in lieu* of the use of trade names.

The test data presented in the following sections will show that different admixtures produce results differing in degree of enhancement; such differences however are a result of the particular nature of the concreting materials and the manner of combining them. Reliable admixtures cannot be said to be inferior or superior to one another; they merely perform differently under particular conditions of use.

COMPRESSIVE STRENGTH

Compressive strength is the most generally accepted criterion of good concrete, and, although such acceptance can be misleading, it is nevertheless true that compressive strength and other quality characteristics are related. Although compressive strength is an indication of other properties and such indication is not of a quantitative nature, it is of value in the absence of tests specifically designed for those other properties in question.

The strength of a concrete will generally increase with the proportion of cement in the mix until the strength of the cement paste or aggregate, whichever is the weaker, is reached. This relationship is, of course, based upon the premise of similar materials and consistencies being used.

Just as important as the cement content is the water content of a mix. Inasmuch as strength is inversely proportional to the water-cement ratio and, unfortunately, workability requirements necessitate two to three times the water required for chemical hydration of the cement, it does seem logical to seek a means of reducing the water content while maintaining equal or improved workability.

This much-desired water reduction can be realized by means of admixtures specifically formulated to achieve such action. The effect of water reduction on compressive strength is in the direction of greater strength when such water reduction is supplementary to that derived from air entrainment alone. This, of course, is to be expected in consideration of strength and void-cement ratio relationships.

Table I, containing data on concrete made with three of the four classes of admixtures, shows the significant increase in compressive strength of the treated concrete redesigned for air entrainment and a change in cement content. The water-cement ratio for the treated mixes is, in some cases, greater than that of the untreated mix; yet the strength data do

TABLE I.—COMPRESSIVE STRENGTH OF CONCRETE CONTAINING WATER-REDUCING ADMIXTURES.

Admixture		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	Sand-Aggregate Ratio, by weight	Compressive Strength					
								1-day		7-day		28-day	
Class	Product							psi	per cent	psi	per cent	psi	per cent
Type I Portland Cement. Natural Sand and Gravel. Slump 3 to 4 in. Treated mixes redesigned for 13 per cent cement reduction. All tests in accordance with ASTM Methods.													
None		...	5.08	7.20	...	2.1	0.49	425	100	1490	100	2380	100
2	*J*	0.44	4.37	7.56	10	4.3	0.47	440	103	1630	109	2620	110
2	*D*[a]	0.25	4.44	6.76	17	5.7	0.45	550	129	2050	137	3390	142
2	*I*	0.20	4.44	7.22	12	5.1	0.45	455	107	1720	115	3020	127
3	*O*	0.20	4.44	7.56	9	3.1	0.47	475	112	1530	103	2670	112
4	*M*	0.20	4.44	6.99	15	5.3	0.45	460	108	1760	118	3110	131
Type II Portland Cement. Same Aggregates and Conditions as Above.													
None		...	5.32	7.20	...	1.3	0.49	440	100	1800	100	3650	100
2	*J*	0.44	4.65	7.56	8	2.3	0.47	495	112	1960	109	3650	100
2	*D*	0.25	4.65	6.87	17	3.6	0.45	715	162	2530	140	4220	116
2	*I*	0.20	4.63	7.22	12	4.4	0.45	520	118	2010	112	3730	102
3	*O*	0.20	4.65	7.56	8	1.8	0.47	470	107	2020	112	3820	105
4	*M*	0.20	4.62	6.99	16	5.0	0.45	505	115	2140	119	3710	102

[a] Plus AEA-3.

TABLE II.—EFFECT OF WATER-REDUCING ADMIXTURES ON EARLY STRENGTH DEVELOPMENT OF CONCRETE.

Admixture[a]		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	Sand-Aggregate Ratio, by weight	Compressive Strength					
								1-day		7-day		28-day	
Class	Product							psi	per cent	psi	per cent	psi	per cent
Blend of Four Type I Portland Cements. Natural Sand and Gravel. All tests in accordance with ASTM Methods. Slump 3 to 3½ in. No cement reduction.													
None		...	5.00	5.86	...	5.2	...	670	100	1385	100	2960	100
1	*A*	0.25	4.99	5.48	7	5.0	...	780	116	1720	124	3805	129
2	*B*	0.25	5.00	5.55	5	4.7	...	930	139	1890	136	3950	133
2	*D*	0.25	5.00	5.57	5	4.7	...	1155	173	2095	151	3885	131
2	*E*	0.25	5.00	5.50	6	4.9	...	1055	158	2105	152	3975	134
Type II Portland Cement. Natural Sand and Crushed Stone. Slump 3 to 3½ in. All tests in accordance with ASTM Methods. 13 per cent cement reduction.													
None		...	6.05	7.21	...	1.3	0.46	1150	100	1640	100	3330	100
4	*P*	0.20	5.14	7.45	12	4.3	0.44	1530	133	2280	139	3920	118
4	*P*	0.15	5.16	7.55	11	3.5	0.44	1450	126	2160	132	4030	121
4	*P*	0.10	5.20	7.89	6	2.8	0.44	1340	116	2130	130	3940	118

[a] Air-entraining agent in each mix (including reference mix).

not reflect this. It is thus apparent that the admixtures have imparted some other effect beneficial to strength development. This effect cannot be achieved by air entrainment and redesign alone; a specific effect has occurred in each case and has given rise to greater strength.

The strength data of Table II are typical of those obtained at early ages. In the first series of mixes the admixture was used as a straight addition and supplemented with a separately added air-entraining agent. Although the reference mix is air-entrained concrete rather than plain untreated concrete, the strength development is noteworthy.

The second series of Table II also presents early strength data with a different type of cement and with a different admixture. This admixture was used at different dosages, and, although control of the air content is thus effected, the

TABLE III.—EFFECT OF CEMENT FACTOR ON COMPRESSIVE STRENGTH OF CONCRETE CONTAINING WATER-REDUCING ADMIXTURES OF CLASS 2.

Blend of Types I and II portland cements. Natural sand and gravel. Slump 3½ to 4½ in. Dosage at producers' recommended rates.

Admixture Product	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	Compressive Strength							
				1-day		7-day		28-day		3-month	
				psi	per cent	psi	per cent	psi	per cent	psi	per cent
CEMENT FACTOR 4 SACKS PER CU YD SAND-AGGREGATE RATIO—0.422											
None.....	8.9	...	2.7	395	100	1660	100	2820	100	3570	100
J........	8.1	9	4.7	505	128	2075	125	3440	122	3960	111
D........	8.3	7	4.9	530	134	1995	120	3310	117	3710	104
CEMENT FACTOR 5 SACKS PER CU YD SAND-AGGREGATE RATIO—0.408											
None.....	7.3	...	2.2	705	100	2540	100	4005	100	5040	100
J........	6.6	10	4.7	835	118	3200	126	4695	117	5500	109
D........	6.7	8	4.9	900	128	3010	119	4370	109	4920	98
CEMENT FACTOR 6 SACKS PER CU YD SAND-AGGREGATE RATIO—0.394											
None.....	5.9	...	1.9	1160	100	3660	100	5365	100	6450	100
J........	5.5	7	3.9	1355	117	4210	115	5950	111	7180	111
D........	5.6	5	3.8	1425	123	4110	112	5840	109	6690	104
CEMENT FACTOR 7 SACKS PER CU YD SAND-AGGREGATE RATIO—0.345											
None.....	5.1	...	1.9	1650	100	4265	100	6120	100	6770	100
J........	4.8	6	3.5	1895	115	5030	118	6750	110	7520	111
CEMENT FACTOR 8 SACKS PER CU YD SAND-AGGREGATE RATIO—0.309											
None.....	4.7	...	1.9	2020	100	5165	100	6410	100	7780	100
J........	4.4	6	3.2	2130	105	5230	101	6930	108	8240	106

TABLE IV.—COMPRESSIVE STRENGTH OF CONCRETE CONTAINING A CLASS 3 WATER-REDUCING RETARDER (PRODUCT *N*).

Type II portland cement. Natural sand and crushed stone aggregate. All tests in accordance with ASTM Methods.

Mix	Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Slump, in.	Air Content, per cent	Sand-Aggregate Ratio, by weight	Compressive Strength					
								3-day		7-day		28-day	
								psi	per cent	psi	per cent	psi	per cent
No. 1	none	8.75	5.30	...	4	1.2	0.43	2240	100	3270	100	5000	100
No. 2	0.15	7.19	5.86	7	3½	1.4	0.43	2460	110	3650	112	5730	115
No. 3	0.23	7.19	5.86	7	5½	1.4	0.43	2410	108	3770	115	5780	116
								1-day					
No. 4	none	6.84	6.42	...	3½	1.4	0.43	700	100	2420	100	4500	100
No. 5	0.23	6.88	6.42	0	7	0.9	0.43	920	131	3060	126	5280	117
No. 6	0.15	6.93	5.98	7	3½	1.4	0.43	1070	152	3600	149	5290	118
No. 7	0.23	6.88	5.98	7	3½	1.4	0.43	1230	176	3780	156	5770	128

TABLE V.—EFFECT OF AGGREGATE AND CEMENT CONTENT ON PERFORMANCE OF A CLASS 2 WATER-REDUCING ADMIXTURE (PRODUCT *D*).

Dosage, lb per sack	Slump, in.	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Air Content, per cent	Sand-Aggregate, Ratio	Compressive Strength, psi	
						7 days	28 days
Natural Sand and Gravel Type I portland cement; no added air-entraining agents; average of 3 tests.							
None	3½ to 4	4.45	7.31	2.6	0.40	3145	4550
None	4 to 5	5.91	5.64	2.5	0.375	4435	5660
0.25	3 to 4	3.91	7.37	4.1	0.39	3520	4760
0.25	3 to 4½	4.91	5.85	4.0	0.37	4225	5790
0.25	4 to 4½	5.84	5.00	3.8	0.36	4890	6240
Expanded Shale Coarse and Fine Aggregate Type I portland cement; AEA-1; average of 3 tests.							
None	2	4.97	6.31	8.9	0.62	860	1425
None	2	6.00	5.35	7.8	0.62	1535	2330
None	2	6.90	4.69	8.7	0.62	1935	2665
0.25	2	4.34	5.93	11.4	0.62	1155	1640
0.25	2	5.38	4.91	9.5	0.62	1800	2500
0.25	2	6.37	4.29	7.6	0.62	2310	2990
Expanded Blast-Furnace Slag Coarse and Fine Aggregate Type I portland cement; AEA-1; average of 3 tests on 6 by 12-in. cylinders made, cured, and tested in accordance with ASTM Methods C 192 and C 39.							
None	2 to 2½	5.55	9.31	10.3	0.64	725	1110
None	2 to 3	7.70	6.70	8.7	0.64	1780	2490
0.25	2 to 3	5.41	8.74	10.7	0.64	890	1480
0.25	2½ to 3	7.13	6.11	10.7	0.64	1920	2790

strength is maintained at a level considerably higher than that of the plain untreated concrete. Again the specific beneficial effect of the admixture is apparent; the water-cement ratios would indicate expected strengths lower than that of the plain mix.

sults obtained with a class 3 admixture, a retarder, at relatively high cement factors. Mixes Nos. 2 and 3 develop approximately equal strengths although of different dosages. However, the degree of retardation was decidedly different in each case.

TABLE VI.—EFFECT OF CLASS 3 WATER-REDUCING RETARDERS ON RATE OF HARDENING AND STRENGTH DEVELOPMENT OF CONCRETE.

Type I portland cement (Mix Nos. 1 to 7); Type II (Mix Nos. 8 to 14). Natural sand and gravel. Slump 3½ to 4 in. Cement factor 5.00 ± 0.03 sacks per cu yd. Sand—total aggregate ratio, by weight, 0.49. All tests in accordance with ASTM Methods.

Mix	Admixture Product	Dosage, fluid oz per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	Compressive Strength								Time to Penetration Resistance at 80 F Ambient Temperature			
						1-day		3-day		7-day		28-day		500 psi		4000 psi	
						psi	per cent	psi	per cent	psi	per cent	psi	per cent	hr	per cent	hr	per cent
No. 1......	none	...	7.67	..	1.3	377	100	874	100	1630	100	2905	100	5.4	100	7.7	100
No. 2......	*N*	3	7.10	8	2.1	504	134	1450	162	2430	149	3500	117	5.9	109	7.9	103
No. 3......	*H*	3	7.00	9	1.4	409	109	1240	138	2180	134	3750	126	6.6	122	8.9	116
No. 4......	*N*	4	6.88	10	2.3	494	131	1510	168	2400	147	3495	117	6.7	124	8.3	108
No. 5......	*H*	4	6.88	9	1.8	406	108	1240	138	2170	133	3645	122	7.6	141	10.0	130
No. 6......	*N*	5	6.65	13	2.3	444	118	1550	173	2710	166	3845	129	7.2	133	9.4	122
No. 7......	*H*	5	6.65	12	1.7	374	98	1250	139	2330	143	3975	133	8.8	163	10.8	140
No. 8......	none	...	7.67	...	1.3	330	100	745	100	1140	100	2660	100	5.4	100	7.6	100
No. 9......	*N*	3	6.65	13	2.4	540	169	1130	152	1780	156	3340	125	6.0	111	7.7	101
No. 10.....	*H*	3	6.43	16	1.8	501	152	1200	161	1840	161	3675	138	6.8	126	9.2	121
No. 11.....	*N*	4	6.65	13	2.3	501	152	1110	149	1690	148	3305	124	7.0	130	8.5	112
No. 12.....	*H*	4	6.43	17	1.9	440	133	1270	170	1830	161	3780	142	8.5	157	11.4	150
No. 13.....	*N*	5	6.31	17	2.3	516	156	1300	175	1910	168	3890	146	7.7	143	9.9	130
No. 14.....	*H*	5	6.31	17	1.7	237	72	1340	180	2090	183	4185	157	11.5	213	15.9	209

The performance of water-reducing admixtures at variable cement factors is illustrated by the comparative data of Table III. These data show unusually low water-reduction values for this class of water reducers. The reason for this lies in the use of a particular aggregate known to show odd behavior. Regardless of the relatively low reduction in water content, the admixture-treated concrete is of superior strength with respect to the untreated concrete at each cement factor.

The data of Table IV illustrate the re-

Mixes Nos. 4 to 7 show the effect of this admixture on the required water content and consequently on the slump. Mix No. 5 has the same water-cement ratio as mix No. 4, shows a considerable increase in slump, and yet shows a marked increase in compressive strength.

In mixes Nos. 6 and 7 the consistency was held constant, with reference to the plain mix, by utilizing the water-reduction characteristics of the admixture. The compressive strength in each case is significantly increased.

Table V contains data illustrative of the performance of an admixture with aggregates of widely different characteristics and at variable cement factors.

Although retarders perform their prime function in the plastic state of concrete, they do nevertheless have a responsibility to meet in the hardened state. To merely retard or delay the rate of hardening is inadequate; following the period of desired retardation, the concrete must be capable of exhibiting sufficient rapid strength-gain characteristics to attain normal strength level at one day.

Properly formulated retarders should delay the rate of initial hardening but not interfere with early strength development. As a matter of fact, a reliable retarder of the water-reducing type should accomplish both functions.

It is not the purpose of this paper to discuss retardation *per se* inasmuch as such is a phenomenon of the plastic state. However, in order to exemplify the fact that hardened concrete does not suffer a strength loss at any age when water-reducing retarders are used, some data are presented to illustrate strength development at different degrees of retardation.

Table VI contains such data for a series of tests with two water-reducing retarders of the hydroxylated carboxylic acid type.

The time-penetration data show the relative retardation at two degrees of stiffening and hardening; these degrees are taken as resistances of 500 and 4000 psi to a standard penetration, as specified by ASTM Method C 403.[3]

It can be readily noted that although the degree of retardation is increased with increasing dosages, the 1-day compressive strength values are generally well above those of the untreated reference mix. At a dosage of 5 fluid oz per sack of cement and in the case of both cements, admixture *H* (mixes Nos. 7 and 14) has strength values lower than those of the reference mix. However, by simultaneous consideration of compressive strength and the relatively large increment of retardation in both cases, such phenomena are not without justification. Mix No. 14 with its high degree of retardation at both the 500- and 4000-psi levels and its relative strength of 72 per cent at 1 day is indicative of an overdosage of this particular admixture at the ambient temperature of 80 F. However, such overdosage effects are only temporary as witnessed by the great strength development over the succeeding 2 days (180 per cent at 3 days).

In early development work on water-reducing and set-controlling agents, the possibility of variable performance of these materials, with different cement, was recognized. Later research on retarders has shown that the compound composition of cements has a great influence on performance. It may be that the lower the C_3A content, the greater the retardation for a given dosage of a retarding agent. A research program was undertaken to determine the performance of a water-reducer of the class 4 type on the properties of concrete, using 19 different cements. These cements were of types I and II from plants widely distributed through the country. Table VII presents the results of this program.

The eight type I cements produced untreated concrete 28-day compressive strengths that varied from 2460 to 3440 psi, whereas the eleven type II cements produced strengths that varied from 2960 to 3980 psi. All untreated concretes contained 6.1 sacks per cu yd and 1.3 to 1.7 per cent air (entrapped). The water-cement ratios for all the untreated con-

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[3] Tentative Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles (C 403 - 57 T), 1958 Book of ASTM Standards, Part 4, p. 712.

TABLE VII.—EFFECT OF DIFFERENT CEMENTS ON THE PERFORMANCE OF CONCRETE CONTAINING A CLASS 4 WATER-REDUCING ADMIXTURE (PRODUCT *M*).

Cement factor 6.1 sacks per cu yd for plain mixes,[a] 5.3 for treated mixes. Natural sand and crushed stone. Slump 3 to 4 in. Dosage 2.0 lb per sack of cement.

Cement	Type	Water-Cement Ratio, gal per sack	Air Content, per cent	Compressive Strength					
				3-day		7-day		28-day	
				psi	per cent	psi	per cent	psi	per cent
A.........	I	7.22	1.3	1250	100	2220	100	3280	100
		6.99	4.6	1660	132	2670	120	3550	108
B.........	II	7.33	1.5	780	100	1520	100	3230	100
		6.99	4.6	940	120	1900	125	3540	109
C.........	II	7.33	1.3	1320	100	2030	100	3640	100
		7.10	4.7	1660	126	2570	126	4060	111
D.........	I	7.33	1.5	1010	100	1650	100	3320	100
		7.10	4.6	1060	105	1920	116	3580	108
E.........	II	7.33	1.5	1210	100	1860	100	3410	100
		7.10	4.9	1410	116	2220	119	3600	105
F.........	I	7.33	1.4	900	100	1710	100	2960	100
		7.10	4.8	1150	128	2140	125	3040	102
G.........	II	7.33	1.4	1170	100	2175	100	3510	100
		7.10	4.9	1230	105	2260	104	3600	102
H.........	I	7.33	1.5	1190	100	1830	100	3210	100
		7.22	4.5	1380	116	2150	117	3580	111
I.........	II	7.33	1.5	1110	100	2080	100	3380	100
		7.10	4.9	1240	111	2190	105	3920	116
J.........	II	7.45	1.6	1130	100	1920	100	2960	100
		7.10	4.9	1240	110	2220	115	3160	106
K.........	I	7.45	1.7	1180	100	2190	100	3440	100
		7.10	4.8	1620	137	2660	121	3970	115
L.........	II	7.45	1.3	680	100	1490	100	3140	100
		7.10	4.6	965	141	1850	124	4060	129
M.........	II	7.45	1.6	1120	100	1810	100	3800	100
		7.10	4.9	1400	125	2180	121	4500	118
N.........	II	7.45	1.6	895	100	1550	100	3980	100
		7.10	4.4	960	107	1820	117	4200	105
O.........	II	7.45	1.3	1150	100	1510	100	3040	100
		7.22	4.5	1220	106	1880	124	3500	115
P.........	I	7.45	1.4	1180	100	1950	100	3340	100
		7.10	4.9	1310	111	1970	101	3110	93
Q.........	I	7.45	1.4	860	100	1315	100	2460	100
		7.10	4.2	1040	121	1700	129	3200	130
R.........	I	7.55	1.5	1200	100	1850	100	3080	100
		7.33	4.8	1530	127	2410	131	3850	124
S.........	II	7.45	1.5	1420	100	2260	100	3200	100
		7.22	4.6	1710	120	2610	115	4200	131

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[a] For each set of data the untreated mix is followed by the treated mix.

crete averaged 7.4 gal per sack. The treated concretes contained 5.3 sacks per cu yd, 4.5 to 5.0 per cent air, and an average water-cement ratio of 7.1 gal per sack. A class 4 water-reducing agent was used in all of the treated mixes. This material was composed of a natural pozzolan containing 10 per cent active ingredient.

With one exception, cement *P* at 28 days, the strengths of all treated mixes were equal to or superior to those of the untreated mixes. This particular cement was the only one having a high alkali content.

FLEXURAL STRENGTH

Resistance to flexure and bending is of major importance in the case of slabs and beams. However, interpretations of flexural test results require a great deal of consideration because of the high degree of sensitivity encountered in the treatment and testing of specimens and because of inherently different aggregate properties (**1**).[4]

With a given set of materials, the relationship between compressive strength and flexural strength can be established in the laboratory. Compressive strength specimens are easier to fabricate, the testing procedures less complicated, and the results more readily interpreted than those dealing with flexural strength. In view of these practical factors, after establishment of the compressive-flexural strength relationship, satisfactory control of flexural strength can be accomplished (**2**). However, with different materials and properties, compressive strength tests are merely an indication of flexural strength to the extent that these parameters are somewhat parallel (**3**,**4**).

The data given in Tables VIII and IX indicate that definite beneficial effects, with respect to flexural strength, result from the proper use of reliable admixtures; increased strength has resulted. This, of course, would be expected in the light of the improved compressive strength of the same concretes.

The air contents of the mixes shown in the upper portion of Table VIII were not measured. However, this particular water-reducing admixture does not have air-entraining properties, and consequently the air contents of all three mixes are essentially the same.

BOND STRENGTH

The resistance to slipping of steel reinforcing bars embedded in structural concrete is a property of considerable significance in flexural members. The character of the hardened paste, particularly with respect to dimensional stability, greatly influences the bond maintained between the paste and the steel.

The quality of the paste can be improved by certain water-reducing admixtures and retarders. Water reduction permits lower water-cement ratios and superior volume change characteristics; settlement or shrinkage away from reinforcing members is reduced during the hardening period, thus providing more extensive adhesion and improved bond strength.

Tables X and XI present data which show respectively slip measurements and relative values of bond strength. Both sets of data show a decided improvement of bond as a result of the use of water-reducing admixtures.

MODULUS OF ELASTICITY

Although the modulus of elasticity of concrete is generally taken as being approximately equal to the compressive strength multiplied by 1000, it is well recognized that no definite relationship holds between these two parameters. The influence of testing techniques on results is of great significance. The moduli

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[4] The boldface numbers in parentheses refer to the list of references appended to this paper.

of aggregates also influence to a great extent the ultimate results and consequently become an important item for consideration.

Water-reducing admixtures and retarders, when properly used, aid in the development of superior elastic properties. These elastic properties are particularly dependent upon the amount and type of paste as well as upon the volume ratio of paste to aggregate. As a consequence these properties are governed to a great extent by the control exerted by the admixture over the water content and, in some instances, over the cement content.

TABLE VIII.—EFFECT OF CLASS 3 AND 4 WATER-REDUCING ADMIXTURES ON FLEXURAL STRENGTH OF CONCRETE.

Admixture		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Air Content, per cent	28-Day Strength			
							Compressive		Flexural	
Class	Product						psi	per cent	psi	per cent
TYPE I PORTLAND CEMENT Natural sand and gravel aggregate. Slump 4 in. All tests in accordance with ASTM Methods.										
None		...	5.65	6.40	...	...	4320	100	654	100[a]
3	*H*	0.5	5.65	6.14	5	...	4890	113	721	111
3	*H*	1.0	5.65	5.89	8	...	5035	116	734	112
TYPE II PORTLAND CEMENT Natural sand and crushed stone aggregate. Slump 4 to 4½ in.										
None		...	5.70	7.7	...	2.1	3210	100	643	100[b]
4	*M*	0.2	4.95	7.8	13	5.2	3180	99	652	101

[a] Third-point loading, 30-in. span, average of five specimens.

[b] Third-point loading, 30-in. span, average of three specimens.

Table XII contains data showing the effect of water-reducing admixtures on the elastic modulus of concrete. Neither of these two particular admixtures has air-entraining characteristics. As would be expected, the modulus of elasticity does vary inversely as the air content and the water-cement ratio. However, the use of water-reducing admixtures with air entrainment and proper redesign of mix to offset the strength loss due to air entrainment provides a means of maintaining strength and desirable elastic characteristics.

RESISTANCE TO FREEZING AND THAWING

A great deal has been published on the resistance of concrete to freezing and thawing, particularly during the past ten years. The data have been primarily developed in laboratory-scale investigations, although a few major studies have been made of concrete subjected to cyclic weathering at field exposure stations.

The greatest factor in improving the resistance of concrete to freezing-and-thawing cycles is the proper distribution of purposefully entrained air voids. Several well-known air-entraining agents have been shown capable of furnishing entrained air in the optimum percentage range and with the void spacing necessary to attainment of maximum resistance to stresses exerted by freezing-and-thawing phenomena.

Although the use of properly entrained air does most toward enhancing the property of weathering resistance, water-reducing admixtures supplement such enhancement.

The test data in the upper portion of Table XIII illustrate to a limited extent the supplementary accruement of advantage from the use of a water reducer in contrast with that of a straight air-entraining agent. Such is generally the case with the use of lignin- or organic acid-type water reducers which have been modified to impart air-entraining characteristics.

TABLE IX.—EFFECT OF CLASS 2 WATER-REDUCING ADMIXTURES ON FLEXURAL STRENGTH OF CONCRETE.

Admixture[a] Product	Dosage, lb per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	28-Day Strength			
					Compressive[b]		Flexural[c]	
					psi	per cent	psi	per cent

Blend of Four Type I Portland Cements

Cement factor 6.0 sacks per cu yd. Natural sand and crushed limestone aggregate. Sand - total aggregate ratio, by weight, 0.49. Slump 2½ to 3 in. All tests in accordance with ASTM Methods.

...	...	5.58	...	5.5	4210	100	688	100
E............	0.3	5.00	10	5.7	4915	117	727	106
B............	0.3	5.07	9	5.4	5130	122	712	103

Blend of Four Type I Portland Cements

Cement factor 6.0 sacks per cu yd. Natural sand and gravel aggregate. Sand - total aggregate ratio, by weight, 0.40. Slump 2½ to 3 in. All tests in accordance with ASTM Methods.

...	...	5.00	...	5.6	4280	100	583	100
E............	0.3	4.61	8	5.3	5170	121	682	117
B............	0.3	4.54	9	5.5	4890	114	644	110

[a] Air-entraining agent AEA-1 used in each mix, including reference mix.

[b] Average of three specimens, 6 by 12-in. cylinders.

[c] Average of three specimens, 6 by 21-in. beams.

Blend of Four Type I Portland Cements

Cement factor 5.0 sacks per cu yd. Natural sand and gravel. Slump 4 ± ½ in.

Admixture Product	Dosage, fluid oz per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Air Content, per cent	Compressive Strength[d]								Flexual Strength[e]							
					7-day		28-day		3-month		1-yr		7-day		28-day		3-month		1-yr	
					psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent
None	...	6.20	...	1.6	2600	100	4230	100	5200	100	5950	100	525	100	680	100	710	100	700	100
J.....	7[f]	5.30	14	5.2	3680	141	5080	120	5930	114	6840	115	595	113	725	107	795	112	795	114

[d] Average of four specimens, 6 by 12-in. cylinders.

[e] Average of three specimens, 6 by 6 by 21-in. beams.

[f] Plus 0.125 fluid oz AEA-2 per sack.

The lower portion of Table XIII presents data which do not lend themselves to a strict comparison of the advantage of water reduction plus air entrainment over air entrainment *per se*. However, the freezing-and-thawing resistance of the admixtured concrete is definitely improved and the benefit of the 14 per cent water reduction is certainly apparent with respect to both compressive and flexural strength, as previously shown in Table IX. The use of an air-entraining agent alone would not contribute the latter benefits.

The reduction in dynamic moduli values of Table XIV shows that even though the use of air entrainment perhaps does most in improving the freezing-and-thawing resistance, the benefits are again supplemented by the characteristic water reduction in excess of that derived from air entrainment.

TABLE X.—EFFECT OF A CLASS 2 WATER - REDUCING ADMIXTURE (PRODUCT *J*) ON BOND OF CONCRETE WITH REINFORCING STEEL.

Blend of four Type I portland cements. Slump 4 ± ½ in. Cement factor 5.0 sacks per cu yd. Plain concrete air content 1.6 per cent, treated concrete air content 5.2 per cent.

Bond Stress, psi	Slip Between Reinforcing Bar and Concrete, in.[a] Horizontal Lower	Horizontal Upper	Vertical	Average
	PLAIN CONCRETE			
200	0.0002	0.0011	0.0012	0.0008
400	0.0009	0.0022	0.0023	0.0018
600	0.0022	0.0040	0.0037	0.0033
800	0.0040	0.0091	0.0056	0.0062
	TREATED CONCRETE			
200	0.0002	0.0004	0.0004	0.0003
400	0.0008	0.0011	0.0010	0.0010
600	0.0022	0.0030	0.0027	0.0020
800	0.0035	0.0053	0.0052	0.0035

[a] ASTM Method C 234 - 54, 1958 Book of ASTM Standards, Part 4.

TABLE XI.—EFFECT OF CLASS 1 AND 2 WATER-REDUCING RETARDERS ON BOND OF CONCRETE WITH REINFORCING STEEL.[a]

Blend of two Type I portland cements. Slump 2½ in. Cement Factor 5.5 sacks per cu yd.

Admixture		Dosage, lb per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent by weight	Air Content, per cent	Bond with Reinforcement,[b] per cent	
Class	Product					Horizontal	Vertical
None		...	6.24	...	0.5	100	100
AEA-1		0.016	5.44	10	4.7	93	96
AEA-2		0.075	5.44	10	4.6	93	95
2............	*C*[c]	0.50	5.25	16	4.5	117	113
1............	*A*[c]	0.25	5.22	17	4.4	121	116

[a] Data from "Experimental Researches on Air-Entrained Concrete," by Yasuo Kondo and Setsuji Hideshima, *Proceedings*, Cement Engineering Assn., Japan, pp. 177-182 (1956).

[b] ASTM Method C 234, 1958 Book of ASTM Standards, Part 4; data for horizontal bars based on the average for bars at the top, middle, and bottom of specimen.

[c] Plus AEA-3.

By utilizing water reductions at improved conditions of workability a more homogeneous concrete is possible; entrained air incorporated into the mix by the water-reducing admixture itself or by the use of a supplementary agent then imparts its share of the enhancement. Measurements of resistance to potentially disruptive cyclic freezing and thawing can be made by means of methods utilizing weight loss, volume change, strength change, or change in elastic modulus. The latter method, as previously discussed, has proven itself adaptable and valuable and has more or less replaced the previously more popular weight-loss methods.

The change in elastic modulus under the influence of freezing-and-thawing cycles has become accepted as an indicative, if not conclusive, means of determining the durability of concrete. The dynamic modulus, as determined from sonic measurements, has become a very useful datum.

Tables XIII and XIV contain data which illustrate the improvement in durability contributed by the use of water-reducing admixtures.

The increased durability of admixture-treated concrete is often overlooked, with strength taking precedence; yet continuity of strength is dependent upon durability. Severe weathering conditions, particularly those involving rapid changes, require concrete of high durability characteristics. Air entrainment plus the advantages of water-reducing admixtures permit concrete to be made with such characteristics and improved strength.

TABLE XII.—MODULUS OF ELASTICITY.

TYPE IV PORTLAND CEMENT

Natural sand and gravel aggregate. Slump 2½ to 3¼ in.

Admixture		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Compressive Strength[a]						Modulus of Elasticity[b]					
						1-yr		2-yr		5-yr		1-yr		2-yr		5-yr	
Class	Product					psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent	psi	per cent
None		...	4.72	7.19	...	3840	100	4209	100	4580	100	5.76 × 10⁶	100	5.93	100	5.57	100
2....	Q	1.25	4.28	7.20	9	3780	98	4161	99	5310	116	5.85	102	6.26	106	5.99	108

TYPE I PORTLAND CEMENT

Natural sand and gravel aggregate. Slump 4 in.

Admixture		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Compressive Strength[c]		Modulus of Elasticity[d]	
						28-day		28-day	
Class	Product					psi	per cent	psi	per cent
None		...	5.65	6.40	...	4320	100	3.50 × 10⁶	100
3....	H	1.0	5.65	5.89	8	5035	124	3.75	107

[a] 6 by 12-in. cylinders.

[b] 3¼ by 4¼ by 16-in. beams; sonic measurements.

[c] Average of three specimens, 6 by 12-in. cylinders.

[d] Average of three specimens, 6 by 12-in. cylinders; measurements in compression.

All tests in accordance with ASTM Methods.

PERMEABILITY

Concrete with greater homogeneity, especially when it is air-entrained, will have lower permeability. The permeability of this type of concrete can be further lowered by water-reducing agents incorporated into the mix. Concrete could be completely impermeable or watertight if it contained no voids. However, in pouring operations it is not possible to produce concrete in which all of the void spaces between the aggregate particles are filled with a solid cementing matrix. To obtain workability, extra water above that which is required for hydration of the portland cement must be used. This excess water causes void spaces, within the matrix, which may be connected to form continuous channels through the concrete.

Another complication that arises is that the products formed through the hydration of portland cement occupy less space than the sum of the absolute volumes of the original cement and water.

Entrained air and entrapped air also produce voids; however, the former permits less water to be used, and therefore, contributes to the impermeability of the concrete. There are extensive data in the literature to support this.

It is quite apparent that all types of hardened concrete are permeable to the passage of water through the matrix yet it is often necessary to subject the concrete to high pressures in order to show a significant efflux of water through the concrete.

Table XV shows the effect of a class 2 admixture on the permeability of concrete when using a low head of water. Table XVI shows the effect of a class 4 admixture on the permeability of lean concrete when using a much greater head of water.

TABLE XIII.—EFFECT OF WATER-REDUCING ADMIXTURES ON FREEZING-AND-THAWING RESISTANCE OF CONCRETE.

TYPE II PORTLAND CEMENT

Natural Sand and Gravel. Slump 3 to 4 in.

Admixture		Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Air Content per cent	Relative Durability at Three-month Period,[a] Number of cycles to Reduce Dynamic Modulus 50 per cent
Class	Product						
None		...	5.30	6.09	...	2.7	26
3........	*O*	0.16	5.20	5.86	6	3.5	56
4........	*M*	0.175	5.20	5.19	16	5.2	143
AEA-2		0.006	5.20	5.64	9	5.2	77

BLEND OF FOUR TYPE I PORTLAND CEMENTS

Cement Factor 5.0 sacks per cu yd. Natural Sand and Gravel. Slump 4 ± ½ in.

Admixture		Dosage, fluid oz per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Air Content, per cent	Freezing-and-Thawing Durability[c]									
						Relative Moduli of Elasticity,[d] per cent at various cycles									
Class	Product					10	20	30	40	50	60	70	80	90	100
None		...	6.20	...	1.6	92	70	53	42	...	...	...	...	...	...
2....	*J*	7[e]	5.30	14	5.2	98	97	93	93	92	89	88	83	82	79

[a] Specimens standard-cured to three months prior to cycling.

[b] 3 by 12-in. cylinders, subjected to six cycles per week according to the following schedule: freeze in water for 40 min at minus 20 F, thaw in water for 40 min at 70 F.

[c] Average of four specimens, 6 by 6 by 21-in. prisms.

[d] Sonic method.

[e] Plus 0.125 fluid oz AEA-2 per sack.

VOLUME CHANGE

The dimensional stability of concrete is of considerable importance to the construction industry. Excessive volume change can be the result of a multiplicity of factors such as thermal movement, unsoundness of materials, length changes resulting from applied loads, moisture expansion and drying shrinkage. Whether such volume changes occur in concrete prior to hardening or after hardening is of great importance. Volume changes in the hardened state, particularly under conditions of restraint, produce tensile stresses and lead to cracking.

The factors affecting drying shrinkage are many (5). This phenomenon, one of major concern, is influenced greatly by the unit water and cement contents and

TABLE XIV.—EFFECT OF WATER-REDUCING ADMIXTURES ON FREEZING-AND-THAWING RESISTANCE OF CONCRETE.

Type I portland cement. Cement factor 5.0 sacks per cu yd. Natural sand and crushed limestone. Slump 3½ to 4 in.

Admixture		Dosage, lb per sack	Water-Cement Ratio, gal per sack	Water Reduction, per cent	Sand-Aggregate Ratio, by weight	Air Content, per cent	Freezing-and-Thawing Durability: Reduction in Dynamic Moduli of Elasticity, per cent, at various cycles of freezing and thawing[a]									Compressive Strength at 28 Days	
Class	Product						11	35	47	59	71	83	108	132	156	psi	per cent
None		...	6.80	...	0.45	1.5	74	...	...	...	...	...	...	...	...	4750	100
...[b]		...	6.14	11	0.41	6.0	11	20	23	23	...	24	26	26[c]	33[c]	3950	83
1....	*A*	0.25	5.53	19	0.43	3.1	19	33	37	39	43	...	...	...	...	5595	118
		0.25	5.50	19	0.41	5.7	12	17	19	20	...	24	25	28	30	4500	95
2....	*B*	0.25	5.59	19	0.43	3.8	15	23	31[c]	22[c]	23[c]	30[c]	33[c]	42[c]	...	6080	128
		0.25	5.51	19	0.41	6.0	11	15	15	15	...	20	22	24	27	4990	105
2....	*D*	0.25	6.02	11	0.43	2.8	21	39	46	...	...	...	...	...	...	6075	128
		0.25	5.74	16	0.41	5.2	12	14	16	16	...	18	21	22	27	5680	120
2....	*E*	0.25	5.65	15	0.43	2.8	19	34	41	...	...	...	...	...	...	5980	126
		0.25	5.52	19	0.41	5.7	11	15	18	18	...	21	22	22	26	4230	89

[a] Specimens moist-cured for 28 days prior to freezing and thawing.

[b] Plus AEA-1. .

[c] One specimen failed; result is based on one specimen.

TABLE XV.—THE EFFECT OF A CLASS 2 WATER-REDUCING ADMIXTURE (PRODUCT *C*) ON THE PERMEABILITY OF CONCRETE.

Type I portland cement. Natural sand and gravel. Slump 2 to 2½ in.

Dosage, lb per sack	Cement Factor, sacks per cu yd	Water-Cement Ratio, gal per sack	Sand-Aggregate Ratio, by weight	Relative Permeability[a], efflux at various ages: 1-day		3-day		7-day		10-day	
				ml	per cent	ml	per cent	ml	per cent	ml	per cent
None.....	6.0	5.83	0.45	16	100	37	100	72	100	93	100
2.0.......	5.0	5.38	0.45	6	38	15	41	33	46	45	48
2.0.......	6.0	5.65	0.45	4	25	12	32	26	36	36	39

[a] 6 by 12-in. cylinders with a 2-in. core hole through the longitudinal axis, standard cured for 18 days; ends then sealed and interior exposed to 60-ft head of water for 10 days prior to recording efflux.

and the elastic properties of the aggregates. The cement factor *per se* has little direct effect. Yet it does have a direct effect on the required water content of the mix; as the water content increases so does the tendency for drying shrinkage.

The paste content and the characteristics of the cement gel are thus primary governing factors, and any step which can be taken to cause reduction of both the paste content and gel formation is one in the right direction. Certain water-reducing admixtures permit such action.

Water-reducing or set-controlling admixtures generally have a tendency to reduce drying shrinkage, thus eliminating or minimizing cracks which are objectionable in concrete structures. Cracks are potential weak spots with respect to applied load. As avenues of ingress they provide a ready means for attack by aggressive solutions and, of course, are detrimental to the appearance or aesthetic value of the concrete member.

ABRASION RESISTANCE

Variations of test procedures for determining relative abrasion resistance of concrete are many and at best only indicative of what may be expected under practical conditions of wear.

TABLE XVI.—EFFECT OF A CLASS 4 WATER - REDUCING ADMIXTURE (PRODUCT *M*) ON THE PERMEABILITY OF CONCRETE.

Water-cement ratio 8.4 gal per sack. Sand - total aggregate ratio, by weight, 0.45. Slump 3½ in. Dosage 0.20 lb per sack cement.

Mix	Cement Factor, sacks per cu yd	Air Content, per cent	Coefficient of Permeability[a]	
			K	per cent
Plain......	3.7	2.4	20×10^{12}	100
Treated....	3.1	6.0	14	70

[a] Average of six 6 by 5½ in. cylinders; standard curing for six months; 100 psi water pressure. *K* cu ft per sec per sq ft per ft head per ft length.

There are extensive data in the literature to show that abrasion resistance is proportional to strength. The conclusion reached is that, other factors equal, the abrasion resistance of a concrete parallels the strength (6).

Retarders when used to delay set under adverse concreting conditions, particularly those of high temperature, permit proper surface finishing; this results in surfaces of greatly improved wear resistance.

Water-reducing admixtures permit use of lower unit water contents and consequently give rise to increased strength. In keeping with the acceptance of compressive strength as a criterion of abrasion resistance, it can be said that the proper use of water-reducing admixtures is conducive to increased abrasion resistance.

SUMMARY

Data have been presented to exemplify the fact that reliable water-reducing admixtures and retarders permit the making of concrete with properties superior to those normally exhibited by plain, untreated concrete.

Such enhancement of properties is particularly noteworthy in the hardened state inasmuch as it is in this state that concrete is subject to final judgment as an engineering material.

Water-reducing admixtures and retarders provide the means for producing quality concrete for more varied construction than is possible with conventional, untreated concrete.

Acknowledgment:

The authors wish to acknowledge with appreciation the assistance of colleagues of the producer group who cooperated in furnishing test data applicable to this paper; these data supplemented those developed by the Johns-Manville Products Corp.

The following producers cooperated in in this joint effort: The Master Builders Co.; W. R. Grace and Co., Dewey and Almy Chemical Division; Sika Chemical Corp.; Johns-Manville Products Corp.

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STP266-EB/Jun.1960

WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES FOR CONCRETE: USES; SPECIFICATIONS; RESEARCH OBJECTIVES

By Richard C. Mielenz[1]

Synopsis

When properly selected and proportioned, water-reducing admixtures and set-retarding admixtures (1) permit control of certain properties of fresh or hardened concrete, (2) aid in producing concrete meeting requirements of specifications when plain air-entrained concrete will not meet these requirements, (3) decrease costs of concrete and of concreting operations, and (4) permit use of design and construction practices not otherwise feasible.

Water-reducing admixtures and set-retarding admixtures should be purchased under specifications which assure uniformity, development in concrete of satisfactory qualities for the intended use, and freedom from deleterious qualities which may adversely affect significant properties of the concrete.

Major producers of these admixtures are engaged actively in basic and developmental research to improve their performance and expand their application.

This paper concludes a series of reports prepared by authors associated with four companies producing and marketing water-reducing admixtures and set-retarding admixtures for concrete. This paper summarizes the applications being made in concrete construction of the four main classes of these admixtures, namely:

Class 1, lignosulfonic acids and their salts;

Class 2, modifications and derivatives of lignosulfonic acids and their salts;

Class 3, hydroxylated carboxylic acids and their salts; and

Class 4, derivatives and modifications of hydroxylated carboxylic acids and their salts.

Water-reducing admixtures and set-retarding admixtures of the four types listed above have been sold commercially and have been used in concrete construction continuously for more than 20 years in all classes and types of concrete under virtually all engineering and physical conditions.

Water-reducing admixtures and set-retarding admixtures can improve the properties and performance of both fresh and hardened concrete, increase uniformity of concrete, and decrease the cost of concrete and concreting operations. They are an example of a self-functioning feature in specifications, increasing quality and speed of construction, with de-

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[1] Director of Research, The Master Builders Co., Division of American-Marietta Co., Cleveand. Ohio.

creased demands on the contractor and inspectors (1).[2]

Presently available water-reducing and set-retarding admixtures are not panaceas for the ills of concrete. Under some conditions and with certain concrete-making materials an admixture may induce or aggravate certain adverse qualities of concrete. In other instances, an admixture may not produce the expected benefits or they may be induced to such limited degree that no benefit commensurate with its cost is realized in the concrete. Hence, the major producers of these admixtures are carrying forward active programs of research to improve the level of performance of these admixtures and to reduce or eliminate their deficiencies. The current objectives of this research are outlined herein.

A variety of water-reducing admixtures and set-retarding admixtures are available from many companies, and the number of distributors appears to be increasing. Such admixtures should be produced and purchased under specifications assuring their quality and uniformity, and the purchaser should be provided with adequate information on their properties and performance in concrete. The nature and content of specifications for water-reducing admixtures and set-retarding admixtures are discussed briefly in this report.

PURPOSES FOR USING WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES

The purposes for which water-reducing admixtures and set-retarding admixtures are used in concrete construction include the following:

1. Economy of proportioning of the concrete mixture, such as use of minimum cement content, use of aggregate characterized by high water requirement, and improved uniformity of concrete.
2. Economy in concreting operations such as reduction of the total cost of concrete-making materials, early form removal and re-use, and ease of placing and finishing.
3. Meeting requirements of job specifications, such as maximum permissible water-cement ratio, early strength development, minimum development of strength and elasticity, and retention of workability.
4. Improvement of the quality of fresh concrete, such as improved and prolonged workability, reduced water content for given consistency or increased slump at constant or reduced water content, improved finishing qualities, control of bleeding and segregation, and control of plastic cracking.
5. Improvement of quality of hardened concrete, such as increased early and ultimate strength and elasticity, decreased permeability and absorption, increased resistance to scaling and deterioration due to freezing and thawing, increased abrasion resistance, decreased crack development, and increased bond with reinforcement.
6. Inducing desirable properties, such as controlled retardation to compensate for adverse ambient conditions or to permit introduction of special concreting practices.

A statistical analysis has been made of 28-day compressive strength of concrete containing a water-reducing admixture of class 2 (product *D*) at the rate of 0.25 lb per sack of cement and equivalent concrete not containing it. The aggregates and cements were obtained from jobs where use of this admixture was contemplated. Product *D* is formulated so as to produce little effect on rate of hardening of concrete at ordinary temperature. The test specimens were 6 by

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

12-in. cylinders made and tested in accordance with ASTM Methods C 192 and C 39.[3] The analysis includes results of all tests of concrete containing this admixture conducted in one laboratory between Sept. 20, 1957, and March 1, 1959, namely, 163 tests of concrete without the admixture and 179 tests of concrete containing the water-reducing admixture, with or without the addition of any of several conventional air-entraining admixtures. The concrete mixtures include 26 portland cements of types I, II, and III and 36 combinations of natural sand and gravel, crushed stone, synthetic lightweight aggregates, and blast-furnace slag. The results are shown in Fig. 1.

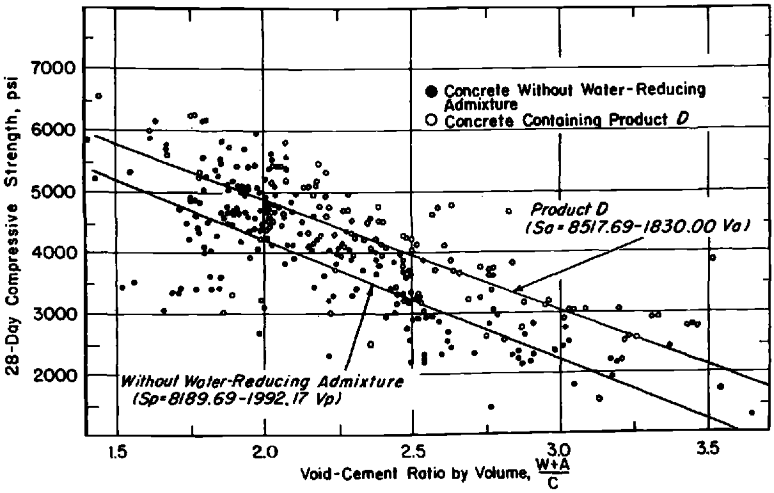

FIG. 1.—Relationship of 28-day Compressive Strength and Void-Cement Ratio of Concrete Containing Product *D*, Class 2, at 0.25 lb per sack of cement.

Analysis of the data by the method of least squares reveals the following relationship between compressive strength at 28 days and void-cement ratio by volume:

$$S_a = 8517.50 - 1830.00\ V_a \ldots\ldots (1)$$

$$S_p = 8189.69 - 1992.17\ V_p \ldots\ldots (2)$$

where:

S_a = 28-day compressive strength of the admixture concrete, psi,

S_p = 28-day compressive strength of the concrete without the admixture, psi, and

V_a and V_p = void-cement ratio by volume of the concretes, respectively.

Void-cement ratio is calculated as follows:

$$V = \frac{W + A}{C}$$

where W = water content, A = air content, and C = cement content, all by absolute volume of the concrete. The coefficient of correlation for Eq 1 is 0.787, whereas that for Eq 2 is 0.805, indicating that the probability that the indicated relationship is by chance is less than 1 in 1000 in each instance.

These relationships indicate that on the average, at constant air and cement content, for air-entrained concrete an in-

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[3] ASTM Method of Making and Curing Concrete Compression and Flexure Test Specimens in the Laboratory (C 192) and ASTM Method of Test for Compressive Strength of Molded Concrete Cylinders (C 39), 1958 book of ASTM Standards, Part 4.

TABLE I.—PROPORTIONS AND PROPERTIES OF CONCRETE USED IN EVALUATION OF TWO WATER-REDUCING RETARDERS FOR APPLICATION IN FABRICATION OF STEAM-CURED PRESTRESSED UNITS.

Item	Air-Entrained Concrete Without Water-Reducing Admixture	Admixture Concrete	
		Product B^a	Product A^a
Materials per cu yd:			
Cement, lb	728	658	658
Sand, lb	956	1033	1033
Stone, lb	2005	2074	2074
Water, lb	278	238^b	228^b
AEA, oz	5.75	0.5	1.0
Air content, per cent	3.2	2.8	5.1
Water-reducing admixture, lb	...	1.5	1.5
Properties of the Concrete:			
Slump, in	2.75	2	3
Unit weight, lb per cu ft	150.7	152.0	147.6
Temperature of the concrete as cast, deg Fahr	72	73	73

[a] Product *B* and product *A* are members of class 2 and 1, respectively.

[b] Including water content of solution in which the water-reducing admixture is introduced.

crease of 19 per cent in 28-day compressive strength can be expected using job-selected materials, even if the water reduction effected by the admixture is only 5 per cent. For concrete containing no air-entraining admixture, the expected average increase in 28-day compressive strength is 15 to 18 per cent if the water requirement is reduced 10 to 15 per cent by introduction of the admixture at the rate of 0.25 lb per bag of cement.

APPLICATION OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES IN CONCRETE CONSTRUCTION

Water-reducing admixtures and set-retarding admixtures are being used widely in all types of concrete construction. However, the specific effects produced in concrete by these admixtures depend to considerable measure on various factors, such as the characteristics of the cement and aggregate, the properties and proportions of other admixtures, and the ambient conditions, particularly temperature. Moreover, their full value and greatest economy frequently can be achieved only by a change in the proportioning of the concrete mixture otherwise employed.

For these reasons, laboratory or field

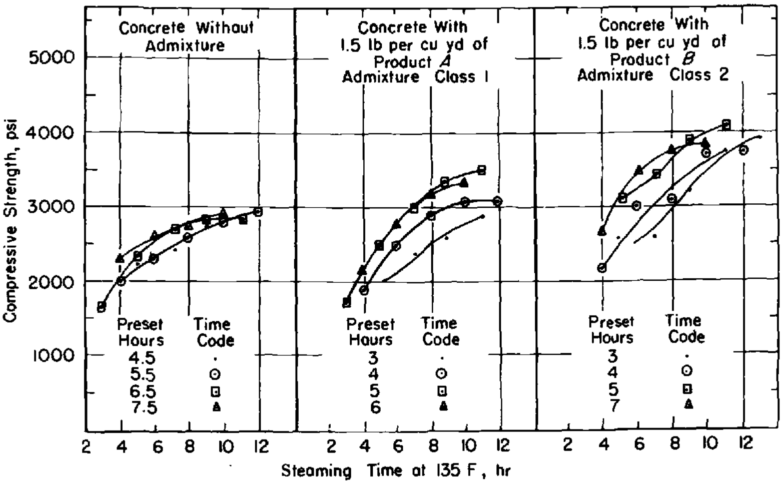

FIG. 2.—Relationship of Early Compressive Strength and Preset and Steaming Time for Concrete Containing Product *A*, Class 1, or Product *B*, Class 2.

trials are essential to select the optimum admixture formulation or proportion of admixture to be used. Every precaution should be taken to assure that the admixture is properly and uniformly dispensed. When engineers, technicians, and concrete crews become familiar with the properties and use of particular water-reducing, set-controlling admixtures, little or no outside assistance ordinarily is required in their application.

Prestressed Concrete:

Water-reducing and set-retarding admixtures have found widespread, beneficial application in prestressed concrete, both pretensioned and posttensioned, both from the standpoints of economy in concrete-making materials, early re-use of forms, ease of placing and compaction, and general quality of the product in terms of early and ultimate strength and reduced cracking. Use of properly selected admixtures of these types produces initial retardation sufficient to permit consolidation of heavily reinforced members into homogeneous units free from discontinuities in the concrete; yet, the compressive strength ordinarily exceeds that of equivalent plain concrete mixtures after about 6 hr of steaming.

Detailed tests were performed at a concrete plant in Illinois during August 1957 to determine the development of early compressive strength of concrete with varying duration of preset time[4] and steam cured at 135 F. A comparison was made between air-entrained concrete without other admixture and air-entrained concrete containing either product *A*, class 1, or product *B*, class 2, at the rate of 1.5 lb per cu yd (Table I and Fig 2).

For the air-entrained concrete without other admixture little increase in compressive strength at early ages is achieved by variation of preset time in the range applied and the maximum compressive strength achieved after 12 hr of steaming at 135 F is less than 3000 psi.

For the admixture concrete, the compressive strength after given time of steaming at 135 F increases with increase in preset time, at least to 5 or 6 hr of preset time.

Both product *A* and product *B* contain only minute proportions of chloride compounds, these being present in residual amounts in the raw materials. The amount of chloride contributed to a concrete mixture by these admixtures is similar to that introduced in mixing water.

A water-reducing admixture was used in fabrication of posttensioned girders for a highway bridge over the Santa Clara river, near Saticoy, Calif. (2). In this work, curing time was cut from 25 to 14 days by use of a water-reducing retarder of class 1, product *A* (3,4). With the admixture used at 0.25 lb per sack of cement, the concrete achieved a compressive strength of 5200 psi in 14 days, the average at 28 days being 6250 psi. Earlier tests of equivalent concrete without admixture indicated that a compressive strength of 5200 psi was not attained until 28 days after placing.

Use of prestressed concrete design of the Gorgas Lane bridge in Philadelphia, Pa., is said to have saved the city 20 per cent of the cost of the originally proposed steel bridge (5). Of particular significance is the novel sequence of concrete placing. The spans of the bridge are 120 ft long and the roadway is 68 ft wide. The contractor developed a procedure by which he could place each span in two halves, that is, 120 ft long and 34 ft wide. The supporting girders are 12 in. wide and 7 ft deep; 260 cu yd of concrete were placed in each continuous pour. Placing time was 8 to 10 hr. By using a retarder of class 3 (product *H*) in the concrete of the girders, the hardening was delayed

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[4] Preset time is the period between completion of placing of concrete in a unit and the application of heat.

until the slab was placed. The concrete then was revibrated along the centerline of the girders, making a slab and girder a homogeneous structural unit. Such a procedure would not have been feasible if a retarder had not been used. Rapid strength gain after hardening permitted early release of tension from the prestressing wires and so contributed to the speed of construction.

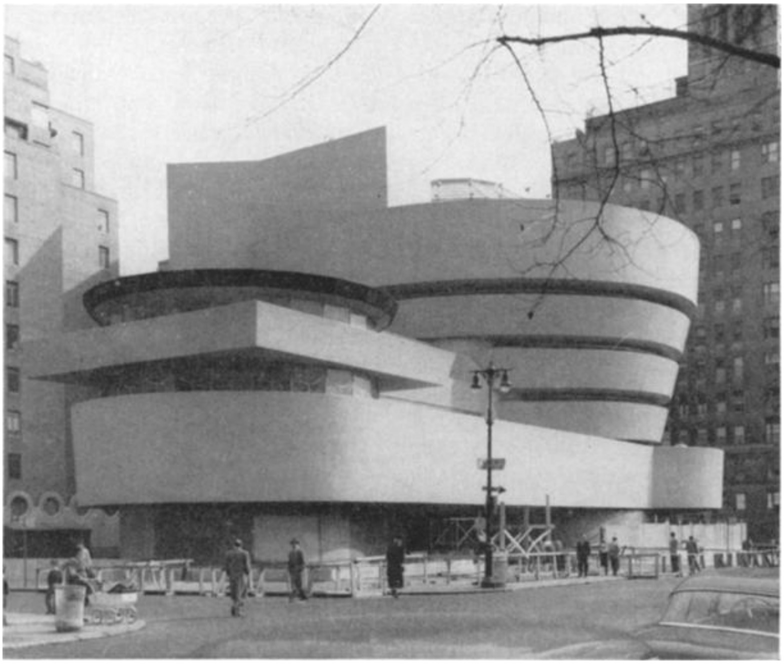

FIG. 3.—View of the Guggenheim Museum in New York City, N. Y.

Buildings; Floating Structures:

Three admixtures of class 2 (products *D*, *E*, and *F*) were used in construction of the Dallas Memorial Auditorium in Dallas, Tex. (6). These admixtures were employed to obtain the required workability at the specified low water-cement ratio (5.0 gal per sack), and rapid strength gain to permit prompt removal of the forms. The specifications required a modulus of elasticity equal to or greater than 2×10^6 psi before removal of the roof form. The average time required was three days. During the summer a water-reducing retarder (product *E*) was used so as to allow ample time for placing and finishing operations. In winter an accelerating water-reducer of class 2 (product *F*) was used. During the spring and fall, a water reducer of class 2 (product *D*) having little effect upon rate of hardening of concrete was used.

The Guggenheim Museum recently constructed in New York City (Fig. 3) (7) has an outer surface in the form of a conical helix increasing in diameter upwardly and an inner surface in the form of a helical cone decreasing in diameter with increase in elevation. Because of this complex design, the contractor chose to use a retarding admixture (class 3, product *H*) to minimize the difficulties resulting from the involved form work and reinforcement. Among the principal considerations prompting use of an admixture was the reduced finishing time and improved workability and strength.

Water and sewerage works place especially stringent demands upon the performance of concrete because of the rigid requirements for resistance to leaching, freezing-and-thawing durability, low permeability, workability and placeability to minimize segregation and to assure a dense structure in the concrete, freedom from cracks, and volume stability. Admixtures of classes 1, 2, and 3 have been used in several hundred water and sewerage treatment plants in the United States and Canada.

Product *H*, a water-reducing retarder of class 3 has been used in many floating concrete structures, such as concrete ships, barges, dry-docks, and piers. This admixture was employed in the majority of floating concrete structures described as "notable concrete structures" by the American Concrete Inst. (8). A water-reducing retarder was used in the concrete ship program during World War II to assist in joining new concrete to old, to increase strength of the concrete, and to decrease water content for given slump (9).

Tunnel Concrete:

Concrete tunnel linings present many problems for which water-reducing and set-retarding admixtures are very valuable. Water-reducing admixtures and set-retarding admixtures of classes 1, 2, and 3 have been used in many major railroad, water, and highway tunnels. Of especial importance in the construction and operation of these tunnels are such properties as workability of the concrete so as to permit extensive handling and consolidation into a dense, homogeneous mass free from segregation and honeycombed portions, retardation of loss of workability and hardening because of delay commonly necessary between mixing and placing, low permeability, volume stability, resistance to abrasion and cavitation, and quality of the finished or formed surfaces.

In construction of the Fort Pitt Tunnel at Pittsburgh, Pa. (10) a water-reducing retarder of class 1 (product *A*) is being employed to increase slump of concrete without increasing water-cement ratio above the specified maximum, increase compressive strength 10 per cent above that obtainable with equivalent air-entrained concrete without the admixture, maintain workability and pumping qualities under the conditions of placing required, and increase unit weight to minimum of 146 lb per cu ft.[5] The optimum air-entrained concrete without the admixture meeting the specification requirements produced a compressive strength of 3000 psi at 7 days but the slump was approximately 2 in.

Use of product *A* in combination with a proprietary air-detraining admixture increased slump to 5½ in. at a cement content of 6¼ sacks and a water content of 31¼ gal per cu yd. Air content is 4 to 4.5 per cent. Typical tests indicate the following development of compressive strength:

2 days	2000 psi	14 days	5200 psi
4 days	3400 psi	21 days	5900 psi
7 days	4500 psi	28 days	6300 psi

Specifications require that the concrete in the tunnel walls develop a compressive strength of 1500 psi before the forms are moved; this strength is consistently developed in less than 48 hr.

In construction of the Tecolote Tunnel a water-reducing retarder was used in combination with a pozzolan (11). Tuthill and Cordon (12) have summarized results obtained in the concreting of the lining of the outlet portion, where air-entrained concrete without admixture

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[5] All data on the Fort Pitt tunnel construction were kindly supplied by the Pennsylvania Department of Highways.

was used in 4000 cu yd and concrete containing an admixture of class 1, product *A* was used in 16,000 cu yd of lining at the rate of 1.75 lb per cu yd. A calcined natural pozzolan was used at the rate of about 100 lb per cu yd. An average of 33 tests of the concrete without admixture and of 134 tests of the admixture concrete indicated that the water content was decreased from 298 to 270 lb per cu yd; slump was held essentially constant at 3.9 and 4.1 in. for the two concrete mixtures, respectively, and compressive strength at 28 days was increased from 4390 to 5474 psi.

Pavements and Other Slabs:

Of prime importance in placing of pavements and other concrete slabs are such factors as minimal water content consistent with adequate workability and placing quality, retardation sufficient to avoid "cold joints" or separations between successive batches of concrete, minimal settlement and cracking of the fresh concrete, finishing qualities, and strength, volume stability, and weathering and scaling resistance of the concrete.

A significant paving job involving use of water-reducing and set-retarding admixtures was construction of the flight apron at Boeing Field in Seattle, Wash. (13). Three requirements were placed upon the concrete: (1) high early strength was necessary so that the load of 200-ton bombers could be applied after 3 or 4 days, (2) a maximum of 1½ in. slump was allowed, (3) good workability was required. These qualities are reported to have been achieved by use of type III portland cement, an air-entraining admixture, and an admixture of class 3 (product *H*). The air content averaged about 3.5 per cent; slump ranged from ½ to 1½ in.; flexural strength averaged 750 psi and compressive strength 5500 psi at 28 days.

A water-reducing admixture of class 1 (product *A*) was used in pavement concrete during construction of a banked high-speed plane turn-off during extension of the Weir Cook Municipal Airport, Indianapolis, Ind. (14). The new paving includes 180,000 sq yd of concrete. Specifications for the concrete required a minimum of 5.5 sacks of cement per cu yd, 3.5 per cent of air, and 0.25 lb of product *A* per sack of cement. The flexural strength by the three-point loading method was required to be at least 700 psi at 28 days. This mixture was workable at a slump of 1½ in. The low-water content and rapid-strength development permitted the contractor to run his spreaders and finishing machines on the pavement after 3 days of curing, without damage to the concrete. The low-slump concrete lay in place on the super-depressed turnouts, without movement to the low side such as usually occurs from the working of the finishing screeds. The average flexural strength at 28 days determined on 101 sets of specimens was 746 psi. It was found necessary to increase the cement content from 5.5 to 6.5 sacks per cu yd when the water-reducing admixture was omitted.

A water-reducing admixture of class 2 (product *J*) was incorporated in concrete in critical sections of O'Hare Field near Chicago, Ill., primarily to reduce placing time. Use of the admixture improved workability and compressive and flexural strength with respect to those properties of equivalent air-entrained concrete without admixture so that the contractor was permitted to use the minimum cement factor allowable under the specifications. Economies were effected through more efficient use of equipment because of high-early strength development in the placed concrete.

Projects C-28 and C-29 of the Ohio Turnpike illustrate the use of product *A*, class 1, at 0.25 lb per sack of cement to achieve high early strength.[6] The initial trial of the admixture was because of the desire of the contractor to use the pavement as early as permissible. Data from the permanent job record for these projects are as follows:

DESIGN CRITERIA

Compressive strength at 28 days	4000 psi
Flexural strength at 28 days	600 psi

AVERAGE RESULTS ACHIEVED

Age, days	Admixture Concrete	Concrete Without Admixture
	Compressive Strength, psi	
7	3716	2807
14	4098	3334
28	4438	3851
	Flexural Strength, psi	
3	612	462
5	643	505
7	667	548

The concrete mixture was unchanged except for a reduction of water content and water-cement ratio with introduction of the water-reducing retarder. Weather and operating conditions are reported to have been identical.

Slip Forming:

Water-reducing admixtures and set-retarding admixtures assist in control of the workability, placeability, hardening, and strength development of concrete essential to efficient and economical slip-forming operations.

A typical example of the beneficial use of retarders in slip-forming construction is the recently completed bleaching plant of the firm of Hollingsworth and Whitney in Mobile, Ala. A retarder aided in avoiding development of cold joints in the concrete and also was found to assure quick development of strength after hardening of the concrete so as to maintain the rate of elevation of the forms at a maximum. The structure contains nine towers which are 14 ft in diameter and 60 ft high. Placing of the concrete was completed in only 7 days. Water requirement was reduced materially by use of an admixture of class 3 (product *H*) while the slump was maintained at 4 in. for optimum workability of the concrete.

Slip-form construction of grain storage elevators for the A. E. Staley Manufacturing Co., Decatur, Ill., illustrates use of water-reducing admixtures of class 2.[7] The elevators are 20 ft in diameter and 145 ft high. The specifications required a compressive strength of 3000 psi at 28 days. Nine to eleven days were required for the placing of concrete in each elevator unit, the longer time being required during −11 to 33 F weather. Slump ranged from 4 to 6 in. and strength ranged from 4000 to 5000 psi at 28 days. By using an accelerating water-reducing admixture on the cold days at 0.5 lb per sack of cement, the contractor was able to jack the forms as fast as on jobs constructed during warm weather. An inspection after three years indicates that these extreme conditions produced no adverse effects on the concrete.

Prefabricated Concrete Units:

Of prime importance in precasting of structural elements are workability, placeability, controlled rate of hardening, rapid strength gain, finishing qualities, and control of cracking both before and after hardening of the concrete. One example of precast of structural elements is the decking of the great highway bridge across Lake Pontchartrain, La. (15). The entire deck and girder element for each span was cast in a single unit. Spans are 56 ft long. Eight such elements were cast each day in a single bed. A water-reducing retarder (product *H*, class 3) is re-

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[6] The ensuing data were kindly supplied by the J. A. Jones Construction Co., Norwalk, Ohio.

[7] The following data on this construction were kindly supplied by the A. E. Staley Manufacturing Co., Decatur, Ill.

ported to have been of great value, particularly because of variable weather conditions. The initial retardation of hardening permitted complete consolidation of the 89 cu yd of concrete in the bridge section even in the hottest weather, and rapid build-up of strength after hardening of the concrete permitted early release of the tension on prestressed wires. For these members, compressive strength at 3 days averaged well over 4000 psi.

Tilt-up wall construction is another important class of prefabricated concrete construction in which water-reducing admixtures have found wide application. During construction of the General Service Administration warehouse in Rome, Ga., a water-reducing, set-controlling admixture of class 2, product *G* was used in all wall panels.[8] Most of the walls were tilted up at 6 days at which time the compressive strength was found to exceed the value of 1800 psi required at 7 days. No panels were lost because of cracking of the concrete. In floor slabs on this project, concrete containing the water-reducing admixture is reported to display less shrinkage cracking than does comparable plain concrete.

Tilt-up panels are used abundantly in southern California, where hot and dry conditions are conducive to loss of workability and development of shrinkage cracks in the plastic concrete. Experience has demonstrated that cracking of plastic concrete can be greatly reduced in some situations by use of an admixture of class 2, either in concrete containing portland cement and a pozzolan or portland cement alone.

Mass Concrete:

Water-reducing retarders can contribute significantly to the quality, economy, and ease of placing of mass concrete. Water-reducing admixtures of classes 1, 2, and 3 have been used in over 100 concrete dams and also in appurtenant works in the United States, Europe, Canada, Japan, and South America.

Projects requiring substantial volumes of mass concrete commonly are in remote areas of rough terrain where the cost of cement is high and where the distance between batching plant and the various features of the project require long haul and great distances of pipeline transportation of concrete. By use of a water-reducing retarder a low water-cement ratio can be maintained or reduced even at reduced cement content. Also, the improved workability, resistance to segregation of the concrete mixture during transportation, and improved pumping quality of the concrete provide important advantages in use of the admixture.

The lower cement content commonly made possible by the admixture not only reduces cost of the concrete but decreases heat generation and temperature rise in the structures. In addition, available data show that water-reducing retarders of classes 1 and 3 delay the liberation of heat by portland cement and reduce the maximum temperature attained during hydration (16,17). The total heat released from a given quantity of cement is not altered appreciably.

The Bersimis-Lac Cassé Project of the Hydroelectric Power Commission of Quebec, in south-central Quebec, exemplifies use of a water-reducing retarder in mass concrete (18,19). Product *A*, class 1, was employed on this project in 400,000 cu yd of concrete, at the rate of 1.5 lb per cu yd. The concrete was mixed at a central mixing plant and transported in open-bodied, 8 cu yd capacity trucks for as much as 8 miles before its deposition in pneumatic placers or pumping machines. The specifications for the 18-in. thick tunnel lining required a compressive strength of 3000 psi at 28 days. With the admixture, the strength ob-

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[8] Data on this construction were kindly supplied by the Johnson and Johnson Construction Co., Rome, Ga.

tained averaged 3900 psi at that age. There was "practically no segregation" of the admixture concrete as it was delivered at the placing machines and workability was maintained for as long as 2 hr after completion of the mixing at the central concrete plant. In the tunnel, the concrete was placed against rock at a temperature about 50 F, yet rapid strength gain permitted slipping of the forms in 11 hr so that they could be reset and re-used on a 24-hr cycle.

The Tri-Dam project, located in east-central California has provided unusually complete data for determination of the relative cost of concrete in large scale construction when a water-reducing admixture is used. Primary features of the project are Donnells Dam, a concrete arch, Tulloch Dam, a concrete gravity structure, and Beardsley Dam, a rolled earth fill dam with a concrete spillway.[9] A total of 518,367 cu yd of concrete were placed on the project. Any of three water-reducing admixtures of classes 1 and 2, and an air-entraining admixture were employed in all of the concrete on the project except for 18,652 cu yd placed during the first several months of construction. The concrete containing a water-reducing admixture was produced at the same slump and water-cement ratio as was the air-entrained concrete not containing a water-reducing admixture, the cement content being reduced but the compressive strength being maintained essentially constant.

Detailed records maintained by the project engineer indicate a net saving of $0.183 per cu yd of concrete in the cost of cement at Beardsley Dam, or a total of $3,982. At Tulloch Dam and appurtenances the calculated savings amount to $102,792 for 236,795 cu yd of concrete placed. Total savings in the cost of cement for the entire project as a result of the use of the water-reducing admixtures were indicated to be $172,475 for the 499,715 cu yd of concrete in which these admixtures were employed. The net savings in the cost of the concrete-making materials is estimated by the author to be about one half this amount in view of the cost of aggregate necessary to compensate the reduction in volume of cement and water incorporated in the concrete. The records take into account such factors as cost of the admixtures employed, transportation charges and taxes imposed on the admixtures, and handling costs.

DEVELOPMENT OF SPECIFICATIONS FOR WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES

As with all engineering materials, water-reducing admixtures and set-retarding admixtures should be purchased under specifications that assure the presence of the desired properties, that demonstrate the absence of deleterious effects, and that permit evaluation of the uniformity of the admixture from lot to lot. So far as feasible, the requirements for concrete admixtures should be based on performance tests in concrete.

Specifications on water-reducing and set-retarding admixtures have been developed and are being used by several public agencies and by numerous private engineering and contracting firms.

Briefly discussed below are general considerations pertaining to such specifications and evaluation of water-reducing and set-retarding admixtures.

Ascertaining Uniformity of Admixture Products:

It is usually essential to include in specifications on water-reducing admixtures and set-retarding admixtures some chemical and physical tests as a means

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[9] All data on the Tri-Dam project were kindly supplied by Mr. B. W. Goodenough, formerly of Tudor-Goodenough Engineers, now President, Goodenough, Sudman and Overholser, Consulting Engineers, Sacramento, Calif.

to compare shipments with previous samples. However, because of the difficulty inherent in chemical analysis or organic compounds and mixtures thereof and because most admixture manufacturers are unwilling to reveal details of the composition of their products, the identification and comparison of admixtures being supplied under specifications usually will be based upon index tests, no one of which is specific or definitive. Physical and chemical tests for this purpose are as follows:

1. Observation of physical nature, appearance, and microscopical characteristics.
2. Moisture content of solid products.
3. Solids content, nature of solvent, index of refraction, or specific gravity of solutions or liquids.
4. Partial or complete chemical analysis, such as content of chlorides, carbohydrates, and other compounds and radicals of especial interest.
5. Infrared and ultraviolet light spectroscopy of active constituents.
6. X-ray diffraction analysis of crystalline solids.
7. Solubility of solids in water or other solvents.

Most of these properties or compositional features indicated above are not of critical importance themselves within broad limits. These are determined mainly to assure uniformity of the product being supplied. In general, there is no merit in specifying water-reducing admixtures by chemical composition because, again in general, it is infeasible to control the properties and performance of admixtures by this means and because difficulties of chemical analysis preclude rapid, reliable, quantitative determination of organic constituents in any but the most completely equipped and staffed laboratories. There is substantial variation in properties and performance, as well as in chemical composition, among the various commercially available water-reducing admixtures within each of the four classes to which reference has been made in this paper.

Under particular circumstances, certain compositional features are important; in these instances, the significant qualities should be cited in purchase specifications. So, for example, the chloride content of water-reducing admixtures proposed for use in prestressed concrete might be restricted to such a level that its use will not introduce into the concrete an amount of chloride equivalent to more than 0.01 per cent by weight of the cement, expressed as calcium chloride ($CaCl_2$). This proportion of calcium chloride is in the range of the proportion of calcium chloride introduced into concrete in mixing water in some cities in the United States and is less than that present in some commercial portland cements.

Performance Tests of Water-Reducing Admixtures and Set-Retarding Admixtures:

The main technical basis for selection of water-reducing and set-retarding admixtures for concrete should be tests of concrete containing the admixtures under investigation. Evaluation of such properties as strength development, water reduction, bleeding, and air-entrainment should not be based upon tests of mortar inasmuch as significantly different results may be obtained than would be observed in concrete.

In general, the tests should be made in concrete containing the cement, aggregates, and other admixtures proposed for use in the work. If the particular cement to be used has not been selected or if samples of the selected cement are not available, the cement used should be of the type specified for the project and preferably should be a blend of several cements conforming with the specifications and available in the project area. The aggregate also should meet the requirements of the project specifications.

In order to secure comparative results in tests of two or more admixtures or of concrete with and without a water-reducing, set-controlling admixture, particular attention must be given to such features as air content, grading of the coarse and fine aggregate, sand content, yield, and slump (and other aspects of consistency pertinent to the work). Obviously, the techniques, apparatus, and conditions of testing employed should conform in every detail with standard specifications and the tests should be repeated sufficiently to provide statistically valid data.

Of great importance is the proportion of the admixture to be used in the test concrete. Variation in proportion ordinarily will affect such properties as water requirement, air content, rate of hardening, bleeding, and early and ultimate strength of the concrete. In general, the factors limiting the utility of a particular rate of use of each admixture are the water reduction, strength development, rate of hardening, and the air content. With most water-reducing, set-retarding admixtures, excessive rate of use induces inordinate retardation. Under no circumstance should a comparison be made between strength of plain or plain air-entrained concrete and that of concrete containing a water-reducing retarder without knowledge of the degree of retardation effected in the admixture concrete. In general, moderate or marked retardation induces increased compressive strength of concrete at 7 and 28 days; yet, unless controlled, the retardation effected in the test may be inconsistent with the requirements of the work.

For the most part, the nature of the work, the ambient temperature conditions, and the distance of transportation required for the concrete will dictate an optimum or necessary range of rate of hardening, such as may be determined by ASTM Method C 403[10] or bond pullout pins (20). The admixture should be employed at the rate recommended by the manufacturer or at such adjusted rate as is necessary to effect the desired acceleration or retardation of hardening and strength development.

The tests stipulated by purchase specifications for water-reducing admixtures and set-retarding admixtures should evaluate such properties as:

Reduction of water requirement,
Air entrainment,
Slump or other pertinent aspects of consistency,
Bleeding of air and water,
Rate of hardening of the concrete at temperatures pertinent to the work,
Compressive strength at ages pertinent to the design requirements,
Flexural strength at ages pertinent to the design requirements,
Resistance to freezing and thawing, and
Volume stability under conditions pertinent to the work.

OBJECTIVES OF RESEARCH BY PRODUCERS OF WATER-REDUCING ADMIXTURES AND SET-RETARDING ADMIXTURES

The major producers of water-reducing admixtures and set-retarding admixtures are sponsoring active programs of research to (1) improve the average or typical performance of their products, (2) reduce the effects of cement and aggregate on performance of the admixture, and (3) develop new or other special qualities in concrete. Research programs of the four producers of water-reducing admixtures with which the authors of the four jointly prepared papers are associated are equivalent to about 2.5 to 5 per cent of the gross business of these

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[10] Tentative Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles (C 403 – 57 T), 1958 Book of ASTM Standards, Part 4, p. 712.

companies in sale and servicing of the products.

Improvement of Typical Performance:

Of primary concern to the admixture manufacturer is the development of basic physical and chemical data which elucidate the mechanisms controlling the effect of water-reducing and set-controlling admixtures on the properties of concrete. Developments such as the reduction of water requirement for given consistency, controlling the retardation and acceleration of hardening under various conditions, improvement of various important engineering properties of hardened concrete, and control of air content and of the air-void system in concrete are of particular interest.

Reduction of Effects of Cement and Aggregates on Performance of Admixtures:

Experience as well as research demonstrates that the performance of water-reducing admixtures depends to substantial degree upon the properties of the cement and occasionally upon the properties of the aggregate. The adverse effects of some cements and aggregates on performance of an admixture are primarily a decrease in water reduction and strength or development of a stiffening tendency in the concrete. The cause of these adverse effects largely is not known at present but considerable research is being devoted to their elucidation.

Difficulty occasionally is experienced with combination of air-entraining water-reducing admixtures and cements or sands which entrain air. Research on this problem has developed several air-detraining agents which may be added to the concrete at the mixer to reduce excessive air content to desired levels.

Development of New or Other Special Qualities in Concrete:

It is occasionally desirable to improve certain qualities of concrete other than those generally thought of as related to use of water-reducing and set-retarding admixtures. One such important property is the finishing quality of concrete slabs and other surfaces. Based upon difficulties experienced with finishing in certain areas where poorly graded sands are in wide use, one manufacturer has developed a formulation which has been shown by field trials and experience to significantly improve finishing quality, primarily by improving workability and increasing the fattiness and cohesive character of the near-surface mortar.

Difficulties of Research on Admixtures:

Research in development of concrete admixtures presents substantial difficulties: (1) Fundamental information on the physical, chemical and physicochemical action of admixtures in concrete is so meager that much of the research and development of new formulations must be empirical; (2) Tests of portland cement mixtures containing water-reducing admixtures for concrete are reliable only if concrete is used, rather than mortar; (3) The well-known limited reproducibility of tests of concrete requires five to ten rounds of tests even under excellent standards of control if relatively small, although significant differences in performance are to be detected; (4) A thorough evaluation of an experimental product requires a wide range of tests before the several important aspects of performance are evaluated and the laboratory tests should be followed by field trials under competent supervision; (5) Selection of the cements and aggregates for use in the research studies presents problems, primarily because of the differing performance of the admixtures with different cements; (6) Certain qualities of concrete cannot readily be evaluated quantitatively in the laboratory, especially such features as finishing quality and shrinkage cracking of plastic concrete.

CONCLUSIONS

Water-reducing admixtures and set-retarding admixtures of various chemical classes provide means to control and improve the properties of concrete, reduce costs of concrete without loss of quality, reduce cost of concreting operations, and make feasible design and construction procedures not ordinarily practicable with concrete not containing such admixtures. These admixtures are not a substitute for portland cement. Rather, they are proposed as a beneficial component of portland-cement concrete which, when properly employed, should improve the competitive position of portland-cement concrete and broaden its application.

No one water-reducing admixture or set-retarding admixture or proportion of such admixture will produce optimum qualities in all concrete mixtures under all conditions. Consequently, evaluation of the merits of these admixtures for individual projects and selection of the admixture formulation and of the rate of use of the formulation in the concrete usually are best determined by tests performed with the proposed concrete-making materials under conditions approximating those anticipated on the job.

Water-reducing admixtures and set-retarding admixtures should be purchased under specifications which stipulate procedures evaluating uniformity and performance in concrete in relation to the anticipated conditions of service. These admixtures are being improved constantly and more is being learned about their properties and performance. Consequently, we look forward to change and strengthening of specification requirements and methods of testing with the passing of time.

Acknowledgments:

This paper is one of a coordinated series of four prepared by representatives of four producers of water-reducing admixtures and set-retarding admixtures for concrete, namely, The Master Builders Co., Division of American-Marietta Co.; the Sika Chemical Corp.; the Dewey and Almy Chemical Division, W. R. Grace and Co.; and the Johns-Manville Products Corp. The author of this paper wishes to acknowledge with appreciation the cooperation and assistance received from these companies in supplying data and other information and in constructive review of the manuscript.

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DISCUSSION

MR. E. A. ABDUN-NUR[1] (*presented in written form*).—The author has assembled an excellent array of applications for these admixtures, and has given a realistic insight into the specifications that are being considered by ASTM as possible standard specifications for this class of products.

In discussing Eqs 1 and 2, the author gives coefficients of correlation of 0.787 and 0.805 respectively. Equation 1 refers to data from concrete with an admixture, while Eq 2 refers to data from concrete without admixture. For practical purposes, the two correlations are essentially the same. However, an evaluation of the reliability of a coefficient of correlation requires a knowledge of the probable error of the coefficient. With the large number of tests represented by these correlations, the probable error is likely to be low, but it would be interesting to know the actual probable errors of these two correlations.

The writer might add another application for water-reducing retarders. This application has found important use in bridge work and might be as applicable to other slabs with extensive areas and long spans. When a bridge deck or a building slab is placed either on steel or on precast beams or girders, a certain amount of deflection takes place in the supporting beams due to the weight of the slab. This progressive deflection causes cracks in any part of the slab that has already attained its final set. By using varying amounts of retarding admixture, it is possible to delay the final set until the whole span has been placed. Thus, deflections can be accommodated by the plastic concrete without cracking.

The writer agrees wholeheartedly with the author regarding the desirability of performance specifications, has repeatedly advocated such specifications, and has made effective use of them wherever possible. However, long-time experience has established the fact that in concrete, field performance tests on the plastic material cannot by themselves guarantee the long-range properties and durability of the structure. Some other limitations developed from experience have to be superimposed and added to the performance tests to assure the desirable long-term properties and durability.

In addition, it is essential for the engineer to know the composition of any of the ingredients that go into the concrete mix. This is necessary so that when problems arise he can trace the cause, whereas, when the components of a mix are not known, as a result of an admixture of unknown composition, it may be impossible to determine what is giving trouble. Specifications which permit the use of proprietary admixtures, the compositions of which are unknown, should not be accepted in good engineering practice. In addition, there is no assurance that an article bought by trade name without any knowledge of its makeup will not have its composition changed without the knowledge of the engineer.

"Proprietary" type of admixtures may be desirable from the standpoint of the

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[1] Consulting Engineer, Denver, Colo.

admixture manufacturer as sales and promotion tools to permit him to claim something that his competition does not have. Actually, these are not only not needed from the engineering viewpoint, but may in the long run be detrimental to good engineering practice.

Some of the papers of this symposium have brought out the fact that fine distinctions in performance of the various trade named water-reducing-retarder type of admixture cannot be confirmed in actual practice. The writer's experience is that given an admixture of classes 1 or 3, an air-entraining agent, and an accelerator, one can obtain any of the properties claimed by the various patented compounds and can control and vary these properties as the need arises. This combination would be ideal for ready-mixed concrete plants in lieu of trying to batch a large variety of admixtures by trade name.

No one would think of taking chemical composition requirements out of cement specifications, or out of pozzolan specifications, so why permit an admixture specification without requiring knowledge of its composition or limiting at least some of its constituents.

The limitation of chloride content suggested by the author is an excellent step in the right direction, but it must be supplemented by knowledge of other chemical constituents to permit a realistic and proper use of these admixtures.

MR. L. H. TUTHILL[2] (*by letter*).—We are particularly indebted to the author for including in his excellent paper such a comprehensive list of concrete construction operations in which some one of these admixtures has been used with notably beneficial results. It is encouraging to find this wide contemporary success with these materials because we have come to believe that when properly used, and the impossible is not expected of them, they can make a significant improvement in the quality of concrete. It has long been recognized that increases in strength usually correlate with general improvement in most other desirable properties.

Least clearly evident among the benefits of these admixtures is improvement in workability when slump and air content is kept the same. Not only salesmen make these claims; they often appear in the comments of engineers and construction men on the performance of these materials. For instance, it is reported that concrete pumps perform with less effort when these admixtures are placed in the mix with the slump and cement content unchanged. If such added workability is not in fact provided, belief that it has been noted may stem from the fact that many may still be making the mistaken assumption we made several years ago that because more time was provided before the vibration limit was reached, slump loss also would be postponed. At least two papers in this symposium have clearly shown the error of such an assumption.

If, however, some added workability is in fact provided despite loss of slump, it may be that it is the result of the prolonged period of plasticity of very low penetration resistance, before this concrete begins to stiffen. It is our hope that reproducible quantitative evidence of such added workability or mobility can be obtained. The difficulty will be to hold slump and air content constant.

In his discussion of specifications the author has provided a thorough outline of what is worth knowing about an admixture proposed for use. For evaluating a product, and for occasional confirmation tests during use of a product, such an outline of tests and determinations provides an excellent guide. It will be

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[2] Concrete Engineer, California State Department of Water Resources, Sacramento, Calif.

necessary in the forthcoming ASTM standards for such materials to follow some such lines.

For routine acceptance of standard products or materials that have been fully evaluated prior to use on the job, it is feared that such fulsome specifications would be unnecessarily cumbersome. Probably all that is actually required is that the materials perform as expected in job concrete. Regardless of their merits elsewhere, this is all that counts to each user. Fortunately this is readily determined on the job by comparing the water requirement, rate of hardening, and strength at ages pertinent to job requirements, of concrete with and without the admixture. If a user is not prepared to obtain such information about the concrete he is using, he is unlikely to be in a position to carry out tests to prove compliance with a comprehensive specification. Such users must rely on the integrity of well known materials supplied under established brand names.

The effect of these admixtures is usually so marked that a performance failure would be conspicuous. For instance, water requirement might increase for no otherwise explainable reason. In such cases, however, it is well to check the job to be sure the cause does not lie in a change in cement or aggregates, error in make-up of admixture solution or failure to stir it with some brands, or under dosage due to malfunction of clogged dispensing equipment—before questioning the character of the admixture as delivered.

It is good to know that research is continuing. As more is known about what is happening in cement paste from the moment it is made until it is part of strong, serviceable concrete, and about how admixtures can favorably modify it, increasingly better workmanship and service performance with concrete will be obtained. An improvement which would go far in this direction would be one that would reduce slump loss so that 80 per cent of the original slump was still present 20 min or so after mixing, without affecting the vibration limit. Ideally, such a factor would be adjustable from a requirement for long hauls of centrally mixed concrete in hot weather, to that for job-mixed concrete in cold weather to minimize form pressures. We hope it will not be long before such a factor is found for modification of presently available water-reducing retarders.

MR. RICHARD C. MIELENZ (*author's closure*).—I am most appreciative of the comments by Messrs. Abdun-Nur and Tuthill, particularly the supplementary information they have supplied.

Mr. Abdun-Nur has expressed an interest in the "probable error" of the coefficient of correlation calculated for the two equations relating 28-day compressive strength and void-cement ratio. I have indicated the significance of the correlation coefficient for the equations by stating that in each instance the probability that the indicated relationship is by chance less than 1 in 1000. This conclusion is based upon tabular data published in texts on statistical methods[3,4] showing the maximum value of the correlation coefficient that can be expected by chance for the amount of data involved if there were no correlation between the variables. An identical result is obtained by application of variance tests of the correlation, such as the t test described by Volk.[4]

By dint of substantial labor, it would be possible to establish confidence limits

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[3] R. A. Fisher and Frank Yates, "Statistical Tables for Biological, Agricultural, and Medical Research," Oliver and Boyd, Ltd., Edinburgh and London (1953) (*See especially* Table VI).

[4] William Volk, "Applied Statistics for Engineers," McGraw Hill Book Co., Inc., New York, N. Y. (1958) (*See especially* Tables 6.1 and 8.2, pp. 234, 235).

of the slope and the least-squares line represented by the equations. This treatment has not been accomplished; it would be worthwhile in a paper dealing specifically with the correlation of compressive strength and void-cement ratio of concrete.

Messrs. Abdun-Nur and Tuthill have discussed briefly the proposed approach to specifications on water-reducing and set-retarding admixtures. In spite of the apparent divergence in their point of view from mine and in their points of view one from the other, I believe we are actually in substantial agreement. A good deal of the apparent difference of opinion results largely from the fact that each has emphasized differing stages in the selection and evaluation of the materials.

In my opinion, specifications on engineering materials must contemplate three general levels of evaluation and selection, namely, (1) evaluation of commercial or natural materials and proprietary products to determine their properties and performance under a range of conditions and, if appropriate, in combination with a variety of other materials, primarily to establish a list of approved materials for general application, (2) evaluation of materials and products with respect to use in specific work, preferably in combination with other job materials and under conditions pertinent to the work, and (3) routine evaluation of materials received at the job site to compare the shipments with previously approved samples and to determine uniformity.

Manifestly, each of these levels of evaluation can feasibly be performed with differing speed and thoroughness. With respect to admixtures, the last must necessarily be predicated upon quick chemical and physical methods, including application of what I have called "index" tests as well as tests in concrete mixtures to determine such properties as water requirement, air-entraining potential, rate of hardening, and compressive strength at early ages.

Mr. Abdun-Nur expressed the opinion that the engineer should know the composition of all ingredients of a concrete mixture. Although this concept appears to be justifiable, it is not entirely feasible with respect to chemical admixtures if the user of these products is to receive at an early time the advantages of research and development by producers. During the period of development and of applying for patents on new formulations, the patentee cannot reveal the composition of his products without danger of prejudicing the obtaining of patent rights. Secondly, in general, without regard to patents, a producer frequently finds it essential to restrict release of information on his formulations so that he can maintain his business and receive the just rewards of his research, development, and experience in preparing his products.

Mr. Abdun-Nur has stated that the composition of the ingredients of the concrete should be known so that the cause of any "trouble" can be ascertained. Speaking of chemical admixtures, it seems to me that the admixture as a whole should be evaluated; if it is causing "trouble" or is not providing benefits commensurate with the cost, it should be rejected. It is not the responsibility of the engineer to provide the admixture producer with information on how to reformulate his product.

Mr. Abdun-Nur states that "no one would think of taking chemical composition requirements out of cement specification or out of pozzolan specifications." It is interesting in this connection to note that the chemical requirements of ASTM Specifications C 150[5] on type I portland cement stipulate limits on only the content of MgO, SO_3, loss on ignition, and

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[5] Specification for Portland Cement (C 150 – 56), 1958 Book of ASTM Standards, Part 4, p. 1.

insoluble residue. A type I portland cement can be certified to conform with these specifications and yet the composition of only 14.25 per cent by weight or less of the cement need be indicated. Also, not only has omission of chemical requirements on pozzolans been thought of, but it has been done. ASTM Specifications C 340 - 58 T[6] on portland pozzolan cement, which may contain 15 to 50 per cent by weight of a pozzolan, include not one chemical requirement on the pozzolan. Rather, the specifications depend upon physical requirements, as is most appropriate, to evaluate the performance of the finished cement.

In my opinion, as has been stated in the text of the paper, limitation of chemical components of chemical admixtures should be restricted to those compounds or elements known or indicated to be deleterious to portland-cement mixtures either in general or specifically with respect to the work at hand. This is the approach taken in development of ASTM specifications on portland cement; the chemical requirements serve primarily to delimit the potentially deleterious qualities and the physical requirement serve primarily to demonstrate that the desired qualities exist at proper levels.

The essential basis for choice and acceptance of admixtures for concrete should be cost-performance ratio and uniformity. Certification by a manufacturer of the presence of certain supposedly beneficial constituents will usually be of no aid to the engineer because chemicals of the same nominal identity may yield substantially different effects in concrete and, in some instances, the significance of the component will be unknown to the engineer. Consequently, revelation of composition of chemical admixtures will not accomplish what Mr. Abdun-Nur apparently hopes to achieve by demand for such information.

Mr. Abdun-Nur has stated that "fine distinctions in performance of the various trade named water-reducing-retarder type of admixtures cannot be confirmed in actual practice." Water-reducing retarders vary substantially in many respects, such as rate of use for given retardation, water-reduction achieved, and influence on strength of the concrete. The variation is even greater if comparison is made among raw materials of the type employed as the main constituents of the manufactured water-reducing retarder products. These conclusions are supported by the abundant data included in this publication, particularly the contributions of Messrs. Wallace and Ore[7] and of Messrs. Tuthill et al.[8]

Mr. Abdun-Nur has noted that he has achieved satisfactory results by combining an admixture of classes 1 or 3, an accelerator, and an air-entraining agent, and varying the amounts of each as the need arises. There is no doubt that with proper selection of materials and control of the formulation of the admixture that satisfactory results can be obtained in this way. The decision must remain with those responsible for the concrete-making operation as to whether they wish to (1) assume the tasks of locating sources of suitable raw materials, determining the composition and properties of successive shipments, and formulating and storing the admixtures, or (2) depend upon a manufacturer of these admixtures for these services as well as for the continuing research which they are carrying forward.

As indicated by Mr. Tuthill, quantitative evaluation of the effect of water-reducing admixtures upon workability of concrete is needed badly. Reports from engineers, contractors, and workmen fre-

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[6] Tentative Specification for Portland-Pozzolan Cement (C 340 – 58 T), 1958 Book of ASTM Standards, Part 4, p. 15.

[7] See p. 38 of this symposium.

[8] See p. 97 of this symposium.

quently indicate improvement in workability when such admixtures are used, not only in decrease in segregation and improvement in placeability but also in the finishing characteristics of floors and pavements. Reference has been made in the paper to reports of this type by engineers in connection with a variety of concreting operations. Probably the main effect of water-reducing retarders on workability is development of retardation sufficient to make possible or to facilitate completion of placing and finishing under difficult conditions. In any event, conclusions of users about the beneficial effect of water-reducing admixtures upon workability are sufficiently firm that they are a determining factor in the continuing use of these admixtures in certain areas and in the choice of the admixture product.

Skeen[9] has reported results of tests of workability of concrete containing any of several selected surface active agents, including (1) an anionic wetting agent based on sodium higher alkyl sulfates, (2) a nonionic surface-active agent consisting of condensation products of polyethylene oxide with substituted phenols, (3) a proprietary air-entraining agent consisting of a triethanolamine salt of sulfonated hydrocarbons, and (4) an impure calcium lignosulfonate. Mixing of the concrete was conducted under reduced air pressure (16 to 17 mm of mercury) to reduce air entrainment to a minimum. Air content was very nearly 2.0 per cent for all of the mixtures, including the plain concrete, except for agents 1 and 3 (above), for which the air content was about 2.3 and 2.7 per cent, respectively. Workability was gaged by a "practical compacting factor," this being the "ratio of the weight of the concrete in the test vessel (after compaction in a standard manner) to the maximum weight attainable by vibration, the latter being adjusted so as to avoid, as far as possible, the loss of entrained air." Based on the results obtained and recognizing the fairly high experimental errors of the procedure, the author concludes that agent 2, above, "improves the working qualities" of concrete and agent 4, above, gives "marked improvement in working qualities as measured in the compacting factor test," in addition to that due to any entrainment of air in the concrete mixture. The calcium lignosulfonate was employed at the rate of 0.15 and 0.30 per cent by weight of the cement; the rate of use of agent 2 was not reported.

I agree completely with Mr. Tuthill's comments on the need for continued research to control loss of slump or other aspects of consistency of concrete. It is especially helpful to have his recommendation on criteria to serve as a goal for the research now in progress on this important characteristic of fresh concrete.

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[9] J. W. Skeen, "Effect of Vacuum Mixing on Concrete Containing Surface-Active Agents," *Proceedings*, Thirty-first International Congress of Industrial Chemistry, Liege, Sept., 1958. (Reprinted by the Building Research Station, England, as Reference QL-622.)

STP266-EB/Jun.1960

SUMMARY

By Bruce Foster[1]

This closing paper is a summary of the main points brought out in the symposium.

Classification and Qualification of Materials

The water-reducing admixtures and set-retarding admixtures discussed were divided into four classes: (1) Lignosulfonic acids and their salts, (2) modifications and derivatives of lignosulfonic acids and their salts, (3) hydroxylated carboxylic acids and their salts, and (4) modifications and derivatives of hydroxylated carboxylic acids and their salts. In each, the primary component has both water-reducing and set-retarding properties. These may be modified by the addition of other components to give various degrees of retardation, no appreciable change in setting time, or acceleration, while at the same time preserving water-reducing properties.

Some of the admixtures are produced by refining sulfite liquors from the wood pulp industry. In these it is necessary to reduce the sugar content, and of course it is desirable to produce a uniform product in all cases.

Data are included on the performance of a number of admixtures of varying sugar contents and it was concluded that the sugar content, *per se*, was not an important factor. However, these data covered only satisfactorily refined products. High sugar content in unsuitably refined products has resulted in excessive retardation.

This summary refers only to materials which have been suitably refined and controlled in their manufacture and which have been used successfully in concrete. It does not necessarily refer to all the many other materials which might be included in one of the four general chemical classes.

Nature and Action of the Admixtures

The admixtures discussed in the symposium are surface active chemicals which are adsorbed on the cement grains, giving them a negative charge. The presence of the adsorbate, and the charge, was pictured as resulting in (*a*) a reduction of the interfacial tension, (*b*) an increase in the electrokinetic potential, and (*c*) a protective sheath of oriented water dipoles around each cement particle. The resulting reduction in natural flocculating tendency of the cement particles then leaves them with increased mobility, and the water freed from the restraining influence of a highly flocculated system becomes available to lubricate the mix. Less water is required, therefore, for a given consistency.

To offer a mechanism explaining set retardation Hansen first advanced a solid state reaction theory to explain the role of calcium sulfate, normally incorporated in portland cement, in modifying the setting properties of cement. He pictured the surfaces of cement crystals as consisting predominantly of Ca^{++} and O^{-} ions. When exposed to water, the Ca^{++} ions attract OH^{-} ions of the water and the O^{-} ions

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[1] National Bureau of Standards, Washington, D. C.

attract the H_3O^+ ions. The rate of chemisorption and migration of these ions from the water into the crystals of the cement minerals was regarded as determining the setting and hardening characteristics of the cement. The rate may be modified by controlling the concentrations of OH^- and H_3O^+ ions available to the surfaces of the cement particles and by controlling the amount of surface available to the ions.

As the large admixture anions and molecules are adsorbed on the cement particle surfaces the hydration is blocked and the hardening process slowed. Later, as a result of reaction between the organic salts and tricalcium aluminate from the cement, the former are removed from the liquid phase of the system by precipitation. This explanation is in qualitative agreement with observations that retarding admixtures are often particularly effective with low tricalcium aluminate cements and that the initial retardation period is followed by rapid hydration and hardening of the paste.

In a prepared discussion, Steinour[2] advanced arguments against the solid state reaction theory on the basis that such reactions could not proceed fast enough. He agreed, however, with Hansen's[3] treatment of the mechanism by which retarding admixtures achieve their effect.

EFFECTS ON PLASTIC CONCRETE

Water Reduction:

Water-reducing admixtures permit the use of less water, with the same slump, and were indicated as being effective with a wide variety of concretes. The water reduction was reported to vary from 5 to 15 per cent, but a portion of the reduction in many cases is due to entrained air which may result from use of the admixture.

The agents have been found to be effective with all types of portland cement, with portland blast-furnace slag cement, with portland pozzolan cement, and with high alumina cement. The range in the performance of a given admixture with a number of cements of the same type is likely to be greater than the difference in performance of a number of properly formulated admixtures of the same type when used with the same cement. Evidence was presented indicating that generally the admixtures are more effective with cements low in tricalcium aluminate and alkali content than with those in which these constituents are higher. The benefits when used with some cements are very small.

It was brought out that the amount of water reduction is also influenced by admixture dosage, cement content, type of aggregate, and presence of other admixtures such as air-entraining agents and pozzolans.

Retardation:

Like water reduction, retardation of set and extension of the vibration limit have been produced with a wide variety of concretes and under a wide variety of conditions. And, in a similar manner, the amount of retardation obtained is dependent upon the specific admixture used, its dosage, and the brand and type of cement. Retarding admixtures were said to retard the set at all temperatures, the amount being dependent upon the dosage.

With class 1 and class 3 agents the degree of retardation can be controlled by varying the dosage, provided that the allowable air content is not exceeded. Overdosage of properly formulated retarders was said to normally cause no permanent reduction in strength of the concrete provided the concrete is protected from drying, and forms are not removed too soon. Other data, however,

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[2] See p. 25 of this symposium.

[3] See p. 3 of this symposium.

showed an average loss in strength of about 25 per cent.

With class 2 and class 4 retarders there may be no retardation or there may even be acceleration, both properties being brought about by the addition of a catalyst or of an accelerator.

Air Entrainment:

The use of class 1 admixtures in normal doses was described as generally entraining about 2 to 3 per cent of air. Tests reported show that the bubble spacing, and hence effectiveness from a durability standpoint, of such entrained air is in the same range as that produced by regular air-entraining agents. Class 2 admixtures may contain an additional air-entraining component or may be used with an air-detraining agent, as required by job conditions. It was pointed out that class 3 admixtures do not normally entrain air, but that they may be used with air-entraining agents or the latter may be included in the formulation of a class 4 agent. Usually when a water-reducing admixture is added to an air-entrained concrete the dosage of air-entraining agent must be reduced to maintain the same air content, even with a class 3 admixture. The degree of the effect may be different in laboratory mixes than in field concrete.

Bleeding:

Water-reducing admixtures that entrain air reduce bleeding. This reduction is due to the entrained air and the lower water content. Water-reducing admixtures that do not entrain air were reported to increase the rate and amount of bleeding. Such bleeding was suggested as being responsible for a portion of the strength increase observed with the use of such admixtures.

Slump Loss:

While reduction in slump loss occurring between mixing and placing was claimed for retarding admixtures, two authors reported data showing no improvement and one case was cited where the problem was aggravated by addition of lignin.[4] However, as will be mentioned later, water-reducing admixtures were indicated as having an application under conditions where slump loss is a problem.

EFFECTS ON HARDENED CONCRETE

Strength:

Strength at 28 days.—The reduction in strength due to entrained air may normally be compensated for by the increase in strength brought about by the reduced water and sand content made possible by the presence of entrained air. The portion of the water reduction brought about by a water-reducing admixture which is in excess of that due to any air which may be introduced through its use results in a net increase in strength. Further, in general, this increase in strength was reported to be greater than would be expected simply from the amount of water reduction produced.

An analysis of one extensive block of data with one admixture in which 28-day strengths were compared with the ratio of water-plus-air to cement contents showed that, on the average, and with air-entrained concrete, a 19 per cent increase in strength resulted from the use of the admixture even with a water reduction of only 5 per cent. For concrete with no air-entraining admixture 15 to 18 per cent increase in compressive strength might be expected with a water reduction of 10 to 15 per cent. In many mixes the strength was considerably lower or higher than the averages given, and the average for other brands and types of admixtures would in general be different.

Water-reducing admixtures were found to be particularly advantageous in mass concrete where pozzolans were used. It

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[4] See under Finishing Characteristics, p. 60 of this symposium.

was suggested that the admixture might increase the pozzolanic activity.

Increases in compressive strength were reported to be accompanied by increases in flexural, tensile, shearing, and bond strength. Usually the improvement in flexural strength is less pronounced than that in compressive strength. The bond strength may be benefited not only by the increase in concrete strength, but also by improvement in bleeding and volume change characteristics. The resistance to abrasion may also be improved.

Strength at Other Ages.—When retarding or accelerating admixtures are employed, the rates of strength gain are altered. In most cases a retarder should be effective only for a limited period, after which the concrete should gain strength rapidly to reach normal or higher levels at 1 day. Properly formulated retarding admixtures were said to perform in this manner unless the dosage is too large. The strength increase, expressed as a percentage, is usually greater at 3- and 7-day than at 28-day and later ages. This is particularly true for type I cements.

Strength tests on hermetically-sealed cylinders at ages up to 5 yr showed that strength advantage due to the admixture is still present at those ages.

Permeability:

Data were presented indicating that concretes made with water-reducing admixtures had a substantially lower permeability to water under pressure as compared to similar concretes without admixture and with the same or higher cement factor.

Volume Change:

Other factors being equal, the dimensional stability of concrete as a function of moisture content depends upon the original water content of the concrete. A reduction in original water content brought about through reduction in water-cement ratio, or a reduction in cement content while maintaining the same water-cement ratio—as shown to be possible by using a water reducing agent—may lead to less volume change with varying moisture conditions. Data presented by two authors showed some reduction in drying shrinkage in some cases, none in others. The effect is not large. It was brought out in the discussion that shrinkage was reduced with higher-SO_3 cements and increased with lower ones.

Resistance to Freezing and Thawing:

Laboratory test data were presented which, in general, showed some improvement in performance when water-reducing admixtures were used, as compared to control concretes with similar air contents, but the test results were not conclusive.

Water-reducing admixtures may increase the resistance of concrete to the action of freezing and thawing because they permit use of a lower water-cement ratio and because they often entrain air. Some modified types contain an air-entraining agent which may furnish a fully-protective air void system.

Resistance to Sulfates:

Laboratory data were reported which showed, in some cases, modest improvement in resistance to sulfate attack for concretes with water-reducing admixtures as compared with those without.

APPLICATIONS

The modifications of concrete properties, both in the plastic and hardened state, made possible by the addition of water-reducing admixtures and set-retarding admixtures were reported to have been taken advantage of in all types of construction. The various advantages have been utilized to overcome a variety of problems, increase the quality of the concrete, and in many cases decrease the cost of concrete and concreting operations. Some applications will be enumerated further under headings descriptive of modifications made possible in concrete properties.

Use of Less Water While Maintaining Slump:

In general, the use of less water was mentioned as being advantageous in all types of concrete, since the strength, dimensional stability, permeability, and other properties are improved. It could aid materially in meeting a maximum water-cement ratio specification requirement. It might eliminate the need to use excess water when aggregates with high water requirements are used.

A particular advantage to the small user was brought out in a prepared discussion which considered the danger of poor quality concrete caused by overly wet mixes.[5] Data presented indicated that considerably less water needed to be added to increase slump from 2 in. to 8 in. when a water-reducing admixture was used than when none was used, and that the decrease in strength resulting from such a change was correspondingly less. Such an admixture property might lead to increased uniformity in other types of concrete.

By contrast, it was stated that the "sticky" appearance which may result from use of an admixture often leads to the addition of unneeded excess water.

Use of Greater Slump While Maintaining Water-Cement Ratio:

The increased workability was described as promoting easier handling and placing of the concrete and better compaction, which are particularly desirable where formwork and reinforcement make placing unduly difficult. Higher initial slump may compensate for loss in slump between mixing and placing of the concrete. This applies to conventional as well as pumped concrete. It was pointed out that by changing the dosage as a function of the fresh concrete temperature, the water-cement ratio may be held relatively constant, thereby promoting uniformity in the concrete.

Use of Less Cement:

The increase in strength which was shown to result from the use of water-reducing admixtures would permit a reduction in cement content while still maintaining the design strength. This lower cement content may increase the dimensional stability of the concrete, result in lower total materials cost, and be of considerable advantage in reducing the temperature rise in mass concrete.

Achievement of Increased Strength at Early Ages:

The strength advantage shown for concrete containing water-reducing and set-retarding admixtures at ages of 24 hr and later would permit early stripping and re-use of forms. It is of particular value in slip-form, prestress, and tunnel-lining operations.

Modification in Bleeding Rates:

Various views have been expressed on the possible advantages and disadvantages of bleeding. Reduced bleeding produced by air-entraining types of water-reducing agents was described as beneficial, from a segregation standpoint, in many types of construction. Induced early bleeding produced by the non air-entraining types was said to help prevention of plastic cracks in concrete placed in hot, arid areas.

Use of Retardation:

The control of the setting time was reported to be a very substantial aid in

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[5] See pp. 148–155 of this symposium.

concreting at elevated temperatures. Advantages accruing from extension of the vibration limit were cited in reducing the incidence of cold joints in a number of types of construction including those employed in tunnel lining, mass concrete, slip-form work, and large cast-in-place bridge girders and decks made monolithic by vibration even up to 10 hr after placing the first concrete.

Longer setting time was credited with minimizing cracking due to form movement under increasing loads as filling proceeds.

Advantages accruing in steam-cured concrete units due to lengthening the period between placing and steaming were reported.

PROCEDURES IN USE

Specifications:

Ideally, water-reducing admixtures and set-retarding admixtures should be purchased under specifications that assure the production of the desired concrete properties, that demonstrate the absence of any resulting deleterious effects, and that permit evaluation of the uniformity of the admixture from one lot to another.

In practice this is difficult because of the variability of results obtained with an admixture when used with various cements, aggregates, mixtures, etc., and because no simple, rapid, reliable tests are usually available to compare one lot with the next.

One procedure recommended consists of comparing laboratory batches of concrete made with each successive lot of admixtures with one made with identical materials and design except for the use of admixture from a reference lot.

Often the uniformity may be roughly judged by observing the uniformity in the rate of hardening, water requirement, and slump in the field concrete.

All tests should preferably be made using the materials and mix design proposed for the work, and should be made on concrete rather than mortar.

Development of a qualitative method for indicating the presence or absence of the reaction products resulting from the use of lignosulfonates in cement paste was described. Such a method applied to hardened concrete should prove useful as an addition to other tests employed in conducting examinations of distressed concrete. The method utilizes optical absorption techniques in the ultraviolet region, applied to extracts from hardened paste.

Dosage:

It was suggested that either the dosage recommended by the manufacturer should be used or laboratory tests should be employed to determine the optimum dosage. Some admixture producers formulate different products for use under different conditions; others recommend use of different amounts, depending on the conditions. Admixtures which also entrain air should not be used in excess of a certain amount unless used in conjunction with an air-detraining agent. Limitation on the desired degree of retardation may limit the usable dosage of water-reducing agents unless catalysts or accelerators are incorporated in the formulation.

A correlation between time of set of cement pastes and rate of stiffening of concrete mortars was reported, which might permit the correct admixture dosage for various conditions to be determined in the laboratory.

Control of Dosage:

It was stressed that the quantity of admixture added must be accurately measured if uniform results are to be obtained. Automatic dispensers are available for liquid admixtures, but these must be kept in good working order and should preferably be of a type in which the volume added may be checked visually. Admixtures in powder form should preferably be accurately weighed out in individual packages.

The handling and dispensing of admixtures may be a considerable problem in a ready-mix plant, one of which was reported to stock 14 different agents.

Possible Reduction in Cement Content:

Recommendation was made that claims made concerning the quantity of cement reduction made possible by addition of the admixture should be checked by making strength tests.

RESEARCH ON ADMIXTURES

Water-reducing and set-retarding admixtures are undergoing improvement, both in performance and reliability. Much remains to be learned about their action in concrete and how this action is affected by the properties of the other concrete ingredients. A substantial amount of research is under way in the laboratories of a number of admixture manufacturers. Even better products and better concretes made possible through their use are anticipated.

THIS PUBLICATION is one of many issued by the American Society for Testing Materials in connection with its work of promoting knowledge of the properties of materials and developing standard specifications and tests for materials. Much of the data result from the voluntary contributions of many of the country's leading technical authorities from industry, scientific agencies, and government.

Over the years the Society has published many technical symposiums, reports, and special books. These may consist of a series of technical papers, reports by the ASTM technical committees, or compilations of data developed in special Society groups with many organizations cooperating. A list of ASTM publications and information on the work of the Society will be furnished on request.