Special Report 119

ADMIXTURES IN CONCRETE

accelerators
air entrainers
water reducers
retarders
pozzolans

subject area

32 cement and concrete

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DELMAR L. BLOEM

A Tribute

This Special Report is dedicated to Del Bloem, who passed away shortly before its publication. From 1961 to 1966 he was Chairman of the Committee responsible for its preparation—HRB Committee on Chemical Additions and Admixtures for Concrete.

Del was born in Hudson, South Dakota, on May 21, 1922, received his secondary schooling in Sioux City, Iowa, and attended Iowa State College (now Iowa State University) from 1940 to 1943 where he received his B.S. in Civil Engineering in 1943 and Civil Engineering Degree in 1950. After working for 2 years with the Chicago Bridge and Iron Company, he joined the staff of the National Sand and Gravel and National Ready Mixed Concrete Associations in 1946. He was associate research engineer in charge of the laboratory, located on the campus of the University of Maryland, until 1949, when he was made assistant director of engineering. In 1954 he became associate director of engineering of the Associations and was director of engineering in 1962.

To all he was a presistent voice for quality and responsibility. In all of his relationships he will be remembered for his keen insight, his objectivity, and his ability to provide leadership in a difficult situation.

Del has been honored for his professional accomplishments on many occasions. In 1967 he received the Award of Merit for Distinguished Service from the American Society for Testing and Materials. On three occasions he received the Sanford E. Thompson Award of the American Society for Testing and Materials, an award presented annually for the outstanding paper in the field of concrete and aggregates.

Del served on a list of over 40 committees and subcommittees of ASTM, ACI, the Highway Research Board, and the American Railway Association. He was elected to the Board of Directors of the American Concrete Institute in 1963 and was vice president from 1969 to 1970.

In the Highway Research Board he served on the Committee on Performance of Concrete—Physical Aspects and the Committee on Quality Assurance and Acceptance Procedures, but above all he is remembered for his strong leadership of the Committee on Chemical Additions and Admixtures for Concrete, attested to by this Special Report concerning the nature and use of admixtures in concrete.

Foreword

Since 1964 the Committee on Chemical Additions and Admixtures for Concrete has been working on summaries for the most commonly used admixtures in concrete. The first of these summaries concerned accelerators and was published in Highway Research Circular 6 in July 1965. It was written by a special subcommittee chaired by Bruce E. Foster. An article on air entrainment in concrete was published in the same circular and was the product of a subcommittee chaired by W. L. Dolch. Highway Research Circular 22, dated May 1966, contained a summary on water reducers and retarders; a subcommittee chaired by W. E. Grieb was responsible for this work.

In 1968, a special subcommittee headed by C. E. Lovewell produced a report on the use of pozzolans in highway concrete. When this last report was completed, the Committee on Chemical Additions and Admixtures for Concrete concluded that the work by the four separate subcommittees should be combined and updated for publication as a Special Report. Thus, the work in this report represents the combined efforts of the four subcommittees as well as the entire Committee.

Contents

Introduction

Any material other than water, aggregates, and hydraulic cement that is used as an ingredient of a concrete or mortar mixture and is added to the batch immediately before or during its mixing is defined as an admixture. Materials, interground or interblended with the hydraulic cement, are defined as additions to the cement. This report deals primarily with admixtures. An admixture is used to make the concrete or mortar more suitable for the purpose for which it is made or to reduce its cost. An admixture should not be used unless the benefits are worth the cost and could not be achieved by other means except at greater cost.

The two most widely used classes of admixtures for concrete—organic chemical materials and active mineral powders (pozzolans)—were known and used by the Romans in classic times. Marcus Vitruvius Pollio in the first century A.D. specified a mortar that called for well-hydrated lime, marble dust, sand, and water, "to which is added either hog's lard, curdled milk, or blood." In 1967, the National Renderers Association and the Fats and Proteins Research Foundation were sponsoring a survey of the utility of inedible fats as admixtures for concrete.

Among the effects that are sought by the use of admixtures are acceleration, the achievement of an earlier setting time; retardation, delay of setting time; water reduction, the achievement of equal workability with lower water content; air entrainment, the provision of entrained air voids in the cement paste; air detrainment, the removal of excessive amounts of air bubbles from the cement paste; permeability reduction; and corrosion reduction, the inhibition of the tendency of embedded metal to corrode.

MATERIALS

Some of the materials used to achieve these effects are discussed briefly in this introduction and are the subjects of this report.

Accelerators

The most widely used accelerator is calcium chloride. Other materials that accelerate the hardening of mixtures of portland cement and water include other soluble chlorides; soluble carbonates, silicates, fluosilicates, and hydroxides; and some organic compounds such as triethanolamine.

Air-Entraining Agents

The materials used for air entrainment are those that make foam during mixing; thus, they are similar to soaps and detergents. They are generally derived from resins, fats, or oils. The primary purpose of air entrainment is to protect the concrete against the damage it may suffer if the paste becomes saturated with water and then freezes. A mature portland cement paste, in which air bubbles are present with a spacing factor of 0.008 in. or less, will not be damaged by freezing unless totally saturated with water, which can seldom occur under natural conditions. The spacing factor is the average maximum distance from any point in the paste to the nearest air void. With the usual air-entraining admixtures, the air-void spacing factor will be within the correct limits if the amount of air in the mortar fraction of the freshly mixed concrete is 9 percent or more. This is equivalent to about $5\frac{1}{2}$ percent air in concrete containing aggregate of $1\frac{1}{2}$-in. maximum size.

Retarders and Water Reducers

All commonly used retarding admixtures are organic chemicals, usually lignosulfonic acid salts or hydroxylated carboxylic acid salts or modifications of them. At normal temperatures, these materials used in recommended amounts will usually extend the setting time by 30 to 50 percent. Greater delays of setting may be obtained by using larger amounts. Retarders are most often used to compensate for the undesired accelerating effects of high placement temperatures, to avoid cold joints, or to avoid undesirable effects of displacements and deflections that might be caused by the loading of forms and supports by subsequent concrete placement in construction, such as composite multispan bridge work.

The same basic kinds of materials used for retarders are generally water reducers. Commercial retarders are usually also water reducers. Agents that are exclusively water reducers are retarders that have been modified to suppress or compensate for their retarding effect.

Pozzolans

One of the most widely used classes of admixtures is pozzolans. A pozzolan is a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperatures to form compounds with cementitious properties. Pozzolans contain a large proportion of silica in a form that will react with hydroxides. The silica may be present as natural volcanic glass, artificial glass (as in fly ash), opal (as in diatomaceous earth), or the disordered forms of silica present in many clays and shales. Concrete can often be produced for some purposes at lower cost with pozzolans than would be possible without them.

BENEFIT

The word "admixture" has sometimes produced a negative reaction. There are some who feel that deliberately putting anything into concrete—other than water, aggregates, and portland cement—is adulterating the mixture. Some of those concerned with marketing portland cement have tended to foster this impression because they believe that, because the use of admixtures often has as one of its benefits the reduction in the unit quantity of cement required per unit volume of concrete, admixtures are competitors of cement. But such is not the case. Any method or material that makes concrete either more widely useful or available at lower cost increases the use of concrete and of cement.

1. *Accelerators in Highway Concrete*

Accelerators have a useful application in concrete when decreased setting time or increased rate of strength development is desired. There is extensive literature on the subject, a selection of which is listed at the end of this report. The objective of this publication is to summarize that portion of the information particularly relevant to highway construction and likely to be useful to the highway engineer.

DEFINITION

As defined in ASTM Specification C 494-68 (Standard Specification for Chemical Admixtures for Concrete), an accelerating admixture is one that accelerates the setting and early strength development of concrete. This specification refers to such admixtures as Type C.

APPLICATIONS TO HIGHWAY WORK

Accelerating admixtures are useful, particularly in cold weather, for modifying the properties of portland cement concrete to (a) expedite the start of finishing operations and, when necessary, the application of insulation (1); (b) reduce the period of time required for proper curing, especially for paving in late fall when early application of de-icing salts may be expected (2); and (c) permit earlier loading or opening of pavements and structures to traffic (3).

The setting and hardening of portland cement result from chemical processes, and, in common with other chemical reactions, the rate of reaction is dependent on the temperature. The rate of concrete strength development drops rapidly with reduction in temperature; near and below the freezing point concrete gains strength very slowly. The benefits of an accelerator are the result of a higher rate of hydration of the portland cement, which reduces the initial setting time of the concrete, releases the heat of hydration more rapidly, and increases the initial rate of development of compressive and flexural strengths.

Cold-Weather Concreting

When an accelerator is properly used, the rate of strength gain is considerably enhanced at low temperatures so that the concrete reaches the maturity required to resist the harmful effects of freezing, with or without the presence of ice-removal salts, much earlier than if no accelerator were used. Likewise, the heat given off as the portland cement hydrates is released earlier and is available to the concrete during the vital early hardening period. In addition, the concrete can be finished sooner so that the loss of heat to the outside during the period between placing the concrete and applying the insulation can be reduced.

The quantities recommended for use later in this section lower the freezing point of concrete only a negligible amount, and hence calcium chloride should never be considered as an "antifreeze." In fact, no materials are known that can appreciably lower the freezing point of the water in concrete without being harmful to the concrete in other respects.

The use of calcium chloride is often not sufficient in itself to prevent damage to newly placed concrete during cold weather. Other measures are often required, and recommendations on preparation of the base, heating the concrete ingredients, insulation, and application of external heat are available (2, 3).

Early Use of Structures

Increasing the rate of strength gain at cold or at normal temperatures will permit the use of the pavement or other structure at an earlier date when an accelerator has been used than if it has not. On some projects this may be of more advantage from the standpoint of allowing movement of the contractor's equipment over completed work at an earlier date, while in others opening to normal or to bypass traffic may be more important. The earlier use permitted by using an accelerator may be particularly advantageous where traffic must be stopped or detoured during repair work. In some patching operations, especially against waterheads, the required quick-set mortar or concrete can be obtained by using an accelerator.

Reduction in Curing Period

To develop its potential properties to the fullest, concrete must be prevented from drying for a period long enough for adequate hydration of the cement to take place. Attempts to maintain the concrete in a moist condition for an adequate period are often ineffective and may entail considerable expense and inconvenience. Because the length of moist-curing required is dependent on the rate at which the cement hydrates, the use of an accelerator may make possible a shorter curing time or at least minimize the damage from insufficient curing.

TYPES OF ACCELERATORS

The best-known and most widely used accelerator is calcium chloride (4). A number of other materials have been found to accelerate the setting of cement, but in general they are little used in the United States. Usually adequate information is not available for judging their probable other effects on concrete, and many are suited only to the preparation of fast-setting patching or plugging compounds. Many of the chlorides, alkaline carbonates, sulfates, nitrates, silicates, and hydroxides of alkaline metals and earths have an accelerating action. Fluorides and fluosilicates also accelerate, as do some organic materials such as triethanolamine (5, 6).

ASTM Specification C 494 furnishes performance requirements and tests for accelerators. Calcium chloride should also meet the requirements of AASHO M 144, ASTM Designation D 98, or Federal Specification O-C-105, all of which cover the two types: type 1, regular flake ($CaCl_2$, minimum 77 percent); and type 2, concentrated flake, pellet, or other granular ($CaCl_2$, minimum 94 percent).

Moderate percentages of high-alumina cement added to portland cement produce acceleration (7) as does the seeding of portland cement with about 2 percent of finely ground, fully hydrated cement paste (8).

Subsequent discussion will be limited almost wholly to calcium chloride. Many proprietary compounds sold as accelerators or as "antifreezes" are largely, if not wholly, composed of calcium chloride or solutions thereof, and the advantages and limitations of calcium chloride also apply to such products.

PROPERTIES OF CALCIUM CHLORIDE

Rate of Use

Usual recommendations limit the dosage of calcium chloride to a maximum of 2 lb of type 1 per bag of portland cement. When substantially larger quantities are used or where the material is not uniformly distributed, there is danger of flash set or formation of disruptive chemical compounds. The actual quantity added should depend on job conditions and on the purpose for which acceleration is sought. At low temperatures the full 2 lb per bag might be used advantageously, while at higher temperatures smaller dosages may be indicated. ACI Standard Recommended Practice for Cold Weather Concreting (2) recommends a maximum of 2 percent calcium chloride by weight of cement. It should be dissolved in a portion of the mixing water before batching, because undissolved lumps may later disfigure concrete surfaces.

The rate of application of proprietary materials should be such that the quantities of calcium chloride actually added are equivalent to not more than 2 percent of the type 1 form by weight of cement. Calcium chloride should not be added to the concrete in addition to such proprietary materials unless it is determined that the total calcium chloride content will not exceed the 2 percent recommended limit.

Calcium chloride can be used with all types of portland cement, but the magnitude of its effect may vary considerably, depending on both the type of cement and the particular source of a particular type of cement.

Unless otherwise indicated, the following statements refer to the use of 1 to 2 percent $CaCl_2$ by weight of cement, whether added as the salt or as a proprietary compound.

Effects on Concrete

Setting Time—Tests and experience with concrete indicate that both the initial and final setting times are reduced significantly. Four percent calcium chloride may cause a very rapid set. In some applications the calcium chloride addition should be adjusted to give optimum setting time for placing and finishing the concrete.

Strength—Many data are available on the effects of calcium chloride on compressive and flexural strengths of concrete (4, 9, 10) and some data are available on tensile strength. Compressive strength is increased substantially at early ages, 3 and 7 days, compared to similar concrete without calcium chloride. The percentage increase in strength is substantially less at 28 days than at earlier ages, but an increase has usually been found to persist over extended periods of moist-curing. The percentage strength gain resulting from the addition of calcium chloride is more pronounced at low temperatures than at higher ones (10). Benefits are greater with rich than with lean concretes. Usually the improvement in flexural strength is less than in compressive strength, and at later ages concrete with no accelerator may be even slightly stronger in flexure than that in which calcium chloride has been added. Excessive additions of calcium chloride are detrimental to strength, particularly at later ages.

Heat Release—Calcium chloride accelerates the early heat development but has no appreciable effect on the total heat of hydration.

Volume Change—The effect of calcium chloride on volume change is not thoroughly established, but the consensus is that it increases the volume change of concrete both during continuous moist-curing and during drying (9, 11). The magnitude of the effect as measured in the laboratory depends on many factors, including the conditions of test. For an objective appraisal, the concretes with or without an accelerator should be compared at equal maturities.

Water Requirement—Calcium chloride usually reduces slightly the water required to produce a given slump.

Air Entrainment—Usually less air-entraining admixture is required to produce a given air content when calcium chloride is used than when it is not. The addition of 1 percent calcium chloride has been found to result in somewhat larger air bubbles and a higher spacing factor (12, p. 359). Calcium chloride is not compatible with some air-entraining agents, and in such cases the two admixtures must be added to the concrete mixture separately.

Resistance to Freezing and Thawing—Calcium chloride has been found to increase the resistance of concrete to the detrimental action of freezing and thawing at early ages and to decrease it at later ages (9). The increased resistance at early ages is of particular importance in winter concreting and in concrete that will be subjected to early application of ice-removal salts (13).

Sulfate Resistance—Calcium chloride has been found to contribute to low sulfate resistance. Its use is not recommended, therefore, where sulfate attack is probable.

Alkali-Aggregate Reaction—Data have shown that the magnitude of expansions produced by the alkali-silica reaction is greater when calcium chloride is added than when it is not. However, when the expansion is controlled through the use of low-alkali cement or addition of a suitable pozzolan, the effect of calcium chloride appears to be unimportant.

Corrosion of Metals—The use of calcium chloride in reinforced concrete has not been found to cause corrosion of the reinforcement, provided that the adequate concrete cover and thorough consolidation required for concrete without calcium chloride are available. However, calcium chloride should not be used in reinforced concrete where stray currents are present. It should not be used when steam-curing is employed unless tests of the specific application demonstrate the absence of objectionable corrosion.

Calcium chloride has been found to contribute to the corrosion of prestressing reinforcing wire, and it therefore should not be used in prestressed concrete. Combinations of metals such as steel reinforcing and aluminum conduit should not be employed in concrete containing calcium chloride (16). Severe corrosion of galvanized steel sheets used as permanent forms has been attributed to the use of calcium chloride (15). In contrast, it has been reported (14) that stannous chloride, when properly used, acts as an accelerator and does not cause corrosion of steel under steam-curing conditions.

METHOD OF USE

Storage

Calcium chloride should be stored in a manner that will prevent the pickup of moisture. Storage conditions suitable for cement are satisfactory. Lumps that may inadvertently develop must be discarded, because they are not readily soluble in solution preparation and, if added to the mixture in solid form, may produce pop-outs.

Use as Solution

Calcium chloride may be added either in solution or dry form, but it is preferable to use the solution. A standard solution containing 1 lb of type 1 or 0.8 lb of type 2 calcium chloride per quart of solution is recommended. When specifications call for 1 percent calcium chloride, 1 qt of standard solution per bag of cement may be added to the mixture. For 2 percent calcium chloride, 2 qt of standard solution per bag of cement are added. Solutions of greater concentration are not recommended because they are more difficult to prepare and because they may not be stable at all temperatures.

The solution is considered as part of the mixing water and often is added to it. Automatic dispensers are available for that purpose. The concentrated solution should not be allowed to come in contact with the cement, because this may cause flash set. In ready-mixed operations, it may be desirable to batch the concentrated solution with the first charge of aggregate to prevent contact of the solution with cement until after water has been added and mixing begun.

Calcium chloride, unless caked, dissolves readily in either hot or cold water. Heat is released during the dissolving period, and the solution may require cooling before use. The calcium chloride should be added to the water, rather than water added to the salt, or else a hard, slowly soluble coating may otherwise result. A small mechanical mixer or air lance is recommended for use in solution preparation.

Dry Use

Completely dry calcium chloride, free from lumps, can be batched and may be measured by volume or weight but as such should not come in contact with the cement before it has had an opportunity to dissolve. When measured by weight, it should be added in amounts not to exceed 2.0 lb of type 1 calcium chloride or 1.6 lb of type 2 calcium chloride per bag of cement. When volume measure is used, it is necessary to calibrate a container for type and form used. In the case of ready-mixed concrete when long hauls are involved, it may be desirable to add to calcium chloride at the destination. To ensure adequate dispersion in the concrete, the dry calcium chloride should be added during the first half of the mixing period.

Addition With Other Admixtures

As mentioned previously, concentrated calcium chloride solutions are not compatible with some air-entraining admixtures. This may also be true with other admixtures. It is preferable, therefore, that calcium chloride and other admixtures be added to the concrete separately.

2. *Air-Entrained Concrete*

Air entrainment has provided great benefits for concrete in many applications but nowhere more dramatically than in highway construction. The improvement in resistance to freezing and thawing, especially when such exposure is aggravated by the use of ice-removal salts, has multiplied in many cases the useful service life of pavements and structures by a substantial factor. The information provided in this report is not limited in its applicability to highway construction but has been developed and arranged to be of maximum use to the highway engineer.

The principle of air entrainment in concrete and the reasons for its use can be stated as follows: Certain substances, when added to concrete in small quantities, bring about the inclusion of a larger amount of air than is found in ordinary concrete. This added air exists in the form of minute discrete bubbles that affect materially the properties of both the freshly mixed concrete and the hardened concrete. Air-entrained concrete is more plastic and workable than non-air-entrained concrete and can be placed and compacted with less segregation and bleeding. Hardened air-entrained concrete is far more resistant to the harmful effects of freezing and thawing and of salt-scaling than is ordinary concrete (see 75 through 96 in particular).

NATURE OF AIR VOIDS IN AIR-ENTRAINED CONCRETE

Non-air-entrained concrete normally contains about 1 or 2 percent air in the form of relatively large voids. This is termed entrapped air. Entrained air, on the other hand, exists as very small bubbles and in an amount that depends on the amount of the air-entraining agent added to the concrete as well as on other variables of the mixture and environment. In air-entrained concrete the total air content recommended for normal uses varies with the maximum size of the aggregate and ranges from about 4 percent for a 2-in. maximum size to about 8 percent for a $^3/_8$-in. maximum size. These values refer to the concrete in place, because the placement process reduces the air content of the concrete discharged from the mixer.

There is a need for variation in air content with aggregate size because the amount of mortar in the concrete is dependent on the maximum aggregate size, and it is the mortar that carries the air bubbles. The air content should be adjusted in air-entrained concrete so that the mortar component contains about 10 percent air. This value has been found to give the desired beneficial effects, including protection from freezing action.

The emphasis on total air content is somewhat misleading and is the result of its comparative ease of measurement. It is possible, although not likely with the air-entraining agents in current use, to obtain the recommended values for air content and yet not the desired protection against freezing action. The reason is that the bubbles must be small in size and well distributed throughout the mortar component of the concrete in order to furnish proper protection. Extensive theoretical and experimental work has fairly well established the importance of a parameter called the spacing factor; that is, roughly, the average distance from any point in the paste to the nearest air bubble. It has been found that if this spacing factor is less than a critical maximum of about 0.008 in., the concrete will have good durability, provided that durable aggregate, suitable water-cement ratio, and proper handling, placing, and curing techniques are used. If the spacing factor increases above this value, the durability can be reduced. Unfortunately, the experimental determination of this factor can as yet be done only on hardened concrete.

Therefore, the only practical approach is to use an air-entraining agent that has been shown to produce the desired bubble system and in an amount that will give the previously mentioned approximate values of total air content. A good procedure to follow is to proportion the trial mixture according to the report of Committee 211 of the American Concrete Institute (75) and to use an air-entraining admixture that conforms to ASTM Designation C 260 (Tentative Specification for Air-Entraining Admixtures for Concrete) or air-entraining cement that meets the requirements of ASTM Designations C 175 or C 595 (Standard Specification for Air-Entraining Portland Cement and Standard Specification for Blended Hydraulic Cements respectively).

EFFECTS OF AIR-ENTRAINMENT ON FRESHLY MIXED CONCRETE

Air-entrained concrete is more workable than ordinary concrete and is less subject to segregation and bleeding. These changes are the result of the ability of the air bubbles to bear short-term loads, to interrupt the movement of bleeding water to the surface, to buoy up the solids, and to change the effective viscosity of the cement paste. The precise mechanisms of these actions are not well understood.

Experience in the use of air-entrained concrete has shown the necessity for some minor changes in certain construction practices. For example, air-entrained concrete is more sticky than ordinary concrete, especially in richer mixes. The concrete may therefore have a tendency to tear under the screeds of the finishing machine. This tendency can usually be corrected by increasing the frequency of the transverse oscillations of the screeds. Sometimes a slight adjustment of the mixture composition, such as a change in the fine aggregate-coarse aggregate ratio, will accomplish the desired results.

Normally, a ⅛-in. backward tilt or lift of the cutting edge of the front screed and a level position of the rear screed have been found best for finishing air-entrained concrete with a transverse finishing machine. Rebound has sometimes been experienced behind the finishing machine. This is caused by too much material passing under the screeds. The condition can be controlled by changing the tilt, as mentioned previously, or by regulating the height of the concrete roll being carried ahead of the screeds. The concrete ahead of the front screed during the first pass of the finishing machine should have a uniform depth of 3 to 6 in.

Because bleeding is reduced and little water rises to the surface of air-entrained concrete, the consistency of the concrete should be kept wet enough to allow finishing operations to proceed without undue difficulty. The placing and finishing operations with air-entrained concrete pavements require no more care and attention than those with ordinary concrete, and the most exacting requirements for surface evenness can be met without difficulty.

EFFECTS OF AIR ENTRAINMENT ON HARDENED CONCRETE

Durability

The principal reason for the inclusion of entrained air in concrete is to obtain a great increase in durability under frost action. Non-air-entrained concrete may have high durability if the mixture is well proportioned and if the concrete is properly placed, finished, and cured, but it cannot resist frost damage when frozen in a critically saturated condition if it does not contain entrained air. Entrained air can be expected to provide protection for the mortar components of the concrete under all ordinary conditions of freezing. It also provides protection against the increased severity of freezing exposure that results from the application of de-icing salts to pavement surfaces. It is especially important to ensure that the surface layers of the concrete, which are most influenced by the salting action, contain the proper quantity and quality of entrained air. Certain procedures, such as overfinishing or overvibrating, may contribute to surface layers that are nondurable for this reason.

Lack of durability of concrete in freezing can be caused by the presence of nondurable aggregates. Although entrained air protects the mortar and usually the fine aggregate, it does not provide protection against difficulty arising from the coarse aggregate, and no reliance should be placed on it for such protection.

Strength

If there is no alteration of the mixture proportions, air-entrained concrete will have a lower strength than that of ordinary concrete. This reduction will be about 5 percent for each percent of air. However, owing to the increased plasticity imparted by entrained air, it is usually possible to reproportion the mixture using lower water and sand contents at constant slump. This is particularly true of lean concretes or those with a small maximum size of aggregate. Such concretes will therefore not have their strengths reduced; they may even be increased by the use of air entrainment.

Because any increase of the air content above the intended amount will result in further loss of strength, it is important to maintain close control of the air content by frequent determinations at the job site. A common error is to neglect the frequent checking of the air content.

Abrasion Resistance, Elasticity, and Bond Strength to Steel

Concrete properties of abrasion resistance, elasticity, and bond strength to steel are influenced roughly in the same manner as is compressive strength. If the use of air entrainment results in a loss of strength, these concrete properties will also be reduced.

Shrinkage and Thermal Expansion

Volume changes resulting from changes of water content or temperature of the concrete are not greatly affected by entrainment of air in the usual amounts.

Absorption

There is conflicting opinion regarding the absorption of water by air-entrained concrete. Theoretically the rate of capillary absorption should be lowered, although the total amount should be about the same as for ordinary concrete. Available evidence shows little difference between the two.

Creep

The small amount of available evidence shows no important difference between the creep of air-entrained concrete and that of ordinary concrete.

General Properties

It should be remembered in considering the properties of hardened concrete that air entrainment permits the placement of a more homogeneous material, free from honeycombing, and will therefore be of indirect benefit to all the properties of the hardened concrete.

MATERIALS FOR PRODUCTION OF AIR-ENTRAINED CONCRETE

Air entrainment can be provided in concrete by means either of an addition interground with the cement or of an admixture added at the time of mixing.

Air-Entraining Cements

Portland and portland blast-furnace slag cements can be interground with agents at the mill to form their air-entraining counterparts. These products are covered by ASTM Designations C 175 and C 595 respectively.

The main advantage of the use of air-entraining cements rather than admixtures is convenience. The addition of another component at the mixer and the attendant problems of accurate measurement of small amounts of material are eliminated. Trouble has, for instance, not infrequently come from failure to properly batch the admixture, either through operator error or equipment malfunction. The use of air-entraining cement eliminates such problems and furnishes some assurance of durability even when there are no facilities to measure the actual air content.

The disadvantage of the use of air-entraining cements is the restriction to a certain amount of addition. These cements are manufactured with sufficient air-entraining addition to give an air content of 19 ± 3 percent in standard mortar when tested by ASTM Designation C 185 (Standard Method of Test for Air Content of Hydraulic Cement Mortar). This quantity of addition has been found to be proper for most average jobs. However, many variables of the mixture, handling, and environment influence the amount and quality of the entrained air. Therefore, to obtain the desired air content it is sometimes found necessary when using air-entraining cement to add an air-entraining admixture at the time of mixing or to add an air-detraining agent or to change some mixture proportion such as the fine aggregate content or grading.

Air-Entraining Admixtures

Many surface-active agents can be used as admixtures incorporated in the concrete at the time of mixing to cause air entrainment. The quality of the bubble system obtained depends on the nature of the air-entraining admixture. Those that conform to the requirements ASTM Designation C 260 will be satisfactory when the other ingredients are properly proportioned.

The main advantage of the use of air-entraining admixtures, as opposed to air-entraining cements, is the flexibility they allow. Alterations can easily be made to compensate for the various conditions that influence air content. The engineer can, therefore, usually keep better control of the concrete mixture when using admixtures.

In order to get the greatest uniformity of the concrete mixture, it is general practice to add air-entraining admixtures in the form of solutions rather than as solids. This point is especially important with reference to the short mixing times used on some classes of concrete work.

Air-entraining admixtures are not usually damaged by freezing, but it is wise to solicit the manufacturer's opinion regarding the effects of freezing on his product.

Other admixtures, for example retarders and accelerators, usually increase the amount of air that is entrained by a given amount of air-entraining admixture, and there may be some reduction in the quality of the concrete. Such behavior is not well understood and, where experience is lacking, a trial batch should be mixed in order to investigate these matters. In general, air-entraining admixtures should be added to the mixer separately from other admixtures being used, unless tests have shown this to be unnecessary.

Finely Divided Materials

The addition of appreciable amounts of finely divided materials, those passing the No. 100 sieve, may seriously inhibit the entrainment of air in concrete. Therefore, when using such substances as fly ash and carbon black, it is frequently necessary to increase the amount of air-entraining admixture. Such an increase may also be necessitated by fines adhering to the aggregate or produced in the mixer by degradation of friable aggregates. It may be necessary in these circumstances to make trial batches to ascertain the correct amount of admixture. It should also be remembered that large amounts of organic materials, such as air-entraining admixtures, may have important effects on the setting and hardening of concrete. These effects should be investigated if large increases in air-entraining agent are necessitated by finely divided materials in the concrete mixture.

Aggregates

The requirements for aggregates used in air-entrained concrete are no different than for those used in ordinary concrete. Good guides are ASTM Designation C 33 (Standard Specification for Concrete Aggregates) and the report of ACI Committee 621.

Any change in the proportions or grading of the aggregate can be expected to cause changes in the air content of air-entrained concrete. However, there is some evidence that the importance of the fine-aggregate gradation is not as great as once was thought, particularly with respect to obtaining a proper spacing factor.

PROPORTIONING OF MIXTURES FOR AIR-ENTRAINED CONCRETE

The proportioning of air-entrained concrete is similar to that of ordinary concrete. The volume of air is merely another component that is added into the summation of absolute volumes along with those of the other ingredients.

It is recommended that, in proportioning air-entrained concrete, the procedure of ACI Committee 613 be followed for the trial batch. This procedure incorporates the reduction in water and sand that the greater workability of air-entrained concrete permits. Small corrections can then be made in the proportions of the trial batch in order to secure the desired properties and maximum economy.

If an air-entraining admixture is used and the manufacturer's recommended amounts do not result in the desired air content, it is usually easy to adjust the amount of agent. However, under some conditions it may be necessary to change the type of air-entraining agent. If an air-entraining cement is being used, it may be necessary to change the brand of cement or add an admixture as well.

EFFECTS OF VARIOUS FACTORS ON ENTRAINED AIR

In this section mention will be made of the factors that influence the quantity and quality of entrained air in concrete. Many of these effects are imperfectly understood, and the following comments are in some instances based on relatively sketchy or even conflicting evidence.

Amount of Fine Aggregate

Increasing the amount of fine aggregate will increase the amount of air. The spacing factor is probably not greatly affected. It is incorrect to attempt to increase the air content by increasing the fine aggregate proportion, especially considering the increased water demand such a change would involve.

Richness of Mixture

Rich mixtures entrain less air than lean mixes for a given addition rate of agent.

Consistency of Mixture

Moderately wet mixtures entrain more air than dry, stiff mixtures. The air content increases with slump up to about 7 in.; with further increases, the air content decreases. Wet mixtures will probably have spacing factors that are larger, and therefore less desirable, than drier mixtures. Excessively dry mixtures may also have comparatively coarse bubble systems and large spacing factors.

Type of Mixing

Machine-mixing will entrain more air than hand-mixing. Mixers with different types of mixing actions entrain differing amounts of air.

Length of Mixing Time

The amount of entrained air increases with mixing time up to a point beyond which it slowly decreases. This variable is especially important for ready-mixed concrete, for which mixing and agitating times of 15 to 90 min are the rule, compared with the 1 or 2 min in a stationary mixer. Experience indicates that the maximum amount of air is entrained in about 15 to 30 min in a truck mixer. However, the ensuing slow decrease in air content is not so critical as to cause undue difficulty in exercising the necessary control especially because the spacing factor is probably little changed.

Temperature of Concrete

The amount of entrained air decreases as the temperature of the concrete increases. The effect of temperature on spacing factor is not known.

Vibration

Placement by internal vibration will usually cause a reduction in the air content of air-entrained concrete. This reduction will be greater when the period of vibration is longer. It has been found, however, that vibration has little effect on the smaller bubbles and therefore does not materially change the spacing factor, and such concrete would therefore have good durability in spite of a lower air content than is normally thought proper.

Admixtures

As was mentioned previously, other admixtures used for various reasons can influence the air content and quality of the bubble system. Very little is known of the details of this influence, and each case should be investigated individually if experience in the particular system is lacking.

TEST METHODS

There are three ASTM standard test methods for the air content of air-entrained concrete. ASTM Designation C 138, Standard Method of Test for Weight per Cubic Foot, Yield, and Air Content (Gravimetric) of Concrete, involves the determination of the unit weight of the concrete. A knowledge of the mixture proportions and the densities of the various components then permits a calculation of the air content. The uncertainties of sampling and of aggregate moisture content that ordinarily exist in the field make this method accurate only for laboratory use with a restricted range of materials.

ASTM Designation C 231, Standard Method of Test for Air Content of Freshly Mixed Concrete by the Pressure Method, involves the determination of the change in volume of a sample of the concrete when a known increase in pressure is applied. The assumption of Boyle's law permits calculation of the air content, because air is the only highly compressible component of the concrete. This method is generally useful except for concretes that contain aggregates with large, air-filled void systems. The method is inaccurate when applied to concretes made with many lightweight aggregates, including blast-furnace slag.

ASTM Designation C 173, Standard Method of Test for Air Content of Freshly Mixed Concrete by the Volumetric Method, is the system in which the air in a known volume of the concrete is displaced by mixing with excess water and its volume determined directly. An adaptation of this method, using the Chace meter and a small sample of mortar from the concrete, is rapid and convenient. It is accurate enough for some routine control purposes but should not be relied on exclusively.

The foregoing methods determine only the total air content and, as mentioned and implied throughout this report, the spacing factor is a more significant parameter than is the total air content. The methods for the determination of spacing factor are given in ASTM Designation C 457 (Tentative Recommended Practice for Microscopical Determination of Air-Void Content, Specific Surface, and Spacing Factor of the Air-Void System in Hardened Concrete). These methods involve microscopic techniques applied to polished surfaces of the concrete and are applicable only to hardened concrete. The field engineer, then, has only the methods for total air content of the plastic concrete to rely on for his control procedures. Undesirable as this state of affairs may be from a theoretical point of view, it has been found that, if the concrete has been properly proportioned according to ACI 613 (75) and if the air-entraining agent qualifies under the appropriate ASTM specification, the resulting bubble system will almost surely have the desired properties. It may be, however, that changes in the total air content caused by the various influential factors do not have as much significance in terms of frost durability as was formerly thought. Even so, the prudent procedure is for the field engineer to maintain control by frequent checks of total air content and investigation of any changes that occur.

BENEFITS OF ENTRAINED AIR IN CONCRETE

The practice of air entrainment in concrete is unquestionably established from the standpoint of increased freezing and thawing resistance and is also used to obtain other desirable improvements in the properties of the concrete. Proper control is importan to ensure maintaining the air content within desired limits—high enough to derive the benefits to durability and workability but low enough to avoid unnecessary decrease of strength and abrasion resistance.

3. *Water-Reducing, Retarding, and Water-Reducing and Retarding Admixtures for Concrete*

Chemical admixtures defined as water-reducers, retarders, and water-reducing retarders are covered in the Specification for Chemical Admixtures for Concrete, ASTM Designation C 494, and given in the following:

1. Water-reducing admixture (Type A)—An admixture that reduces the quantity of mixing water required to produce concrete of a given consistency.
2. Retarding admixture (Type B)—An admixture that retards the setting of concrete.
3. Water-reducing and retarding admixture (Type D)—An admixture that reduces the quantity of mixing water required to produce concrete of a given consistency and that retards setting of concrete.

It is estimated that water-reducing and set-retarding admixtures have been used in over a half billion cubic yards of all types of concrete in the United States and Canada and are being used presently in 50 to 60 million cubic yards of concrete per year in these countries.

Water-reducing, retarding, and water-reducing and retarding admixtures are used to modify the properties of fresh and hardened concrete, such as increasing the fluidity and working qualities of a given mixture without an increase in water content, delay in setting, or increase in strength. Their proper use may decrease the cost of the concrete and concreting operations or permit certain adverse conditions to be overcome. Use of admixtures does not minimize the need for proper proportioning of the concrete, proper control and inspection practices, and good workmanship. Before its use in construction, an admixture should be tested under conditions simulating those anticipated on the job and in concrete preferably containing cement and aggregates proposed for use in the work. Because most highway agencies must supervise a large number of comparatively small jobs and use cements and admixtures from many sources simultaneously, this may not be feasible. It should be noted that all cements of a given type may not be compatible with a given admixture and that the effects of a given admixture vary greatly from one element to another. Attention should be given to the instructions and recommendations of the manufacturer of any admixture product considered for use, especially with respect to its preparation for use and rate of use.

In addition to the selected references, the reader is directed to the comprehensive annotated bibliography published by the Highway Research Board (17). This bibliography lists 86 papers and reports that provide original data and information on the properties, effects, and uses of these materials in concrete.

CLASSIFICATION OF MATERIALS

Materials that are readily available for use as water-reducing or water-reducing and retarding admixtures Types A and D of ASTM Specification C 494 may be classified chemically into five classes, as follows:

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; and
5. Carbohydrates and modifications and derivatives thereof.

The common constituents of classes 1 and 2 are calcium, sodium, or ammonium salts of lignosulfonic acid, produced during the sulfite process of wood-pulping. In general, the effluent from the wood-pulping operation is not suitable for use in concrete;

the raw sulfite liquor solids must be refined to produce a uniform product containing a minimum of impurities. The essential constituents of admixtures of classes 3 and 4 are sodium, calcium, or triethanolamine salts of such compounds as hydroxylated adipic acid and gluconic acid. Compounds of class 5 can be produced by fermentation or oxidation of carbohydrates such as glucose, dextrose, and starch.

In classes 2 and 4, these compounds are combined with organic or inorganic compounds, which act as accelerators, retarders, catalysts, air-entraining agents, or possible air-detraining agents to produce special effects in the performance of the admixtures.

Class 5 carbohydrates, such as sucrose (table sugar), glucose, and maltose, cause retardation of setting of portland cement and concrete when used alone. In general, carbohydrates must be used with caution because widely varying retardation can be obtained with relatively small changes in rate of use with respect to the proportion of cement in the concrete. Also, the effects on retardation, water requirement, and strength development vary widely among carbohydrates; however, these effects can be modified by combining the carbohydrates with suitable accelerators or catalysts. Good performance can be obtained with the use of a satisfactory carbohydrate of uniform composition at proper rates relative to cement content.

Type B retarders of ASTM Specification C 494 comprise a wide range of inorganic and organic admixtures that can produce retardation of setting without adverse effects on compressive strength, flexural strength, bond strength, volume change, bleeding, and freezing and thawing resistance of concrete. The specifications for Type B retarders include no requirement on water reduction. Hence, chemicals meeting the requirements of ASTM Specification C 494 for Type D admixtures will meet the requirements for Type B admixtures. Therefore, a chemical classification of Type B retarding admixtures must include the five classes stipulated previously as well as admixtures based on various inorganic compounds, such as salts of zinc and water-soluble borates and phosphates.

EFFECT ON FRESH CONCRETE

The effects of the admixture on the properties of fresh concrete vary with the type of admixture and the materials composing the concrete. The properties that are most affected are slump, air content, water requirement, bleeding or sedimentation, rate of hardening, workability, and strength.

The slump, air content, and water requirement of concrete are interrelated so that the specific effect of admixtures on each of these properties is difficult to separate. Indication of the individual effects can, however, be gained by considering the behavior when two of the variables are controlled. The cumulative effects may then be related in a rational manner.

Admixtures modify workability of concrete through improved mobility and by lengthening the hardening period. For equal water and air contents, the slump of concrete containing an admixture with water-reducing properties is increased up to 100 percent as compared with comparable reference concrete within the range of slump ordinarily used in highway work. The change in slump with given change of water content is usually more pronounced in admixtured concrete than in conventional concrete, and relatively small changes in water content in some cases may markedly affect the fluidity of the mixture. Under these conditions, the relatively rapid increase in slump is not detrimental to the properties of the hardened concrete, provided that the fluidity is not sufficient to cause segregation. The placeability of concrete at a given slump is generally improved for concretes containing these admixtures.

Some admixtures of these types entrain air in concrete, although in general a supplementary quantity of conventional air-entraining admixture is required to produce air content such as required by ACI 613 (75) and other nationally recognized specifications. When the admixtures are used at rates recommended by the manufacturer for ordinary purposes, admixtures of classes 1 and 2 typically produce air contents 1 to 4 percentage points higher than those of equivalent concrete not containing the admixture; however, some products of these classes entrain more air than these amounts when employed at rates sufficient to effect even mild retardation of setting of concrete. Admixtures of classes 3, 4, and 5 do not entrain air in concrete unless a separate air-entraining substance is included in the product. When a separate air-entraining admixture is needed in concrete containing a water-reducing, set-retarding, or water-reducing and set-retarding admixture, the amount required to produce a given volume of air is usually less than that for concrete without the admixture. Certain admixtures interact if intermixed prior to their introduction into the concrete, but the fact that individual admixtures interact in this manner does not indicate that they will not be fully effective if dispensed separately. This affects the method of addition, as discussed later. The influence of the admixtures on the characteristics of the air voids is treated in the subsequent discussion of hardened concrete.

For concretes of equal slump and air content, the use of Types A and D admixtures (ASTM Specification C 494) will permit a reduction of the water content of up to 12 percent. The corollary properties associated with reduction in water requirement are also important, because a given water-cement ratio can be maintained while producing concrete of a higher slump, or a specific strength may be obtained with a cement content proportionately lower than in concrete not containing the admixture.

The bleeding characteristics of concrete may be modified in any of several ways by the use of these admixtures. Admixtures of classes 1 and 2 may reduce bleeding and settlement of the concrete as compared with concrete having the same slump and mixture proportions but not containing the admixture. This reduction in bleeding is attributed to the entrainment of air, reduction of the amount of water in the mixture, and other more complex factors. Admixtures of classes 3 and 4 may increase the rate and capacity to bleed water at early ages. This rapid bleeding reduces the water content of the concrete in place and retards the drying of the surface of the concrete. However, excessive bleeding is not desirable and should be avoided. The user of concrete containing admixtures should be aware of the differences in bleeding characteristics and provide for them accordingly.

Types B and D admixtures (ASTM Specification C 494) extend the setting time as measured by the various empirical methods used in specifications. The amount of retardation is largely a function of the chemical nature and the amount of admixture added, so that practically any degree of retardation may be achieved. The maximum practical dosage of any given admixture is often limited by the amount of air that is entrained. On the other hand, for the degree of retardation that frequently may be desirable for highway concrete, air entrainment related to use of these admixtures is rarely a problem. When experienced, excessive air entrainment may be controllable by use of non-air-entraining cement in lieu of air-entraining cement or by reduction in the proportion of air-entraining admixture that otherwise would be employed or by use of an air-detraining admixture. However, care should be exercised in the use of air-detraining admixtures so as to avoid undue reduction of air content and adverse effects on the air-void system (18). As shown in Table 1 of ASTM Specification C 494, requirements for Types B and D admixtures dictate that the initial setting time must be delayed over comparable plain concrete at least 1 hour and no more than 3½ hours under conditions specified. The retarding admixtures delay setting, but, after setting has occurred, the hydration reactions, hardening, and strength development proceed at normal or accelerated rates.

EFFECT ON HARDENED CONCRETE

Concrete prepared with these admixtures will normally give compressive strengths that at 24 to 48 hours are equal to and at later ages are higher than those of concrete of the same cement content, air content, and slump without the admixtures. The amount of strength at early ages is somewhat dependent on the amount of retardation, and for concrete in which the setting time is abnormally long an increase may not be achieved. The increase at 28 days is usually 10 to 20 percent. Increases at ages from 3 to 28 days are somewhat greater and at later ages somewhat less when expressed as a percentage of the strength of a corresponding reference concrete. A factor influencing the increase in compressive strength is the amount of water reduction, but the increase is usually greater than would be expected from the reduction in water-cement ratio. Factors such as more complete hydration of cement also have beneficial effects on strength gain.

Flexural strength of concrete usually is increased by the use of these admixtures relative to that of equivalent reference concrete, but the increases so obtained are not proportionally as great as the increases in compressive strength.

Because drying shrinkage of concrete is primarily a function of total water content, admixtures that reduce the water requirement usually effect a slight reduction in drying shrinkage. However, under laboratory conditions, some admixtures may reduce or increase drying shrinkage, depending on their specific chemical composition and the test procedure used.

The resistance to freezing and thawing of concrete containing chemical admixtures is primarily related to the amount and characteristics of the air-void system that is entrained. The resistance increases with increasing air content and decreasing air-void spacing factors. Improvement of resistance to freezing and thawing beyond that resulting from the entrained air would be dependent on the amount of water reduction and increase in strength achieved. Air-detraining admixtures should not be used in concrete to be subjected to freezing and thawing unless their use is shown not to be harmful to the size and distribution of the air voids, as may be demonstrated by a laboratory freezing-and-thawing test or microscopical evaluation of the air-void system (ASTM Designation C 457, Tentative Recommended Practice for Microscopical Determination of Air-Void Content, Specific Surface, and Spacing Factor of the Air-Void System in Hardened Concrete).

In general, the modulus of elasticity and bond to reinforcing steel are increased and creep of the concrete is decreased by the use of a Type A, B, or D admixture (ASTM Specification C 494), but the changes appear to relate to the improvement in compressive strength. Increases in abrasion resistance and decreases in permeability have been obtained that are also related to the degree to which other properties, such as strength and density, are improved.

APPLICATIONS OF ADMIXTURES

Water-reducing, retarding, and water-reducing and retarding admixtures should be used when it is desirable or necessary to modify the properties of concrete in any of the ways previously discussed. The economic considerations of using admixtures are discussed by Committee 212 of the American Concrete Institute (1).

The major use of admixtures in the highway industry has been in structural concrete for bridges and tunnels, but some significant paving projects have also utilized them successfully. An extensive summary of specific applications has been presented by Mielenz (19).

Water-reducing and retarding admixtures (ASTM Specification C 494, Type D) that cause both water reduction and retardation are the most commonly used in the highway industry. Where retardation is desired or can be tolerated, simultaneous water reduction is always beneficial. For this reason Type B admixtures that affect only setting time are not extensively employed. When retardation is not required, water-reducing admixtures (ASTM Specification C 494, Type A) are used.

The following applications of the water-reducing properties of admixtures are important:

1. Economy of proportioning of the concrete mixture, including use of lower cement content and minimizing of problems associated with aggregates that result in a high water requirement.
2. Meeting job specification requirements such as maximum permissible water-cement ratio and early development of strength and modulus of elasticity. Numerous examples may be drawn from experiences in production of prestressed concrete.
3. Improving quality of fresh concrete as a result of improved workability, reduced water content for a given consistency, or increased slump at constant or reduced water content. This is particularly desirable in cases of concrete that is to be placed in heavily reinforced sections, under water, or by pumping.

The following applications of retardation of setting are important:

1. Compensation for adverse ambient conditions, particularly in hot-weather concreting. Extensive use is made of retarding admixtures to permit proper placement and finishing and to overcome damaging accelerating effects of high temperatures.
2. Increase in the permissible period of as much as 45 min between batching and placing.
3. Control of setting of large structural units to keep concrete workable throughout the entire placing period. This is particularly important for elimination of cold joints and discontinuities in large structural units and for prevention of cracking of concrete beams, bridge decks, and composite construction caused by form deflection or movement associated with placement of adjacent units. Adjustment of the dosage as placement proceeds permits various portions of a unit (a large post-tensioned beam, for example) to attain a given level of early strength at approximately the same time.

FACTORS AFFECTING PERFORMANCE

The specific effect of water-reducing and retarding admixtures varies with composition of cement, water-cement ratio, temperature of the concrete, ambient temperatures, and other job conditions.

Different brands and types of cement, because of variations in chemical composition, may require different amounts of the admixtures to obtain the desired results. The effectiveness of the admixture (20) seems to be related primarily to the amounts of tricalcium aluminate (C_3A) and the alkali (Na_2O and K_2O). The sulfur trioxide (SO_3) content also may have a very marked influence on the effect of the admixture on the time of setting of the concrete (21, 22, 23).

In general, the quantity of water-reducing admixture required to produce the desired results will vary less with changes in cement composition or other mix conditions than is true for the retarding admixtures. These latter types are designed to delay the set of the concrete for a predetermined period of time at a given temperature. Slight changes from this temperature do not require a change in addition rate, but, if either the temperature of the concrete or the ambient temperature varies more than 10 F (6 C) from that contemplated, a change in addition rate is generally necessary to maintain the desired retardation. The higher the temperature is, the more admixture will be required to hold a constant degree of retardation.

The effectiveness of water-reducing admixtures varies with the water-cement ratio of the mixture. Concrete of excessive water content and high water-cement ratio cannot benefit by this type of admixture to the extent realized in a medium- to low-slump concrete. The use of water-reducing admixtures (ASTM Specification C 494, Type A or D) causes the concrete to be more sensitive to change of water content so that approximately 50 percent less water is required to increase slump a given amount than is required by similar concrete not containing such an admixture (24).

The addition of these materials to the mixture in liquid form is highly desirable to obtain a more uniform distribution throughout the concrete mass within the time required to mix the concrete. Care should also be taken when using liquids to avoid adding them directly to the cement or dry, absorptive aggregate. A fixed procedure for the method and time of dispensing the admixture should be followed for each job.

The time of addition of set-retarding admixture has a marked effect on the resulting mixture (25, 26, 27). A delay of ½ to 2 min in adding the admixture after all other materials are batched and mixing started will often result in an increase in slump and retardation.

TESTING METHODS AND SPECIFICATIONS

The testing of water-reducing, retarding, or water-reducing and retarding admixtures should be conducted on concretes prepared with and without the admixture to be evaluated in accordance with the procedures outlined in ASTM Specification C 494. The admixture should be added in the manner recommended by the manufacturer and in the amount necessary to comply with the applicable requirements of the specifications. The requirements are given in Table 1 of ASTM Specification C 494.

The time of setting should be determined in accordance with ASTM Method C 403 (Standard Method of Test for Time of Setting of Concrete Mixtures by Penetration Resistance) in order to ensure reproducibility of results. Attempts to correlate data obtained from a mortar mixture with those obtained from mortar screened from a concrete mixture have been unsatisfactory to date.

The specification limits given in Table 1 of ASTM Specification C 494 take into account the variability of test data, which is more critical when comparing concretes than when no comparison is required, as is the case in usual specifications (28).

UNIFORMITY

To ensure uniformity of shipments or to ensure shipments that are identical to samples submitted for tests, quality-control procedures should be implemented. Complete chemical analysis of admixtures is usually very time-consuming and ordinarily is not practical for control of uniformity. Conventional methods of chemical analysis may take a week or more to complete. It has been suggested that infrared spectroscopic analysis be employed for this purpose. This procedure may be applicable to admixtures of the hydroxy carboxylic acid type, but it does not differentiate between the various admixtures of the lignosulfonic acid type that differ markedly in their effect on concrete. Furthermore, with all admixtures infrared techniques may not indicate the presence of essential or detrimental compounds that either should or should not be present in the admixture under test.

The most practical means of ensuring quality would be based on index tests, which, although not specific or definitive for direct evaluation, can be used to control uniformity of the product. Suggested tests for this purpose are as follows:

1. Observation of physical nature;
2. Moisture content of solid products;
3. pH of solutions of selected concentrations;
4. Specific gravity or solids content of liquid admixtures;
5. Analysis for specific ingredients such as percentage of chlorides, carbohydrates, or other compounds of special interest; and
6. Infrared analysis or ultraviolet light spectrum of active constituents.

These tests can establish uniformity or variability of the product. A water-reducing or set-controlling admixture can be specified by chemical class, but in general it is not practical to specify them by exact chemical composition. This is because the performance of these admixtures cannot be controlled by these means, and the difficulties of chemical analysis preclude rapid and reliable quantitative determinations.

ACCEPTANCE TESTING

The requirements outlined in the two preceding sections will reasonably ensure the constancy of the admixture. The previously discussed influence of cement composition on the performance of the admixture in a particular concrete places an added responsibility on a highway agency that must simultaneously supervise a wide variety of jobs. The establishment of an approved list of admixtures must recognize the possibility of unusual behavior of a particular cement-admixture combination. Likewise, enforcement of specification limits for cements does not preclude such unusual behavior. The time and expense of a complete test program in accordance with ASTM Specification C 494 for each possible combination with periodic updating are prohibitive.

Many states accept an admixture on the basis of one series of tests in accordance with ASTM Specification C 494. Compatibility with job cement is established on the basis of very limited tests for water reduction, retardation, and absence of obvious difficulty.

Such an approach will generally suffice, and lack of compatibility can usually be corrected by changes in dosage or addition sequence. Infrequently more serious incompatibility such as false set or excessive retardation is encountered (22, 23, 25, 29). Such an occurrence might be encountered in spite of conformance to the general requirements set forth in this document and requires special attention.

ADDITION

Water-reducing and set-retarding admixtures are generally used in relatively small quantities. It is therefore important that suitable and accurate dispensing equipment be used. These admixtures are available as both liquids and powders. Water-soluble powders should be dissolved in water prior to use so that they can be dispensed as liquids. Unless complete solution of the admixture is obtained, the solutions should be agitated before being taken from storage or shipping tanks or containers, and agitation should be provided before and during dispensing into the concrete mixture. Manufacturers' recommendations should be followed.

Admixtures furnished as liquids by the manufacturer may not require such agitation; however, the manufacturer's instructions should be followed. Powdered admixtures that are not completely water soluble may be manually dispensed dry by volume or weight. In this case, they should preferably be added to the fine aggregate. All admixtures can be added after the concrete has been partially mixed; however, the same sequence and timing of addition of the admixtures should be used throughout a given project because available data indicate that time of addition may affect the efficiency of these admixtures.

Accurate and durable dispensers for liquid admixtures are available. These dispensers work on either a time-flow or a positive displacement principle. The time-flow type of dispenser should be equipped with a transparent measuring tube, and each addition should be dispensed through this tube, because any inaccuracy in flow rate with this type of dispensing equipment will change the volume delivered. A positive displacement type of dispenser does not depend on flow rate for accuracy but is generally adaptable only to dispensing fixed quantities of the admixture.

It may be necessary to add an air-entraining agent to the concrete in addition to the retarding or water-reducing admixture. The admixtures should not be mixed together prior to addition, because, in most instances, they will react causing precipitation, loss of effectiveness, and clogging of the dispenser lines. The incompatibility of air-entraining admixtures and other chemical admixtures when mixed together does not indicate that such admixtures will not be effective when added separately to the concrete.

STORAGE

Powdered admixtures generally have an indefinite shelf life if stored dry. Liquid admixtures may freeze or precipitate at low temperatures. Freezing may permanently damage some liquid admixtures. Other liquid admixtures may be frozen and thawed without damage. The manufacturer's storage directions should be followed.

4. *Pozzolans in Highway Concrete*

The literature on the use of pozzolans in concrete is voluminous. The pozzolan used most extensively and on which the most research has been done is fly ash. Only selected references are mentioned in the interest of brevity. For a more comprehensive evaluation the reader is referred to the extensive additional literature published by the Highway Research Board, the ASTM, the ACI, the Federal Highway Administration, the U.S. Bureau of Reclamation, the U.S. Army Corps of Engineers, several highway departments, and several universities. One Highway Research Board publication (30) alone reviews 275 papers.

Pozzolans are not widely used in portland cement concrete for pavement construction in the United States except in Alabama where fly ash pozzolan is specified regularly. Georgia now includes fly ash in its published standards as an alternate for use in concrete pavement. A survey published in 1963 (31) of pavements containing fly ash estimated a total of 250 lane-miles in the United States of which about 200 miles were in Alabama. Alabama alone now has over 300 lane-miles plus several major highway bridges containing fly ash. Experimental roads with fly ash pozzolan, some dating back to 1938, are found in Illinois, Nebraska, Wisconsin, Michigan, and Kansas (32). An experimental project with fly ash was recently completed in Kentucky (33), and one is proposed in West Virginia. In Nebraska and Kansas, where much sand-gravel aggregate (essentially coarse sand with some pea gravel) is used, concrete pavement frequently suffers from map-cracking and destructive expansion. Pozzolan is helpful in greatly reducing volume change and minimizing deterioration. In the McPherson Test Road built in Kansas in 1949, three pozzolans were used: fly ash, Mowry shale, and Monterey shale. All were effective in reducing but not eliminating map-cracking and abnormal expansion after 10 years of exposure and service (31, 34, 35).

The experimental road planners in Illinois, Wisconsin, Michigan, and Kentucky were not concerned with alkali-silica reaction. They studied strength development, crack resistance, placing and finishing qualities, and long-term wear resistance, as revealed by condition surveys comparing control sections with sections containing fly ash pozzolan. All these roads have performed well (31).

Despite the generally satisfactory performance of concrete with pozzolans in experimental pavements and in Alabama (36), pozzolans are still not generally used in pavement concrete in the United States. This is not the case in Europe, where the use of portland cement in combination with fly ash and with blast-furnace slag and fly ash is increasing rapidly each year in all types of construction (37) including pavements.

The judicious use of a suitable pozzolan can assist in the attainment of the desirable qualities of portland cement concrete and can often result in a substantial reduction in the unit cost of the concrete in place. The use of pozzolan is especially effective in concrete for highway structures because the pozzolan has the ability to progressively convert calcium hydroxide generated during the cement hydration to calcium silicates, lessening the probability of lime salts leaching to the surfaces to form the unsightly deposits seen on so many highway bridges and retaining walls.

NATURE OF POZZOLANS

Pozzolan is defined in ASTM Standard Definition C 219 and elsewhere (42) as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Pozzolans may be divided into two classes (39)—natural and artificial—and the natural materials into three groups—those owing their activity to (a) acidic volcanic glass, (b) opal, and (c) products of calcination of clay minerals. Some of the natural materials in the three groups may require calcination to render them pozzolanic to an optimum degree (42). It is likely that calcined materials will contain several combinations of substances.

Artificial pozzolans are fly ash (ash from burning powdered coal, produced in such operations as steam power plants, and ash caught in precipitators) or silica from the treatment of bauxite, ground brick or tile, and burnt ground oil shale. Fly ash is the most important of this group commercially and economically, because it is available near population centers in large quantities wherever coal is burned to produce electricity.

Fly ash consists largely of generally spherical particles of fused glass with some unburned granules of coal (30). It is usually finer than cement and usually requires no grinding or processing before being used in concrete. The natural pozzolans, except some of the pumicites, usually require drying, grinding, calcination, or a combination of these treatments before being suitable for use (39, 40). Appearance of four different pozzolans under the miscroscope is shown by Blanks and Kennedy (40). Grain shapes range from spherical particles of glass in fly ash to the flat angular plates of pumicite and to the highly porous cellular structure of diatomites. The particles of crushed chert or obsidian, although not shown, would be expected to be in the form of sharp angular shards.

The predominant constituent of all recognized pozzolans is silica (39), but other materials are present. Some pozzolans contain up to 35 percent alumina and 20 percent iron oxide. Some may contain as much as 10 percent total alkali (sodium and potassium oxides). The presence of alkali appears to be beneficial, as does a moderate amount of alumina and iron oxide.

The chemical composition of typical pozzolans (43) and the average of a number of Type I cements (40) are as follows:

Component	Range in Composition (percent)				
	4 Fly Ashes	4 Volcanic Glasses	3 Shales	1 Uncalcined Diatomite	Type I Cement
SiO_2	38.2 to 48.3	68.1 to 74.8	61.2 to 71.1	76.7	21.0
Al_2O_3	14.7 to 34.0	13.8 to 15.8	12.5 to 19.3	12.0	6.5
Fe_2O_3	6.5 to 18.9	0.85 to 1.9	4.1 to 5.9	0.60	2.5
CaO	2.3 to 8.5	0.27 to 1.9	0.22 to 8.6	0.70	64.0
MgO	0.4 to 2.1	0.00 to 0.97	0.85 to 3.0	0.05	2.5
Na_2O	0.31 to 1.62	3.52 to 7.38	0.88 to 1.21	1.72	
K_2O	1.02 to 2.0	2.94 to 4.96	0.61 to 1.56	1.68	
Ignition loss	0.8 to 12.0	0.69 to 6.6	1.26 to 6.8	3.2	
C_3S	0.8 to 12.0	0.69 to 6.6	1.26 to 6.8		48.0
C_2S					27.0
C_3A					12.0
C_4AF					8.0

It is seen that calcium oxide is abundant in cement while the pozzolans, by contrast, are relatively rich in silica, alumina, and iron and are deficient in lime.

EVALUATION OF POZZOLANIC ACTIVITY

The chemical composition of a pozzolan alone affords little information on its reactivity (39, 40, 41). It would seem logical that materials with high silica content would be better than those with low silica content, but some good pozzolans may have as little as 40 percent silica; others may have as much as 10 percent alkalies, 20 percent calcite, 30 percent alumina, 20 percent iron, and even 15 percent carbon (40).

Petrographic examination (40) of pozzolans sometimes is made for the purpose of establishing the mineralogic and phase composition of materials so that the chemical analysis might be more realistically interpreted or for independent evaluation of the likelihood that the material can be processed to produce a satisfactory pozzolan. However, results of petrographic examination cannot quantitatively predict pozzolanic activity (40) because materials of the same petrographic classification may contain many combinations of active constituents.

Because pozzolans as a class include a wide variety of materials, there is no single test or examination procedure diagnostic of all the qualities and changes in the properties of concrete that will be wrought by use of a specific pozzolan (44, 45).

STANDARDS FOR POZZOLANS

Specifications for pozzolans differ among the organizations using them, but all are based on chemical composition and performance in physical tests designed to evaluate pozzolanic activity, uniformity of product, and the effect on the strength and stability of mortar.

The ASTM has a combined specification for fly ash and natural pozzolans (ASTM Designation C 618-68T) and a separate standard for sampling and testing fly ash (ASTM Method C 311). The states of Alabama and Georgia have their own specifications for fly ash (46, 47) differing in a number of respects from ASTM. The two largest federal users of pozzolan, the U.S. Bureau of Reclamation (48) and the U.S. Army Corps of Engineers (49), both have specifications for pozzolans, and an interim federal specification (50) for pozzolan was issued in 1967 that may supplant the specifications of the USBR and the Corps of Engineers. The ASTM, USBR, Corps of Engineers, and interim federal specifications all contain provisions intended to ensure uniformity of some of the physical characteristics of the product to facilitate control in the concrete, especially of the water content and quantity of air-entraining admixture required for proper air entrainment. It is interesting to note that none of the specifications cited makes provision for measuring the effectiveness, or lack thereof, of a pozzolan for increasing the resistance of mortar or concrete to the action of sulfate-bearing soils or water or to seawater, although this virtue is claimed for pozzolans and much has been written on the subject (30, 51, 52, 53).

EFFECT OF POZZOLANS ON CONCRETE

The effects of pozzolans on the properties of freshly mixed concrete vary with the type and fineness; the chemical, mineralogical, and physical characteristics of the pozzolan; the fineness, composition, and constitution of the cement; the ratio of cement to pozzolan; and the quantity of cement plus pozzolan used per unit volume on concrete (30, 36, 39, 40, 41). A review (29) of the use of fly ash based on 275 papers shows that a good fly ash used in optimum quantities does not increase the unit water requirements of concrete but does improve workability (ease of finishing) and plasticity, reduces segregation and bleeding, slows setting time slightly, and reduces heat of hydration. Other sources concur with these findings (36, 39).

The effect of pozzolans on the water content and the amount of neutralized vinsol resin solution required to maintain a constant air content and workability varies with the type, quantity, and fineness. Selected data (43) involving substitution of pozzolans for cement in 0.5 water-cement ratio concrete follow:

Cement (lb/cu yd)	Pozzolan			Surface (sq cm/g)	Water (lb/cu yd)	Neutralized Vinsol Resin (ml/cu yd)
	(lb/cu yd)	Percent	Designation			
532	0	0	None	3,550	265	485
346	116	30	Fly ash 1	3,565	247	379
416	103	25	Pumicite 1	4,410	277	529
404	156	35	Tuff	10,460	310	800
346	139	35	Obsidian	3,415	266	378
458	91	20	Calcined shale 1	13,685	286	670
423	141	30	Calcined diatomite	10,450	302	1,018
462	64	16	Uncalcined diatomite	12,125	274	540

Extensive work (51) on fly ash concrete mixtures containing up to one part pozzolan to one part of cement led to the conclusion that properly constituted mixtures with good-quality fly ash require about the same water content as similar mixtures without pozzolan and less than most natural pozzolans.

When one visualizes the wide range of grain shape of pozzolans, from the predominantly spherical grains of fly ash to the shards of crushed volcanic glass or chert, and the striking differences in surface area, from fly ash near the surface area of cement to some calcined shales or uncalcined diatomites with as much as four times the surface area of cement, it is not surprising that observations about the effect of the use of pozzolans on the properties of concrete must be qualified to account for their circumstances of use.

When fly ash is used to replace an equal amount of cement (30), curing time to maintain equal strength should be longer than normal, but, if fly ash is used in larger amount than the amount of cement removed, curing need not exceed that afforded concrete with straight portland cement. Intergrinding fly ash and cement and curing at temperatures somewhat higher than normal are helpful in shortening curing time.

Concretes with 5.5 bags of Type I and Type IS cements were compared to concrete with 4.5 bags of Type I portland plus 141 lb (essentially 2 bags) of fly ash under varying curing conditions (54). Under the most adverse conditions, with no moist-curing at all, the concrete containing fly ash developed greater strength at all ages from 1 day to 1 year than the concrete made with Type IS cement and greater strength at all ages tested except 3 and 7 days than the concrete made with Type I cement. This indicates that proper proportioning with fly ash can produce concrete that can perform as well as or better than concrete made without fly ash, even under adverse curing conditions.

Lower strength at early ages (51) and higher strength at later ages under normal moist-curing conditions and substantially higher strengths with curing at 100 F result when fly ash is substituted for 30 percent of the cement. In richer mixtures, 6 bags/cu yd, 10 percent or more replacement of cement with pozzolan reduces early strength and possibly later strength as well (39). In leaner mixtures early strength is reduced, but later strength of pozzolan concrete exceeds straight portland cement. The replacement of a part of the cement with pozzolan effects an increase in the water-cement ratio, which generally reduces early strength. However, the loss is soon recovered and overcompensated as the pozzolanic action proceeds (41). Five bags of straight cement concrete and concrete containing 4 bags of cement plus 94 lb fly ash/cu yd respond almost equally to dry-curing or curing at 45 F (55). Under conditions of normal curing, mixtures suitable for paving to have equal 3- to 28-day strength must have a total weight of cement plus fly ash greater than straight portland cement mixtures (54), although the quantity of portland cement in the blended mixtures can be appreciably less than in the straight portland cement mixtures.

The effect of a good pozzolan can be quite pronounced, especially at later ages when the contribution of the cement to strength has leveled off. Highway concrete is seldom deliberately given prolonged water-curing; however, moisture is constantly being supplied by the subgrade and rain except in a few arid regions. Moisture is therefore usually present to enable the pozzolanic action to proceed long after the pavement has been laid.

Flexural strength of concrete with pozzolans appears to be affected in a manner similar to compressive strength (30, 55) so that changes in compressive strength will be reflected in corresponding changes in flexural strength. The replacement of cement by pozzolan (43, 55) generally results in lower flexural strength at 7 and 28 days, with the reduction becoming progressively less with age. However, if well-established proportioning techniques are employed (usually using a greater total amount of cement plus pozzolan but actually using less portland cement than in a comparable mixture containing no pozzolan and with aggregates reproportioned to accommodate the increased volume of cement-sized fines), any desired early compressive or flexural strength can be achieved within reasonable limits.

Tensile strength of portland-pozzolan briquettes (51) at 28 days is generally higher than that of straight cement. The ratio of tensile to compressive strength is always higher (5) for portland-pozzolan concrete than for straight portland cement concrete. This is applicable at both low and high levels of strength. Abrasion resistance correlates directly with compressive strength and is affected only as that strength is affected.

The effects of fly ash and other pozzolans on the resistance of concrete to freezing and thawing and to the action of chemicals for de-icing depend on how the pozzolan is used, the strength of the concrete, moisture condition of the concrete, and the adequacy of air entrainment at the time of exposure. Data (56) obtained from freezing tests on adequately air-entrained concrete with straight cement and with fly ash and other pozzolans show that, regardless of age or water-cement ratio, the durability in freezing and thawing correlates directly with compressive strength. Proper air entrainment, strength, and adequate curing (30) appear to produce in concrete containing fly ash resistance to freezing and thawing and to de-icing with salts equal to that in concrete made with straight cement. Equal strength and equal air-entrainment mean equal durability in freezing (57), and extensive tests (58, 59) in which fly ash was used in concrete generally suitable for paving indicate equal resistance to freezing and thawing and scaling for concrete of about equal strength and adequate air entrainment, whether made with straight cement plus fly ash or blast-furnace slag portland cement plus fly ash. It should be noted that in these tests concrete made with the same ingredients, but with $33\frac{1}{3}$ percent of the cement by absolute volume replaced with fly ash, gave lower strength and less resistance to scaling, but, when reproportioned to give equal strength and equal air entrainment, even with $\frac{3}{4}$ bag less portland cement per cubic yard, the fly ash mixtures had equal or superior resistance to scaling.

Concrete with pozzolans may expand slightly more under continuously wet conditions and shrink slightly more on drying (30, 39, 40), but it would appear that the effects on expansion and shrinkage would vary with the effect the pozzolan had on the unit water content of the concrete. A pozzolan that resulted in lower unit water content might experience less volume change (58). The volume change resulting from loss of heat, as the heat from the hydration process is lost, is usually less because the pozzolan contributes about half as much heat, pound for pound, as cement (30, 39, 40).

The modulus of elasticity appears to be affected as the strength and seems to be a little lower for fly ash concrete at early ages and somewhat higher at later ages (30, 39, 51) than straight portland cement concrete.

Creep or plastic flow seems to be affected in a manner similar to modulus of elasticity, and concrete with pozzolans seems to have somewhat increased strain capacity or resistance to cracking over straight portland cement concrete (5, 29, 40, 51).

The use of pozzolans appears to enable concrete to better resist acid waters, sulfate-bearing waters, and seawater, especially when Type I cement is used (5, 30, 40, 41, 51, 53, 54, 55, 60, 61, 62). Corps of Engineer studies (63) show that the use of a good pozzolan in adequate amount is of great benefit in delaying or preventing destructive expansion and deterioration when concrete containing reactive siliceous aggregates and high-alkali, high-tricalcium aluminate cement is exposed to seawater. Marked improvement in the resistance of concrete containing cement high in tricalcium aluminate to the action of sodium or magnesium sulfates in soils or groundwaters is obtained by use of pozzolan (52). The U.S. Bureau of Reclamation found improvement of resistance to sulfates when fly ash was used with Types II and V as well as with Type I cement (53).

Among the reasons postulated for improved resistance to sulfate when a pozzolan is used is removal of calcium hydroxide by the pozzolanic reaction, which sets up conditions where calcium sulfoaluminate can form without causing expansion of the concrete (5). Reaction between set calcium aluminate and sulfate solution produces etringite and causes expansion, but if the calcium aluminate passes into solution it will react with sulfate and precipitate without expansion. Removal of calcium hydroxide by the pozzolanic reaction makes conditions favorable for the solution of calcium aluminate hydrate. Other explanations for the increased resistance to disruption by sulfate (5) are that the concrete is rendered impermeable by a protective film formed over the aluminate compounds, and in seawater lime may be removed by solution and unstable lime-alumina-silica compounds may be converted into stable silica and alumina gels. The increased water tightness, widely acclaimed in the literature, is no doubt a factor contributing toward increased resistance to acid and sulfate attack.

The corrosion rates of mild steel plates embedded in mortars, in which 20 to 40 percent by weight of the portland cement was replaced by fly ash, were observed to be about the same as for plates in solutions of calcium hydroxide with a pH of 12 or more (64). The pH of water slurries of pulverized blended cement mortars with several pozzolans were not significantly different from each other regardless of the pozzolan or clinker content, age, or curing condition (65). These studies indicate that enough calcium hydroxide appears to be present at all times to ensure the high pH that is required for corrosion resistance.

The usefulness of pozzolans in preventing or ameliorating the effects of alkali-aggregate reaction involving soluble silica in the aggregates are well known, and the literature is voluminous. It has been stated (60) that many pozzolanic materials, but not all, have been found to be effective in counteracting the alkali-silica reaction. Recent work indicates (66) that, if used in sufficient quantity (10 percent for synthetic silica glass, 19 to 29 percent for calcined shales, 32 to 36 percent for volcanic glasses, and 39 to 45 percent for ground blast-furnace slags and fly ash), almost any pozzolan is capable of preventing excessive expansion, but certain pozzolans if used in too small quantities (40) may actually increase the detrimental effects of alkali-silica reaction.

Closely allied to the problem of the alkali-silica reaction is the reaction between cement and sand-gravel aggregate so prevalent in the Kansas-Nebraska area. The McPherson Test Road built in 1949 contains many combinations of cementing medium and sand-gravel aggregate with and without crushed limestone "sweetening." An evaluation of the 10-year results is given elsewhere (34, 35). It appears, however, that the effective pozzolans, including fly ash, are beneficial in reducing or eliminating map-cracking and expansion, and it is conjectured that the use of fly ash plus a small amount of crushed limestone coarse aggregate might prove to be the answer to the sand-gravel problem (31).

PROPORTIONING HIGHWAY CONCRETE WITH POZZOLANS

There are a number of ways in which highway departments may specify use of pozzolans in concrete paving and structures, depending on the criteria to be met. For years the U.S. Army Corps of Engineers has used pozzolans and refers to the cementitious material content of the concrete in terms of absolute volume (total), including both portland cement and pozzolan. The U.S. Bureau of Reclamation refers to cement and pozzolan content in terms of bags at 94 lb each. Both agencies replace cement with pozzolan and attempt to use the minimum amount of cement-pozzolan blend to achieve their objectives in mass concrete. Low early strength, which may be acceptable in mass concrete, may result and probably would be unsatisfactory for highway concrete.

Highway departments frequently specify minimum 14-day strengths as one of the major requirements for paving concrete. This usually requires a greater total of cement plus pozzolan than of cement alone, but correct proportions are easily and readily developed (33, 36, 54, 55, 58, 59, 68, 69). For projects of considerable volume or importance, the proportions of the blend should be established by laboratory testing and proper yield as well as properties established with the materials involved.

Early strength will suffer and, even though properly air-entrained, concrete in which cement is removed and pozzolan substituted on an equal volume or weight basis will be weaker and less resistant to scaling at early age (70). If, however, a 6-bag mixture is reproportioned to contain 5.25 bags of cement plus 100 lb of fly ash and the aggregate proportions are adjusted to fit a 6.58-bag mixture (which is what the new mixture is equivalent to in cement-pozzolan blend), the new mixture will be as strong as or stronger than the old and will show equal or greater resistance to scaling, provided that equal to adequate air entrainment is maintained in both mixtures. Approximately equal strength from 3 to 28 days will be obtained if not more than 1 bag of cement is removed and it is replaced by more than an equal volume of fly ash (33, 54, 55, 68, 69, 74). The Alabama State Highway Department follows similar methods in proportioning mixtures. The following data are from studies (6) dealing with comparable 1-bag batches with sand and gravel aggregates:

Component	Mixture X lb	Mixture X cu ft	Mixture Y lb	Mixture Y cu ft
Cement	94	0.478	94	0.478
Fly ash	0	0	18	0.141
Water	50	0.800	50	0.800
Sand	196	1.192	204	1.237
Gravel	283	1.884	380	2.328
Air		0	(4 percent)	0.208
Total		4.354		5.192
	Cement factor, 1.555 bbl/cu yd		Cement factor, 1.30 bbl/cu yd	

Water-reducing admixtures (ASTM Specification C 494) have been found extremely effective in lean mass concrete in increasing early strength of pozzolan concrete (71) and in relatively low-cement-factor concrete (72) with fly ash and small aggregates. Unpublished studies (73) of nominal 3.5-, 4.5-, 5.0-, and 5.5-bag concrete with and without fly ash and a chemical water reducer indicate that approximately 282 lb of a 23 percent fly ash-cement blend by weight with a water reducer produce strength equal to a 3.5-bag mixture with cement alone at 28 days, and that 3.75 bags of cement plus 100 lb of fly ash plus a water reducer gives strength at 28 days equal to a 5.0-bag mixture with cement alone. A water-reducing retarder was used successfully in construction of the lining of the Tecolate Tunnel (74) where calcined opaline shale pozzolan was employed.

PROBLEMS ASSOCIATED WITH USE OF POZZOLANS

The use of pozzolans includes the practical problems associated with the use of an additional material, unless of course the pozzolan is preblended or interground with the cement. ASTM Designation C 595 covers such blends called portland-pozzolan cement and designated Type IP and Type IP-A. Little economic advantage could be expected from its use unless the Type IP and Type IP-A cements were appreciably cheaper than Type I and Type IA cements. This has not been the case to date of this report.

Fly ash, because it is composed mainly of spherical particles of glass, tends to flow more freely than cement; therefore, dust can be a nuisance (30) when handling and batching equipment is not tight and in good condition.

Problems of uniformity of fineness and specific gravity are not serious and are covered in the specifications and in the provisions for sampling and testing. Control of slump presents no more difficulty than when straight portland cement is being used.

The amount of air-entraining admixture required for adequate air entrainment may increase appreciably (30, 39, 43, 58) with the use of a pozzolan. (Generally the finer the pozzolan is, the greater will be the amount of air-entraining admixture needed.)

Fly ash, when very low in carbon, will not cause an increase in the amount of required air-entraining admixture (43) per unit of cementing material, but those fly ashes with moderate to appreciable amounts of carbon will increase the amount needed. To avoid frequent changes in carbon content of fly ash as well as to ensure uniformity of other properties, the Corps of Engineers includes the following provision in specifications: "If more than one source of fly ash is to be used, shipments from the various sources shall be in accordance with a schedule approved in advance."

ECONOMICS IN THE USE OF POZZOLANS

Pozzolans are usually cheaper than cement. The processing required is relatively simple, and the capital outlay for mining, processing, and storage is relatively low compared to that required for the manufacture of cement. Most fly ashes and some pumices require no processing. Usually the largest item of cost for pozzolan delivered to the job site or ready-mixed plant is transportation. However, it should not be assumed that transportation costs will prohibit the use of a certain pozzolan without investigation, because it has frequently been possible to deliver fly ash to a work site exceeding 1,000 miles from the source for approximately half the price of cement.

Sources or potential sources of pozzolan are available (40) throughout the United States. Some would require calcination, and others would require only drying or grinding, while most fly ashes require no processing and are available wherever coal is burned for the generation of electricity.

If pozzolan is to be batched separately, additional handling, storage, and batching equipment nearly comparable to the equipment required for cement will be needed on the project or at the ready-mixed concrete plant. This requires capital outlay and must be amortized. In established ready-mixed plants, such equipment will frequently be found and may have already been written off, or, in the case of large highway projects, the cost of the added equipment will add little to the unit cost of the concrete.

Taking into consideration the cost of extra handling equipment and storage facilities, the unit cost of pozzolan concrete will probably be less than the cost of straight portland cement concrete of the same 28-day strength, because the saving in unit quantity of cement effected through judicious mixture proportioning will outweigh the cost of the added pozzolan. However, the economics of each situation must be evaluated separately.

SUMMARY

It appears that pozzolans can be used in highway concrete to improve workability (placeability and finishing), improve resistance to sulfate and acid groundwater and seawater, minimize the effects of certain siliceous aggregates reacting with the alkalies in cement, contribute to the volume stability of concrete with sand-gravel aggregate, generally reduce cracking, and effect economies in the unit cost of concrete.

To achieve these effects it will seldom if ever be possible to use pozzolan as a replacement for cement on a pound-for-pound or equal solid-volume basis. However, by judicious mixture proportioning, possibly coupled with the use of a water-reducing admixture, it will frequently be possible to achieve a reduction in the quantity of cement per unit volume of concrete supplemented by an increased volume of pozzolan, with the cost of the resulting cement blend being less per cubic yard than the cost of using cement alone.

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