129

NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM
SYNTHESIS OF HIGHWAY PRACTICE 129

FREEZING AND THAWING RESISTANCE OF HIGH-STRENGTH CONCRETE

TRANSPORTATION RESEARCH BOARD
National Research Council

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FREEZING AND THAWING RESISTANCE OF HIGH-STRENGTH CONCRETE

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NATIONAL RESEARCH COUNCIL
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PREFACE

A vast storehouse of information exists on nearly every subject of concern to highway administrators and engineers. Much of this information has resulted from both research and the successful application of solutions to the problems faced by practitioners in their daily work. Because previously there has been no systematic means for compiling such useful information and making it available to the entire highway community, the American Association of State Highway and Transportation Officials has, through the mechanism of the National Cooperative Highway Research Program, authorized the Transportation Research Board to undertake a continuing project to search out and synthesize useful knowledge from all available sources and to prepare documented reports on current practices in the subject areas of concern.

This synthesis series reports on various practices, making specific recommendations where appropriate but without the detailed directions usually found in handbooks or design manuals. Nonetheless, these documents can serve similar purposes, for each is a compendium of the best knowledge available on those measures found to be the most successful in resolving specific problems. The extent to which these reports are useful will be tempered by the user's knowledge and experience in the particular problem area.

FOREWORD

By Staff
Transportation Research Board

This synthesis will be of interest to materials engineers, bridge designers, and others concerned with mixture proportioning, structural design, and construction of concrete bridges and highway appurtenances of high-strength concrete. Information is presented on the durability of high-strength portland cement concretes, particularly those made by using high-range water-reducing admixtures or silica fume.

Administrators, engineers, and researchers are continually faced with highway problems on which much information exists, either in the form of reports or in terms of undocumented experience and practice. Unfortunately, this information often is scattered and unevaluated, and, as a consequence, in seeking solutions, full information on what has been learned about a problem frequently is not assembled. Costly research findings may go unused, valuable experience may be overlooked, and full consideration may not be given to available practices for solving or alleviating the problem. In an effort to correct this situation, a continuing NCHRP project, carried out by the Transportation Research Board as the research agency, has the objective of reporting on common highway problems and synthesizing available information. The synthesis reports from this endeavor constitute an NCHRP publication series in which various forms of relevant information are assembled into single, concise documents pertaining to specific highway problems or sets of closely related problems.

Recent developments (high-range water-reducing admixtures and silica fume) have made the use of high-strength concrete routine. This report of the Transportation Research Board describes these developments and their effects on the durability of high-strength concrete used in highway structures. The synthesis explains the effects of high-range water-reducing admixtures and silica fume and makes recommendations with respect to the durability testing of high-strength concrete made with these products. The conclusions and recommendations are specifically applicable to highway bridge structural elements. Use of entrained air in concrete pavements and bridge decks to provide resistance to scaling caused by de-icing chemicals is not addressed in this report.

To develop this synthesis in a comprehensive manner and to ensure inclusion of significant knowledge, the Board analyzed available information assembled from numerous sources, including a large number of state highway and transportation departments. A topic panel of experts in the subject area was established to guide the researcher in organizing and evaluating the collected data, and to review the final synthesis report.

This synthesis is an immediately useful document that records practices that were acceptable within the limitations of the knowledge available at the time of its preparation. As the processes of advancement continue, new knowledge can be expected to be added to that now at hand.

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FREEZING AND THAWING RESISTANCE OF HIGH-STRENGTH CONCRETE

SUMMARY

Highway concrete structures are typically constructed with thin sections permanently exposed to the weather, subject to both wetting and freezing, and thus are vulnerable to atmospheric freezing. The highway industry pioneered the development and practical use of air entrainment as the primary defense for concrete against the ravages of freezing and thawing. For the low- and medium-strength concretes that have traditionally been used in highway applications, the use of entrained air has served very well where the exposure has not been complicated by corrosion of reinforcement caused by the application of deicing salts, as in bridge decks, or by the inclusion in the concrete of coarse aggregates of unfavorable pore characteristics, which may produce the phenomenon generally called "D-cracking."

Recent developments have made a new generation of high-strength concrete a viable material for routine construction. The two principal developments are high-range water-reducing admixtures (HRWRAs), which permit the placement of concrete of very low water-cement ratio, and silica fume, a pozzolan of extremely high fineness. The advent of this high-strength concrete has put requirements for strength and durability in conflict. Because entrained air reduces the strength of concrete, builders seek to eliminate or limit the use of entrained air. There are those who argue that high-strength concrete is of such a quality that entrained air is unnecessary. Much of the high-strength concrete is used in buildings where the probability of freezing in a saturated condition is remote; hence, relatively little attention need be given to durability. The problem cannot be avoided in exposed highway structures. Although the biggest use of concrete in highway applications, pavements, has not benefitted from the development of high-strength concrete, there are several applications that have, including bridge structural elements, dense bridge-deck overlays, and precast concrete pipe.

The resistance to freezing is directly dependent on the concrete's capacity for and its probability of containing freezable water. Even the strongest concrete now in use cannot withstand the hydraulic pressure of more than 30,000 psi (205 MPa) generated by the freezing of water. Concretes of commonly used water-cement ratios inevitably have a capacity for freezable water, even at complete hydration, and must be protected by entrained air if they have access to water. Concretes of very low water-cement ratio may have no capacity for freezable water if ambient conditions permit continuous hydration for a long period of time so that all the available space is filled with hydration products; or, short of complete space-filling, they may become so impermeable that saturation by water is unlikely in most natural exposures.

HRWRAs do not alter the pore structure of cement paste; they merely extend traditional cement technology into a range of low water-cement ratios that were previously impractical. The addition of silica fume does alter the pore structure and places more of the pore volume in pores that are so small that water cannot freeze in them at ordinary atmospheric temperatures. It offers some hope of achieving frost resistance without entrained air.

The normal test for evaluating frost resistance, ASTM C 666 (AASHTO T 161), exposes specimens to freezing at an intermediate level of maturity with no opportunity for drying before the test and exposes them to a very rapid freezing cycle. High-strength specimens without air, which may ultimately become durable, cannot be expected to do well in the test. Although the test is excellent for assessing the frost resistance of young saturated specimens to severe exposure, the resistance of mature specimens to more typical exposures might better be assessed by altering the age-at-test and specimen-conditioning requirements in C 666, or by replacing it with a critical dilation test such as ASTM C 671.

CHAPTER ONE

INTRODUCTION

Most uses of concrete in highway applications, and indeed most uses of concrete in any application, have traditionally concentrated on strengths in what is now considered to be the rather moderate strength range of 3,000 to 5,000 psi (20 to 35 MPa). Highway structures are typically constructed with relatively thin sections that are continually exposed to the weather and thus are vulnerable to durability problems. These structures, when there is a potential for exposure to freezing, are universally protected by air entrainment in North American practice. This 40-year old technology has served well to protect pavements and other structures where the exposure is not complicated by corrosion of reinforcement caused by chloride applications, as in bridge decks, or where the concrete has not contained aggregates of unfavorable pore characteristics, which are associated with the phenomenon in pavements known as "D-cracking."

There is now a trend toward higher strengths in concrete. Strengths of 8,000 psi (55 MPa) are not uncommon, and some large structures have been designed for a strength of 11,000 psi (75 MPa). The highway application that uses the most concrete, pavements, does not benefit greatly from the higher available strengths, but there are some highway applications that do. The principal beneficiaries are structural members of bridges, dense concrete overlays on bridge decks, dry-cast concrete paving units, and machine-produced, precast concrete pipe. Wherever high-strength concrete is used, a question arises as to the need for entrained air. Air voids reduce the strength of concrete and, therefore, either limit the strength obtainable or increase the cement content with a concomitant increase in cost. Much of the high-strength concrete currently being used is in buildings, where the question of durability is minor. The question, however, cannot be avoided in exposed highway structures. There are those who argue that high-strength concrete is of such high quality that it is immune to damage from freezing and thawing, but service records of non-air-entrained high-strength concrete exposed to freezing are not conclusive. Hence, this report synthesizes the available knowledge on the subject. Its aim is to provide guidance to those who wish to use high-strength concrete in typical highway applications and to indicate where further information is needed.

BACKGROUND

Assuming the use of durable aggregates, the vulnerability of mature concrete [compressive strength of at least 3500 psi (24 MPa)] to freezing is a function of the pore structure of the cement-paste phase and the moisture condition of the concrete when it is exposed to freezing.

The understanding of both the pore structure and its contribution to physical properties is still basically that developed by Powers and his coworkers in the 1940s and 1950s and reported in PCA Bulletin 22 (*1*), and several subsequent papers on the freezing phenomenon (*2–4*). The National Materials Advisory Board (*5*) states in reference to the Powers work: "This work has served as a basis for developments and modifications of the properties of concrete ever since."

A principal finding of the Powers work was that when a unit volume of portland cement hydrates, the hydration product is a colloidal solid occupying about 2.2 unit volumes. The hydrated mass is a "gel," about a quarter of which consists of very small pores. From these two simple facts much of what needs to be known about cement-paste microstructure can be deduced. For example, because the only place the gel may be formed is in the space originally occupied by cement and water, it may be seen that a water-cement ratio of 1.2 by volume is a critical value. At this value there is exactly enough space available to accommodate the products of hydration. If the water-cement ratio is higher, there will be empty space even after all the cement has hydrated. If the water-cement ratio is lower, there is insufficient room to accommodate the products of hydration of all the cement. Even under ideal conditions for hydration there will forever be unhydrated cement in the concrete. For a cement specific gravity of 3.15 the critical water-cement ratio of 1.2 by volume is 0.38 by mass.

The basic theory does not permit one to calculate pore sizes, but the observations were that the voids left as empty space between gel particles, which became known as capillary pores, were much larger than the pores within the gel. One observation particularly pertinent to the present discussion is that the gel pores are so small that water in them will not freeze at temperatures experienced in winter weather conditions, whereas the capillary pores are of such a size that water in them will freeze near, or only a few degrees below, its normal freezing point. Because gel pores are the finest pores in the system, they will imbibe water if any is available anywhere in the system. This affinity for water has the effect of removing available water from the system as hydration proceeds. To evaluate the effect, two more observations are necessary: the amount of water chemically combining with cement is about 22 percent of the mass of the unhydrated cement, and when water enters gel pores its specific volume decreases about 10 percent. Thus it may be calculated that if no water is provided from the outside, a cement paste with the critical value of water-cement ratio of 0.38 by mass will run out of water when 90 percent of the cement is hydrated.

This process of running out of water has been termed self-dessication. The water-cement ratio must be at least 0.42 by mass for there to be enough water to withstand the effects of self-dessication and still produce complete hydration. Water-cement ratios close to 0.42 probably will not permit complete hydration in the absence of outside water because a high relative humidity (above 85 percent and preferably above 90 percent) is required for continued hydration. As the water disappears, internal humidity drops.

All the above is pertinent to a discussion of the vulnerability of concrete to freezing. Any concrete having a cement paste containing capillary pores has a capacity for freezable water. When water freezes, it undergoes an increase in volume of 9 percent. If the volume of water in the capillary pores exceeds 91 percent of the volume of the capillary pores, the expansion of the water cannot be accommodated in the capillary pores. The excess water will be expelled. Because of the relatively low permeability of cement paste, the movement of water over rather short distances requires high pressures. In fact, for normal strength concretes it has been found that movement on the order of 0.2 mm (0.008 in.) is sufficient to develop pressures approaching the tensile strength of hardened cement paste. This observation, of course, provides the rationale for air entrainment. If air bubbles can be dispersed within the cement paste with a spacing between bubbles of 0.4 mm (0.016 in.), as determined by ASTM C 457, concrete has proved to be immune to damage from freezing. The air bubbles, of course, must remain at least partially empty to accommodate the excess water. But because the air bubbles comprise the coarsest pore system in the concrete, they are the first to give up their water when concrete dries. Thus concrete that undergoes some drying is protected because there is space in the air voids to receive water expelled from capillary pores. On the other hand, concrete that does not dry may not need protection. Much concrete that does not dry is permanently submerged in water, and such concrete normally is protected from freezing. There are, however, a few very severe exposures produced by rapidly fluctuating water levels where concrete in a saturated or nearly saturated condition may be exposed to freezing.

The above discussion is not confined to fresh water. In fact, there is no such thing as fresh water in the pores of concrete except, perhaps, in the ice particles freezing in the air voids. All the pore water is a solution of some concentration of the salts available within concrete and, in fact, part of the driving force that directs water to the air voids results from the concentration gradient between the pore water and the ice in the air void. Thus, exposure to salt water is not a special case. It contributes to the salt concentration in the pores, but the effect is the same as with fresh water. The principal concern for salt water is its contribution to the corrosion of steel in reinforced concrete.

As the strength of concrete increases, the required bubble spacing factor may or may not change. The tensile resistance to hydraulic pressure increases, which is good; but the permeability decreases, which, once the concrete has become critically saturated, is bad. There seems to be no possibility, however, that the spacing factor can be increased until it is comparable to structural dimensions; i.e., even the highest strength concrete cannot contain the freezing of freezable water, which exerts a force in excess of 30,000 psi (205 MPa). High-strength concrete containing freezable water, like normal strength concrete containing freezable water, must contain entrained air, possibly with a different bubble-spacing factor. If high-strength concrete is to be durable without entrained air, it must contain no freezable water. Freezable water may theoretically be excluded from concrete in three ways:

1. Eliminate capillary pores by employing a water-cement ratio below 0.38 by mass and providing moist curing until all the available space is filled with hydration products.
2. Modify the manner in which hydration products are laid down so that the capillary pores are too small to contain freezable water.
3. Produce hydrated cement pastes of such low permeability that after self-dessication has dried the interior it is impossible for water to reenter under normal conditions of exposure.

The production of concrete with zero capillary porosity is simple in theory but not necessarily simple in practice. Hydration is an asymptotic process in which the rate of hydration approaches zero as the unfilled space approaches zero. It may take a very long time, even under ideal curing conditions, to achieve zero capillary porosity. It probably cannot be achieved with a water-cement ratio of 0.38 by mass because statistically half the concrete will have a water-cement ratio exceeding 0.38; thus it will contain capillary porosity even after achieving full hydration unless one is willing to wait eons for the process of diffusion to fill the voids with hydration products from other parts of the concrete. As the water-cement ratio is decreased, the statistical problem is eliminated and the final hydration process is probably accelerated since there is an excess of cement and therefore more potential hydration sites for the available water to find, but problems in workability are introduced. One pertinent truism is that concrete that is gaining strength has a capacity for freezable water, because a concrete can gain strength only if there is available space for depositing hydration products. Thus, one cannot answer categorically the question, "Does 12,000-psi (83-MPa) concrete have capacity for freezable water?" If 12,000 psi (83 MPa) is as strong as it is ever going to be, it may well have no capacity for freezable water. If it is 12,000-psi (83-MPa) concrete on its way to 15,000-psi (103-MPa) concrete, it certainly has room for freezable water.

The discussion has recognized three types of pores. Although they are distinguished primarily by their origin, they may be roughly categorized by size (*6, 7*) as follows:

Type of pore	Diameter
gel	less than 3.2 nanometres
capillary	3.2 to 3,000 nanometres
entrained	greater than 3,000 nanometres

RECENT DEVELOPMENTS

In the past there was no wholesale effort to routinely place concrete with a water-cement ratio below 0.38 by mass (because of both workability and economic restraints) and no known way to reduce permeability significantly other than by reducing the water-cement ratio. Two recent developments, however, have changed the situation. One is the introduction of high-range water-reducing admixtures (HRWRAs), the so-called "superplasticizers;" the other is the availability of very fine forms of silica, predominately condensed silica fume from the metallic silicon and ferro-silicon industries.

The high-range water reducers represent an extension of the water reducing technology that has been available for many years. Although conventional water reducers make possible a 5 percent reduction of mixing water, the new materials make possible a water reduction four times that large with no undesirable side effects except for a propensity for rapid slump loss. With these materials, conventional concrete with a water-cement ratio of 0.20 has been shown to be possible on a routine basis with somewhat lower water-cement ratios in special situations.

Silica fume is an interesting material in that its particle sizes are two orders of magnitude finer than those of portland cement. Because of its high fineness it has an adverse effect on workability of concrete. It is only the advent of HRWRAs that has made it a viable product. It is highly pozzolanic, but some proponents argue that its principal benefit to concrete is its space-filling ability and consequent ability to alter the microstructure of the hardened cement paste.

THE CURRENT PROBLEM

Very-high-strength concrete made necessarily with a very low water-cement ratio is now being placed in the field. Most of it contains an HRWRA; much of it contains a pozzolan; some of it contains silica fume. Questions requiring answers are:

1. For those concretes containing freezable water, is a different air-bubble spacing factor applicable than that applied to normal strength concrete?
2. Can the existing technology produce concrete devoid of freezable water either by filling all the available space in the paste with hydration products, by reducing capillary pores to a size incapable of holding freezable water, or by reducing the permeability to a level that will not permit capillary pores in once-dried concrete to become 91 percent saturated?

The available literature was reviewed with these questions in mind. The review was based on the literature rather than on an examination of field structures because there are not enough documented durability studies of structures of sufficient age available for a statistically valid sample. In addition, Chapter 2 provides additional data on HRWRAs.

CHAPTER TWO

PHYSICAL STRUCTURE OF CONCRETE CONTAINING A HIGH-RANGE WATER-REDUCING ADMIXTURE

The technology of concretes containing HRWRAs is an extension of the technology of conventional water-reducing admixtures, which have been in common use for more than a generation, which in itself is merely an extension of the technology of concrete without admixtures. The properties of hardened concrete depend almost entirely on water-cement ratio and air content, regardless of the presence or absence of admixtures and regardless of the type of water-reducing admixture used. Thus, the effect of water-reducing admixtures on hardened concrete is primarily the physical effect of water reduction itself. The only significant chemical effects are those that occur during the very early reactions in the unhardened state (*8, 9*).

Because most of the properties of concrete with a water-reducing admixture are similar to those without, the only properties requiring detailed examination are those directly related to the reduced water content. In the unhardened state these are the properties directly related to the rheology of the low-water-content suspension and include workability, the maintenance of workability over a period of time before setting, and the ability to produce a satisfactory air-void system when mixed with standard air-entraining admixtures. In hardened concrete it includes a small effect on strength and other properties related to the degree of hydration, discussed under the heading Mechanism of Action, but primarily those properties such as shrinkage, which are dependent on the amount of water in the hardened concrete, and properties associated with very low water-cement ratios, which are generally unobtainable in concrete without water-reducing admixtures. A brief summary will be given of all common properties.

MECHANISM OF ACTION

There is general agreement that water-reducing admixtures perform their function by deflocculating the agglomerations or clumps of cement grains. In the normal state the surfaces of cement grains contain a combination of positive and negative charges. As they are agitated and bump into each other, they are repelled if like charges approach each other and attracted if unlike charges approach. If powders are fine enough, the surface forces are large compared to gravity forces so that agglomerations continue to grow until they become too large to sustain themselves. Admixtures are adsorbed on the surfaces of the cement particles causing them to become predominantly negatively charged. Thus, they repel each other and flocs do not form. The way to detect this phenomenon is to measure the zeta potential of solid surfaces in contact with an aqueous solution. Adding an HRWRA to a cement suspension produces a high repulsive effect as evidenced by a change in the zeta potential from −10 mV to −30 mV (*10, 11*). As a result, water is used more efficiently. This is particularly true in the unhardened state where less water is needed to provide a given consistency when the cement particles are dispersed. There is also a favorable effect in the hardened state. Because the cement is more evenly distributed, more of its surface is accessible to water; and hydration can proceed more expeditiously. This is the probable explanation for a moderate increase in strength even when a water-reducing admixture is used with no change in water-cement ratio.

There is still a need to differentiate between HRWRAs and conventional water-reducing admixtures that have long been in use. The easiest way to classify them is by water reduction. Conventional admixtures permit a reduction in water at a fixed workability of from 5 to 10 percent. An HRWRA may produce as much as 30 percent reduction. It is instructive to note dosage quantities. HRWRAs are commonly batched in quantities such that the solids in the admixture are equal to 0.5 percent of the mass of the cement, and on occasion the dosage rate may be twice that. This figure is several times the dosage rate of conventional water-reducing admixtures. It has long been known that batching conventional admixtures in ever-increasing quantities would lead to large water reductions, comparable to those now attained with the high-range product. But such massive dosages always led to undesirable side effects, chief of which were greatly prolonged setting time and excessively high air contents. Thus, HRWRAs are not different in kind from conventional water-reducing admixtures. The chemical industry has merely found materials that provide the water reduction without the detrimental side effects. This has been done by compounding condensates containing a small number of moles or by adding air-detraining agents such as tributyl phosphate or dibutyl phthalate (*12*).

REVIEW OF CONCRETE PROPERTIES

The experience with HRWRAs, with emphasis on North American practice, has been summarized by Malhotra in two 1981 papers (*8, 9*) and updated by Mielenz in 1984 (*12*). They trace the origins of these materials in Japan and Germany, discuss the chemical formulations that have been found satisfactory, indicate the uses to which the materials have been put, and review the resulting concrete properties.

Although a number of organic compounds or combinations of compounds have demonstrated successful behavior, almost all commercial formulations belong to one of four families:

- Sulfonated melamine-formaldehyde condensates
- Sulfonated naphthalene-formaldehyde condensates
- Modified lignosulfonates
- Polycarboxylate derivatives

The first two are sodium salts of high molecular weight condensates and may be augmented by set-controlling chemicals. All four are compounds of complex, high-molecular-weight organic groups.

Development of the naphthalenes started in Japan in 1958. Production of melamines began in Germany in about 1970. The modified lignosulfonates are most closely associated with recent North American practice. Other materials reported to have been used include a mixture of saccharates and acid amides, sulfonic acid esters, polybenzoaromatics, and sulfonates of aromatic polycyclic condensates.

There are basically three ways to use HRWRAs, although combinations of the three are possible:

1. To produce concrete of unusually high strength. Because low water-cement ratios are possible that are not attainable with concrete without admixtures, or even in concrete with conventional water-reducing admixtures, a new generation of strengths is now available.
2. To produce concretes with reduced cement contents. This use parallels normal practice with conventional water-reducing admixtures where the economic incentive is to produce concrete with the same workability and water-cement ratio as the control concrete by the addition of an admixture that costs less than the cement removed. For this application the cost savings of using an HRWRA is generally not as great as in using conventional admixtures because of the cost of the admixture and the dosage required, but there are places where reduction of cement has advantages other than economic, such as the reduction of temperature rise.
3. To produce "flowing concretes." A new term has been coined to describe concrete in which the slump has been increased from 75 mm (3 in.) to more than 200 mm (8 in.) with no change in cement content or water-cement ratio. Such concrete is necessarily more expensive than the control concrete, but the economic advantage lies in reduction of placing costs. The technical advantage is the achievement of high slump without the use of water. Concrete may be placed with little or no vibration and can be placed with greater assurance of freedom from honeycomb in congested forms.

In Japan interest is primarily in high-strength concrete in accordance with Method 1. In Germany flowing concrete is clearly the method of choice. It is not yet clear what the primary use will be in North America. To date the most popular application has been in precast plants in what might be considered a fourth application. It has been found that concretes of low water-cement ratio gain strength rapidly. Thus, a fast turnaround time for forms can be maintained with no cost for energy to supply heat for accelerated hydration. The material has been used in some bridge decks, but it has not been generally adopted in highway structures. There are understandable reasons. One of the principal problems with the use of HRWRAs has been fairly rapid slump loss during mixing and placing. This is not a problem in precast plants, but it does plague ready-mix operations. In Germany, where the emphasis is on flowing concrete, the practice is to add the admixture at the jobsite just before dumping. This procedure works well because flowing concrete without the admixture is a workable concrete. Flowing concrete has not become popular in North America, possibly because many specifications do not permit high-slump concrete.

Unhardened Concrete

Because much HRWRA is used only to improve the placeability of concrete, it is pertinent to examine its effect on setting time, bleeding, segregation, and requirements for vibration.

Setting times can be a bit erratic. Many HRWRAs are formulated with set-controlling chemicals to overcome a propensity for an adverse effect on setting time in the active ingredients. But because the dosage depends on a particular workability characteristic desired, the dosage may not provide optimum setting performance. Typical data (*13*) show both acceleration and retardation with a maximum departure from the control of 1½ hours, as shown in Figure 1.

The same reference gives data on bleeding, shown in Figure 2. The reference concrete has a water-cement ratio of 0.5. The test concretes have the same cement content and slump, but a water-cement ratio of 0.40. Possibly because there is so much less water to bleed, the concretes with the HRWRA demonstrate much less bleeding.

Segregation is particularly critical. Flowing concrete with no admixture would be completely out of the picture because of

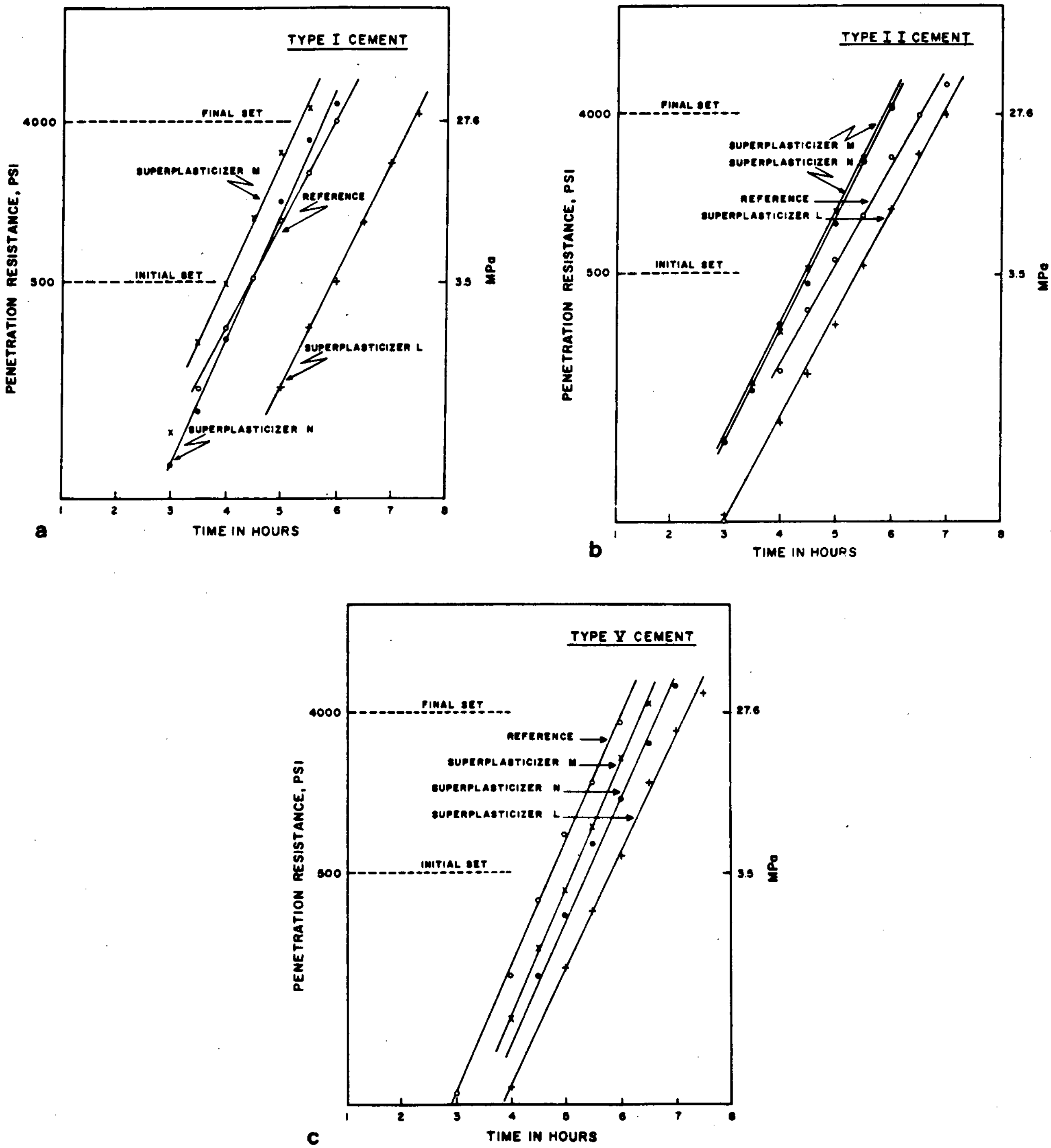

FIGURE 1 Setting time characteristics of reference and superplasticized concretes (a) Type I cement, (b) Type II cement, (c) Type V cement (from Ref. *13*).

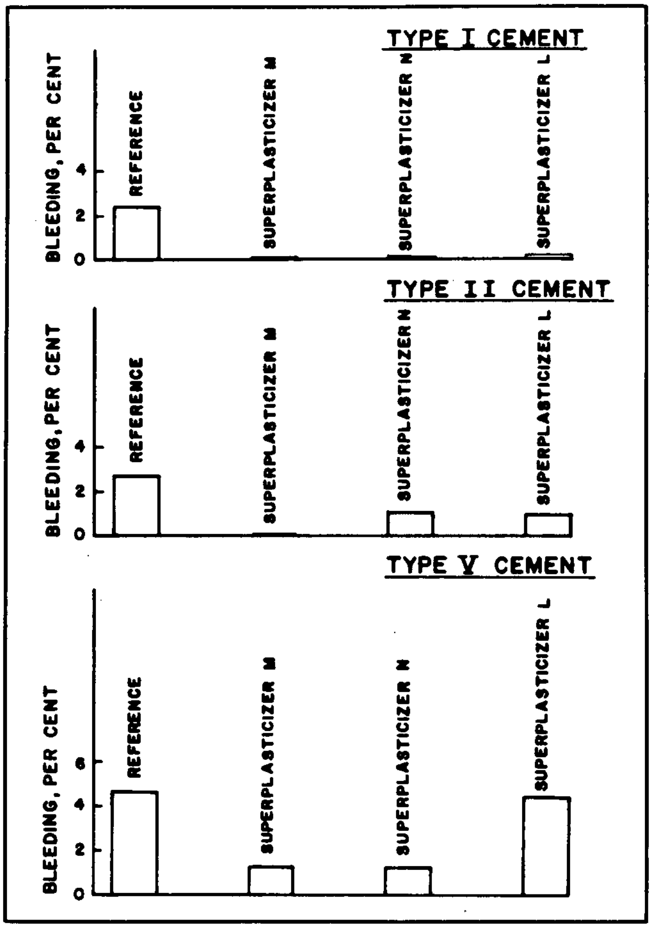

FIGURE 2 Bleeding characteristics of reference and superplasticized concretes (from Ref. *13*).

excessive segregation. Field observations generally confirm that one of the principal benefits of HRWRAs is the absence of segregation at high slumps. An extensive laboratory study of segregation by Soshiroda (*14*), in which he measured segregation by a remolding apparatus and differences in coarse aggregate content between the tops and bottoms of specimens, demonstrated that excessive dosages of HRWRA could induce segregation, but even when segregation was induced there was little effect on the physical properties of the hardened concrete.

The theory of flowing concrete is that concrete can be placed essentially without vibration. In two interesting series of tests reported by Malhotra (*15, 16*), flowing concrete was placed in cylinder molds with and without vibration. The results shown in Figure 3 demonstrate some advantage in vibrating, but they indicate that very acceptable concrete resulted when no vibration was provided.

Hardened Concrete

Although some HRWRA is used to obtain strengths essentially unattainable otherwise, it is instructive to examine the effect on strength where a direct comparison is possible. Such data are shown in Table 1 where the water-cement ratio and slump were held constant and the cement content was adjusted as necessary (*12*). Even at the age of one year all the concretes containing HRWRA were stronger than their control, although in one case by only 1.6 percent.

Modulus of elasticity follows compressive strength (*13, 18*). At all ages the concrete with HRWRA tends to be somewhat stiffer than concrete without. The effect is compounded by the fact that under most conditions of comparison the concrete with the admixture has a smaller paste content with a corresponding larger aggregate content. The effect on creep is not readily identified with the data available. Ghosh and Malhotra (*13*) and Brooks et al. (*18*) both ran comparisons between control concretes and admixtured concretes with identical cement contents and slumps. Because the concrete with the admixture had a lower paste content, a lower creep might have been anticipated. Ghosh and Malhotra found virtually identical creep. Brooks et al. found a variety of behavior, depending on storage and loading conditions. In most cases the concrete with the admixture showed more creep than the control. They concluded, however, that except for one case where concrete was stored continuously in water, the specific creep of the two concretes was the same. They attributed the greater creep in the admixture concrete to the fact that at all ages of loading the concrete with the admixture had attained a greater fraction of its ultimate load than the control. As a result, the control, by virtue of the fact that it was gaining more strength during the test, manifested less creep. As always, part of the creep phenomenon must be related

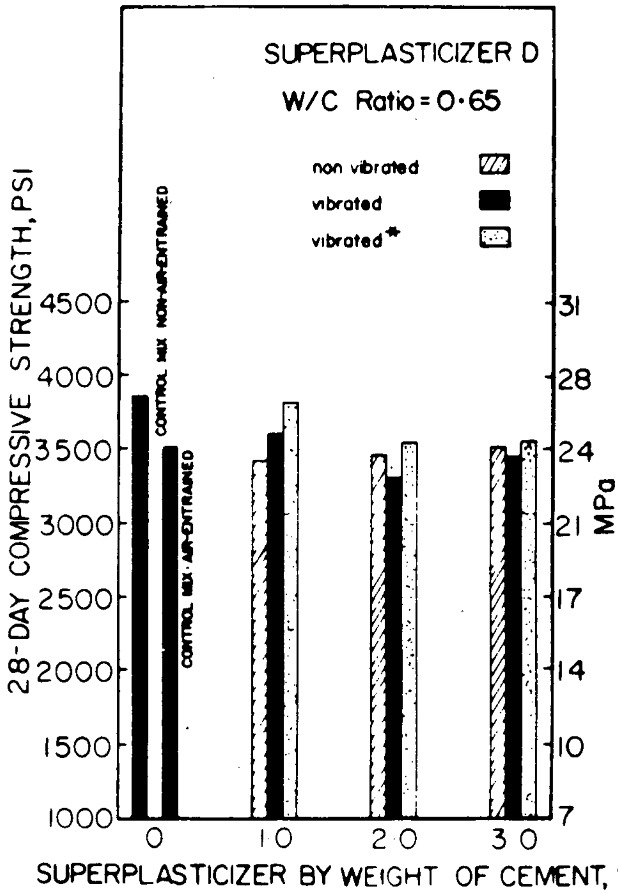

FIGURE 3 Example of compressive strengths of vibrated and nonvibrated cylinders at 28 days (from Ref. *16*).

TABLE 1

PERCENTAGE INCREASE IN COMPRESSIVE STRENGTH OF SUPERPLASTICIZED RELATIVE TO CONTROL CONCRETE WITH SAME WATER-CEMENT RATIO (FROM REF. *12*)

	Increase in strength relative to control mix, %			
Age days	Concrete containing superplasticizer A	Concrete containing superplasticizer B	Concrete containing superplasticizer C	Concrete containing superplasticizer D
7	28.6	33.8	5.4	20.8
28	10.9	18.1	6.5	3.3
183	13.7	28.0	7.6	3.3
365	15.8	13.7	5.4	1.6

Notes: 1. All mixes including control had a water to cement ratio of 0.50, a slump of 100 ± 25 mm and an air content of 6 ± 1 percent immediately before the casting of test specimens.
2. Maximum size of gravel was 13 mm and cement was ASTM Type I.
3. The mix proportions for the control and superplasticized mixes were as follows:

	C.A.	F.A.	Cement	Water
(i) Control mix, kg/m³	882	813	393	196
(ii) Superplasticized mix kg/m³	872	982	290	145

4. Superplasticizer A refers to a melamine formaldehyde condensate.
Superplasticizer B refers to a high M.W. naphthalene condensate of Japanese origin.
Superplasticizer C refers to a sulfonated polymer of Canadian origin.
Superplasticizer D refers to a polymerized naphthalene condensate of U.S.A. origin.

to shrinkage, which is discussed below. The available data seem to warrant two observations:

1. Concrete containing HRWRA may be expected to creep at least as much and possibly more than concrete without, and
2. More information on creep is needed.

SIGNIFICANT PROBLEMS

Although experience with HRWRA's has been good, two problems have dominated discussions between investigators and practitioners: slump loss and development of an adequate air-void system. In addition, with every admixture there is concern for the volume stability of the concrete in which it is used.

Slump Loss

All concrete undergoes some slump loss as it waits to be placed. The dormant period following the initial quick reactions when cement comes in contact with water is not completely dormant. Any phenomenon that robs the concrete of water, whether it is evaporation or chemical reaction, is certain to be accentuated in a concrete containing a small amount of water, because there is less total water available to maintain workability. The normal experience with HRWRAs is that they increase the slump about 150 mm (6 in.) within a few minutes after their addition but that the increased slump is maintained for only 30 to 60 minutes, at which time it returns to the original slump over a like period of time.

The mechanics of slump loss in concrete containing admixtures was described by Lieber and Richartz in 1972 (*19*) and is often cited. When hydration begins, the initial reactions are between SO_3 and C_3A to form ettringite. The reaction proceeds very slowly and requires about 24 hours to reach completion. But it is the only reaction occurring in the first couple of hours of the concrete's life, and it proceeds with little effect on workability. Eventually the formation of calcium silicate hydrate starts the solid structure. Organic admixtures, including both those that accelerate or those that retard the setting time, tend to accelerate the formation of ettringite so that substantially all the SO_3 may be reacted in an hour. The rapid ettringite formation produces stiffening. If the admixture is a water reducer, it may prevent the early reaction of the C_3S because of its adsorption on the C_3S particles. Thus there may be slump loss accompanied by very little strength gain. On the other hand, Hattori (*20*) argues that the effect is physical rather than chemical. He believes that the cement agglomerates during the dormant period as the adsorbed layer disappears. His argument is bolstered by zeta potential measurements, by the observation that redosing of the concrete with HRWRA restores the slump, and by photomicrographs that demonstrate a change from the agglomerated to dispersed state before and after redosing.

There have been several studies of redosing to restore slump. Data from a study by Malhotra (*21*) are shown in Figure 4. In that report he recommended against a third dosage because the concrete loses its workability in spite of the recovered slump. This observation may argue against the premise that the effect is entirely physical. In fact Ramachandran (*22*) treated the problem entirely as chemical and added a series of retarders to concrete containing HRWRA. He found that sodium gluconate worked best. However, it solved the problem not by maintaining the initial slump but by adding to the initial slump and subsequently undergoing slump loss over a period of two hours to return to the original value. Although there are both chemical and physical aspects to the problem, the evidence suggests that the physical effects predominate.

Air-Void System

The normal requirement for concrete that must be resistant to freezing and thawing is a maximum spacing factor of 0.2 mm (0.008 in.) when determined microscopically by the method given in ASTM Standard Practice C 457 (*23*). These factors are routinely and easily obtained in concrete without water-reducing admixtures by adding to the concrete an air-entraining admixture meeting the requirements of ASTM C 260 (*24*). It has been stated that when conventional water-reducing admixtures are used the spacing factor is slightly increased (*25*). With HRWRAs the problem is compounded. Although it has not

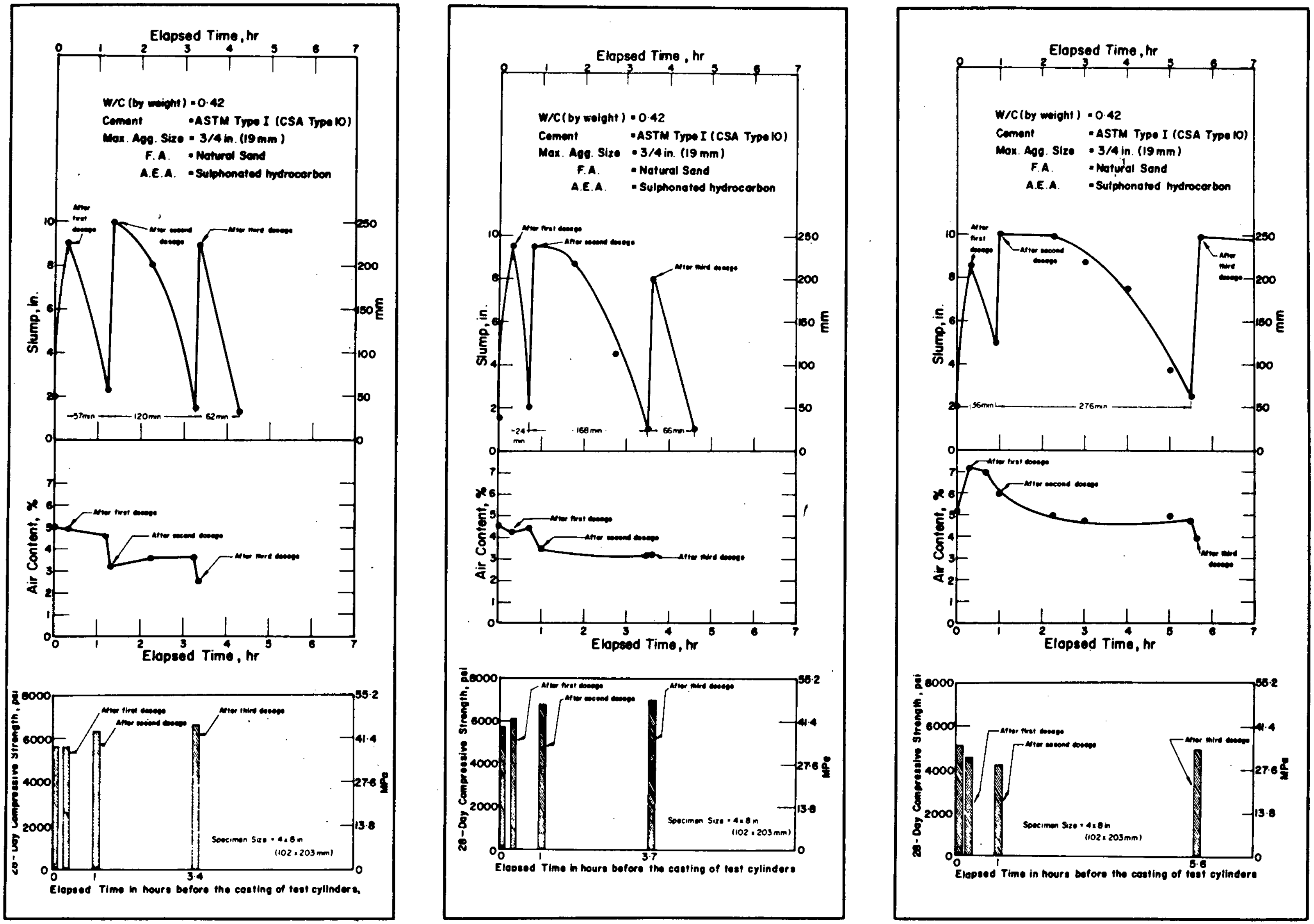

FIGURE 4 Effect of repeated dosages of three different superplasticizers on slump, air content, and 28-day compressive strength of concrete (from Ref. *21*).

been difficult to obtain specified air contents, it has proved very difficult to satisfy the normal criterion for spacing factor. At least 20 papers in the literature give results demonstrating noncompliance. Very few demonstrate compliance. Typical of those showing noncompliance are the paper by Roberts and Scheiner (*26*), which shows spacing factors 0.367 mm and 0.41 mm for concretes containing HRWRA, having air contents of 4.8 percent and water-cement ratios of 0.54 and 0.50, respectively; and the paper by Kobayashi et al. (*27*), in which 17 of 18 results for air-entrained concretes, containing HRWRAs and having water-cement ratios ranging from 0.27 to 0.55, were in the range 0.245 mm to 0.825 mm. Among the few demonstrating compliance, Okada et al. (*28*), as shown in Table 2, found five of seven below or substantially equal to 0.2 mm for HRWRA concrete having 4 percent air and water-cement ratios from 0.25 to 0.55. Malhotra (*29*) found, in comparing two HRWRAs at three water-cement ratios with corresponding concretes without admixture, five of the six possible comparisons showed higher spacing factors with HRWRA than without, but half also had results below 0.2 mm, ranging from 0.151 mm to 0.259 mm.

TABLE 2

STRENGTH, DURABILITY, AND AIR-VOID SYSTEMS OF CONCRETES CONTAINING HIGH-RANGE WATER-REDUCING ADMIXTURES (FROM REF. *28*)

Mixture Number	W/C	Target Air (%)	Durability Factor[b] (300)	Durability Factor[b] (1000)	Weight Decrease (%)[b] (300)	Weight Decrease (%)[b] (1000)	Air-Void System[a] A_h (%)	n (mm^{-1})	α (mm^2/mm^3)	$\bar{L}$ (mm)	Strength (28-day) (MPa)
1	0.25	1	102	105	-0.1	0	0.40	0.019	18.96	0.774	104.1
2	0.25	2	102	105	0	0	1.29	0.063	19.58	0.459	99.8
3	0.25	3	102	105	0	0.1	2.10	0.153	29.82	0.246	101.0
4	0.25	4	99	105	0.1	0.1	3.02	0.243	31.96	0.191	97.8
5	0.30	1	102	105	-0.1	0	0.70	0.022	14.08	0.958	100.9
6	0.30	2	100	103	0.3	0.5	1.40	0.063	18.17	0.484	89.7
7	0.30	3	100	105	0.4	0.7	2.09	0.186	36.81	0.200	93.4
8	0.30	4	101	103	0.3	0.7	3.78	0.361	19.78	0.140	85.0
9	0.35	1	101	24	0.2	-	1.09	0.026	9.86	1.029	82.4
10	0.35	1	101	104	0	0	1.03	0.031	12.09	0.882	91.4
11	0.35	2	101	102	0.6	0.8	1.22	0.070	30.38	0.382	80.1
12	0.35	3	101	102	0.5	0.9	2.72	0.252	37.47	0.172	78.0
13	0.35	4	100	103	0.6	1.0	5.62	0.376	27.08	0.168	73.0
14	0.40	1	56	17	-0.1	-	0.92	0.023	9.86	1.065	75.4
15	0.40	2	56	17	0	-	1.17	0.044	15.81	0.623	73.9
16	0.40	2	99	54	0.7	4.1	1.42	0.055	16.93	0.541	75.2
17	0.40	3	96	98	0.7	2.7	2.10	0.142	28.21	0.265	72.5
18	0.40	4	101	102	0.1	1.4	2.72	0.209	30.86	0.206	69.4
19	0.45	1	31	9	-	-	0.70	0.027	18.57	0.729	65.6
20	0.45	2	76	23	4.2	-	0.95	0.046	19.58	0.527	57.4
21	0.45	2	89	29	0.7	-	1.12	0.049	17.14	0.556	65.7
22	0.45	3	93	19	2.1	-	1.65	0.122	29.78	0.269	59.7
23	0.45	4	99	100	1.0	4.5	-	-	-	-	57.3
24	0.50	1	11	3	-	-	0.55	0.011	8.11	1.681	56.3
25	0.50	2	34	10	-	-	1.17	0.033	11.32	0.829	53.4
26	0.50	2	30	9	-	-	0.81	0.035	18.07	0.678	57.0
27	0.50	3	54	16	1.9	-	1.28	0.073	22.80	0.393	54.2
28	0.50	3	98	84	1.2	-	1.66	0.143	34.88	0.234	54.1
29	0.50	4	99	101	1.4	6.2	2.00	0.130	26.14	0.281	52.0
30	0.55	1	4	1	-	-	0.62	0.014	8.66	1.456	52.0
31	0.55	2	46	14	-	-	0.81	0.036	17.63	0.623	54.3
32	0.55	2	92	76	3.8	-	1.42	0.104	30.45	0.296	48.6
33	0.55	3	99	89	1.6	8.9	1.63	0.107	26.47	0.307	50.6
34	0.55	3	98	88	1.5	7.1	2.82	0.224	35.52	0.200	47.9
35	0.55	4	101	100	0.8	6.3	2.19	0.189	7.48	0.203	49.3

[a]A_h = Air content in hardened concrete
n = Average number of air-void sections intersected per mm of traverse
α = Specific surface area
$\bar{L}$ = Spacing factor

[b]For 300 and 1000 cycles of freezing and thawing.

Volume Stability

There are two forms of volume instability that are of concern to concrete practitioners: plastic shrinkage and shrinking and swelling of hardened concrete. Plastic shrinkage occurs primarily on slabs, before the concrete has set, when the rate of evaporation from the surface exceeds the rate at which water is supplied to the surface either by bleeding or by an external source, such as a fog spray. Drying of the surface puts it in tension and, because the tensile strength of the unhardened concrete is near zero, cracking is likely. The cracking usually does not impair the serviceability or the durability of the concrete, but it is esthetically objectionable. Cracks are most likely to occur in hot weather when the humidity is low and wind velocity high. Concretes that do not bleed much are especially vulnerable. Concrete containing an HRWRA is such a concrete, and it has demonstrated plastic shrinkage cracks in unfavorable weather conditions. The standard preventive measures of establishing windbreaks and supplying water to the surface or preventing evaporation from the surface should be followed.

Data on shrinking and swelling of hardened concrete are limited. Ghosh and Malhotra (*13*) published results of 112 days' shrinkage of concretes of equal cement contents and consistencies, with the water-cement ratios adjusted. The results are plotted in Figure 5 with shrinkage plotted as a function of water loss. For a given water loss (expressed as a fraction of the original mixing water), there is considerably more shrinkage in the concrete containing admixture. Absolute shrinkage at a given age was about the same for both types of concrete, although all other things being equal the concrete with admixture might be expected to shrink less because of its smaller paste content. Brooks et al. (*18*) in a similar comparison found a greater shrinkage for concrete containing the admixture on the first drying but essentially equal swelling and shrinkage on subsequent rewetting and drying. These results are consistent with the observation of Feldman and Swenson (*30*) that on the first drying the dispersion of the gel caused by the HRWRA facilitates desorption of the interlayer water but that there is no particular effect on behavior on subsequent wetting and drying cycles. The Ghosh and Malhotra data also seem to support this observation.

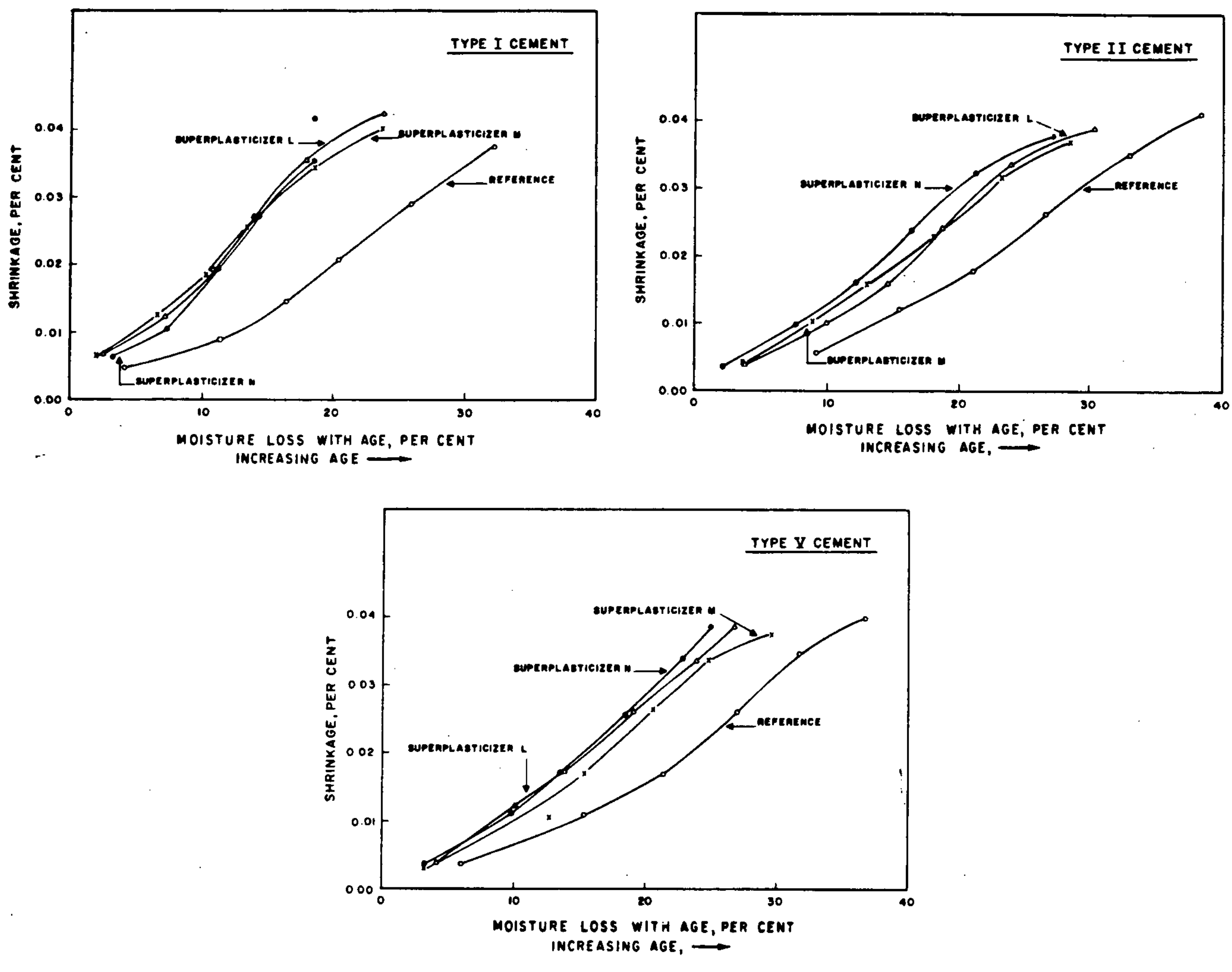

FIGURE 5 Shrinkage as a function of moisture loss for reference and superplasticized concretes (from Ref. *13*).

PORE STRUCTURE

A key question that must be answered to interpret freezing and thawing as well as other physical properties is whether HRWRAs alter the pore structure other than in the manner in which they affect the air-void system. Litvan (*31*) determined pore size distributions by mercury porosimetry of mortars with and without HRWRAs and with and without air entrainment. The results are shown in Figure 6. At this time the curves of interest are the solid curves, which represent non-air-entrained mortars. Specimen 461 contains no HRWRA. The pair of curves in each of the upper three diagrams represents the use of a particular HRWRA at two different dosages, in all cases the lower dosage being that recommended by the manufacturer. All mortars had identical mixture proportions with a water-cement ratio of 0.65. The workability was allowed to vary. Thus, the batches containing HRWRA may be considered as representative of flowing concrete. It may be easily seen that grossly overdosing the mortars had little effect on pore-size distribution. A closer examination also discloses that there is little difference in pore sizes between the admixtured concrete and the concrete without admixture. For example, the concrete with neither air entrainment nor HRWRA had a porosity volume of 7.5 percent in pores with a diameter of less than 0.1 micrometre. For the six non-air-entrained mortars containing HRWRAs the corresponding values were 7.1, 6.2, 7.2, 7.5, 7.0, and 8.6 percent. The range for the mortars with the admixture contain the value for the concrete without admixture, and there is no consistent trend. It should be noted that these data were obtained for mortars with a water-cement ratio of 0.65, which does not take advantage of the peculiar properties of HRWRAs. From the available data it may be concluded that HRWRAs do not affect the size distribution of capillary pores at a given water-cement ratio. The advantage of HRWRAs, as far as porosity is concerned, is that they permit placing the very low-porosity concretes associated with low water-cement ratios, which are essentially impossible without admixtures.

SUMMARY

HRWRAs function by placing an adsorbed layer on cement grains to produce a surface that is predominately negatively charged with the result that cement particles repel each other and do not flocculate. The difference between the high-range and conventional water-reducing admixtures is that the high-range may be used in larger dosages without harmful side effects, thus providing more water reduction. The adsorbed layer is temporary and may degrade while concrete is awaiting placement with a resulting flocculation and loss of slump. HRWRAs are used to produce very-high-strength concrete, to produce concretes with reduced cement contents, or to produce flowing concrete for easy placement. The principal effects on freshly mixed concrete, in addition to the problem of slump loss, are a propensity for plastic shrinkage cracking and the difficulty in entraining an air-void system that meets conventional void spacing criteria. The effects on hardened concrete are primarily those associated with a reduced water content, except where flowing concrete is used, in which case there is little effect on the hardened concrete other than the characteristics of the air-void system. On the first drying there might be more shrinkage in concrete containing HRWRAs than in corresponding concrete without admixture because dispersion of the gel facilitates desorption of the interlayer water. This effect can be largely overcome by the lower paste content made possible by use of the admixture. There is no effect on subsequent wetting and drying. At equal water-cement ratios, capillary porosity is essentially unaffected by HRWRAs. The same principles that relate physical properties to microstructure apply whether or not an HRWRA is used.

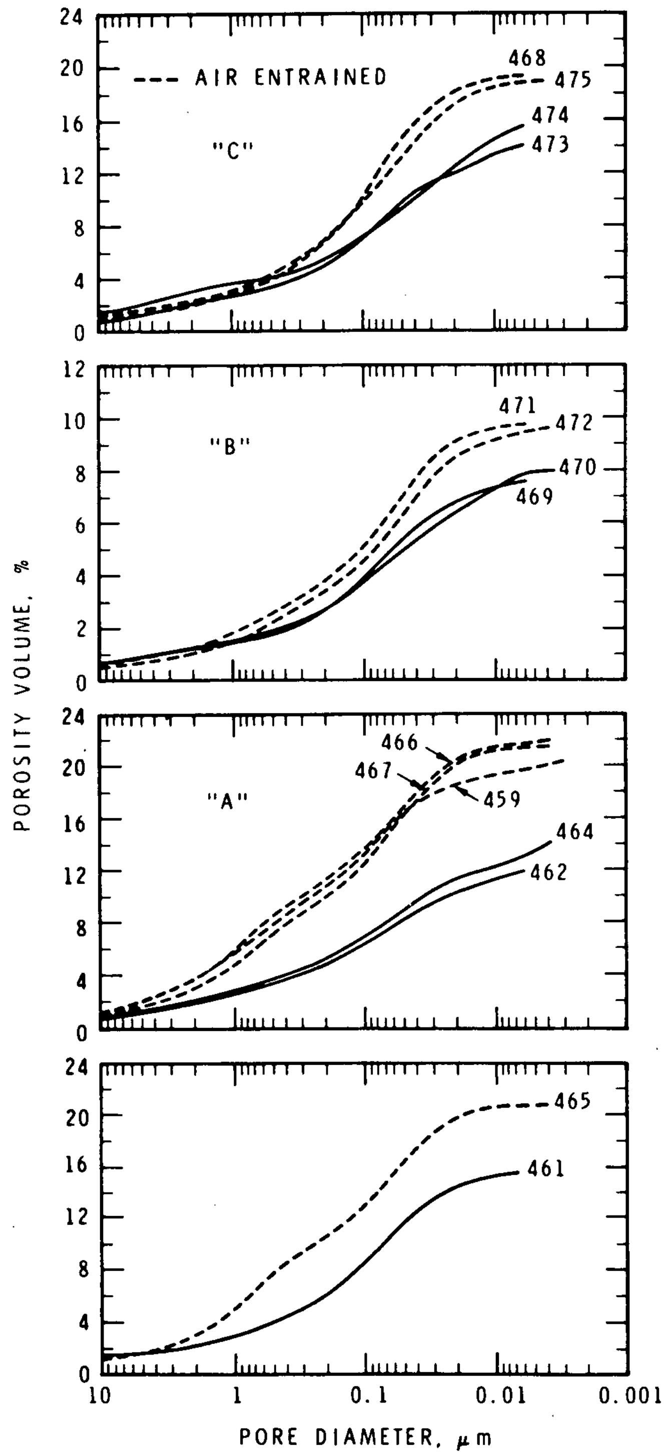

FIGURE 6 Pore size distribution of specimens by mercury intrusion porosimetry (adapted from Ref. *31*).

CHAPTER THREE

PHYSICAL STRUCTURE OF CONCRETE CONTAINING SILICA FUME

Silica fume is most readily obtainable as a byproduct of the production of elemental silicon or ferro-silicon alloys. It consists of extremely fine spherical glassy particles with a silica content of from 85 to 98 percent and an average particle size of about 0.1 μm, or two orders of magnitude finer than cement particles. When added to concrete it affects many properties, the most notable of which are an increase in strength, a decrease in permeability, and a decrease in electrical conductivity. The dosage may be as high as 20 percent by mass of cement, although usually it does not exceed 10 percent. It may be used as an addition or as a cement replacement. It has been found that when used as a replacement one part of silica fume may replace three or four parts of cement to yield the same 28-day strength. Because of its fineness, silica fume has an adverse effect on water requirement of concrete. For that reason, an HRWRA is usually used in concrete containing silica fume.

There are two possible explanations for the effects of silica fume: the fine particle effect and the pozzolanic effect. The most comprehensive study to determine the relative effects of these two mechanisms was that carried out by Sellevold et al. (*32*). They prepared cement pastes with water-cement ratios of 0.40 and 0.60 by mass and with additions of silica fume ranging from 0 to 20 percent of the mass of cement. In addition, they included a calcium carbonate with a fineness comparable to that of silica fume, added in the amount of 12 percent by mass of cement, to make it possible to distinguish between fineness effects and pozzolanic effects. The water-cement ratios selected did not make possible very-high-strength concrete, but they made it possible to place the pastes without the addition of admixtures. Thus, the effects on structure were those caused by silica fume alone without the complicating effects of other admixtures.

The authors were particularly interested in the pozzolanicity of silica fume and in the effect of silica fume on pore structure. Pozzolanicity was established by the thermal-gravimetric analysis shown in Figure 7. The calcium hydroxide content of mature pastes is a function of silica fume addition. Extrapolation indicates that 24 percent silica fume would consume all the calcium hydroxide. They studied pore structure in three ways: mercury intrusion, water sorption, and low-temperature calorimetry. Specimens were water-cured until tested. Details of the experiments are given in Appendix A. Their results are summarized in Figure A-7 in the appendix, where it is demonstrated that all three methods show that gel porosity is an increasing function of silica content. The authors define porosity by size, not by origin. Thus, the introduction of silica fume reduces some of the capillary pores to the size of gel pores. Hence, the paste component of concrete is changed qualitatively when silica fume is added.

Recently Cheng-yi and Feldman (*33,34*) have studied the pore structure of pastes containing portland cements with and without silica fume. Their mercury porosimeter results were very similar to those of Sellevold et al. But they performed several additional tests. They removed the mercury and reintruded specimens in accordance with a technique previously developed by one of the authors (*35*), and mortar specimens as well as paste specimens were included. The reintrusion technique is intended to detect unconnected pores. A greater intruded volume on the second intrusion indicates that the mercury broke through pore

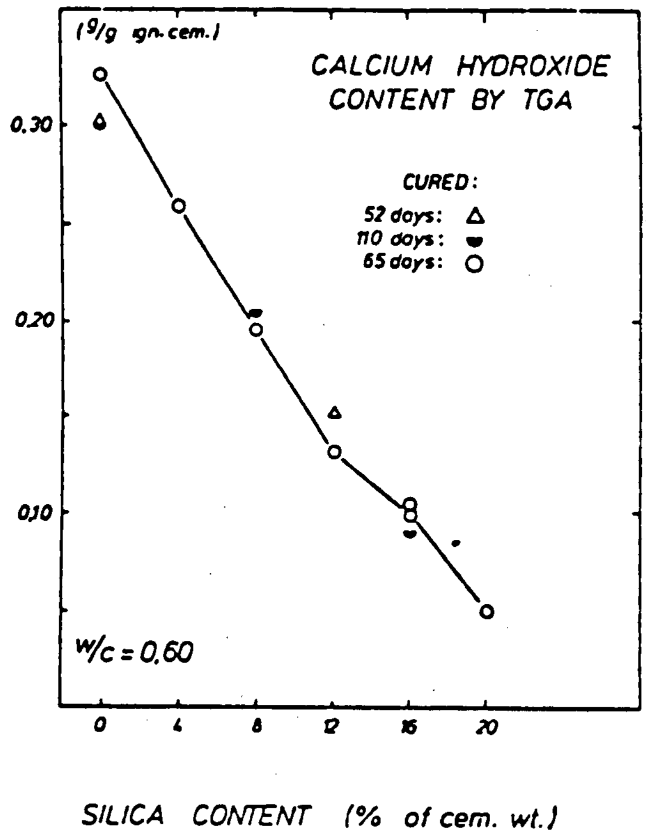

FIGURE 7 Calcium hydroxide content of mature pastes with different silica fume contents (from Ref. *32*).

walls to reach pores that were not accessible during the first intrusion. Because they had to heat the specimens to remove the mercury, they may be observing the same effect of drying reported by Sellevold et al. Plots of the first and second intrusions for a water-cement ratio of 0.45 by mass and silica fume contents of 0, 10, and 30 percent are shown in Figure 8. The spread between the curves is an indication of the quantity of discontinuous pores. It is seen that there are few discontinuous pores in the paste without silica fume, and the quantity of such pores increases as the quantity of silica fume increases. The same conclusion is reached when comparing total porosity by mercury porosimetry and by drying. The advantage of the second intrusion technique is that it estimates the sizes as well as the total quantity of discontinuous pores. The lack of continuity provides an explanation of the low permeability of concrete containing silica fume.

The comparison between pastes and mortars is interesting. Mortars contain more and larger discontinuous pores than paste. The authors conclude that in the early stages of hydration calcium hydroxide crystals form preferentially along the surfaces of fine aggregate particles. The reaction of the silica fume with these crystals improves what otherwise would be a relatively weak bond between paste and fine aggregate. In mortars, then, strength as well as impermeability is improved by the addition of silica fume.

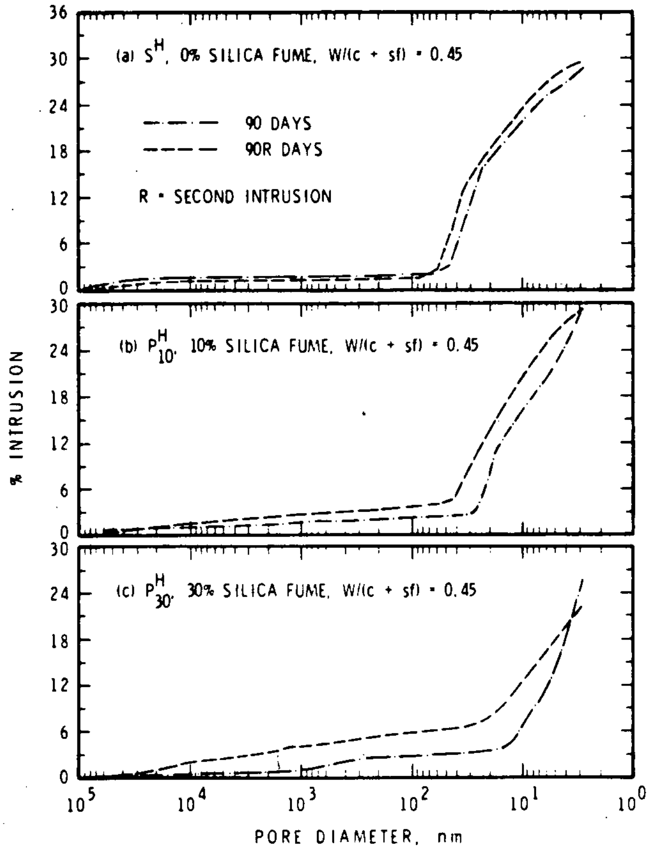

FIGURE 8 Pore-size distribution of cement paste with different silica fume contents, two intrusions, (w/c+sf) = 0.45, 90 days curing: (a) 0% silica fume, (b) 10% silica fume, (c) 30% silica fume (from Ref. *34*).

SUMMARY

The effect of silica fume on concrete depends both on its fineness and pozzolanic activity. The fineness apparently creates more hydration sites for cement and produces a hydrated structure that is a scale model of the hydrated product without such dispersion. Thus, it reduces the size of capillary porosity and provides a greater probability of discontinuous porosity without affecting total porosity. The pozzolanic activity increases the amount of gel porosity. Both effects decrease the number of pores in which water can freeze in winter ambient conditions. The probability, then, of creating concrete with no freezable water is greater for concrete containing silica fume than without, and the greater discontinuity of porosity decreases permeability. Strengths in mortars and concrete are increased by the reaction between silica fume (as well as other pozzolans) and the calcium hydroxide crystals that preferentially form along inclusions such as aggregates.

CHAPTER FOUR

RELEVANCE OF AIR-BUBBLE SPACING IN HIGH-STRENGTH CONCRETE

There is an abundance of data on tests for freezing and thawing of high-strength concrete, most of which contains an HRWRA. Interest was sparked by an early paper by Tynes (*36*), the data from which were repeated by Mather (*37*). Tynes studied concretes containing 517 pounds of cement per cubic yard (307 kg/m^3) with a nominal air content of 6 percent, both with and without HRWRA. The water-cement ratio was 0.45 by mass for the concrete without HRWRA and in the range of 0.34 to 0.37 for concretes with admixture with compressive strengths of about 5,000 psi and 11,000 psi (34 and 76 MPa), respectively. The concrete without admixture had a spacing factor of 0.08 mm, well below the value of 0.2 mm frequently recommended, and a durability factor of 84, a very acceptable value. The concretes containing the admixture had spacing factors ranging from 0.2 to 0.3 mm with durability factors ranging from 14 to 55. The author attributed the poor performance of the concrete containing HRWRA to the inability of the air-entraining admixture to entrain a proper air-void system in the presence of the HRWRA. At about the same time Mielenz and Sprouse (*38*) and Perenchio et al. (*39*) concluded that HRWRA may, indeed, produce a spacing factor higher than desirable by conventional criteria but that it produces durable concrete at the higher spacing factors. Since then a controversy has continued as to whether HRWRA necessarily produces higher spacing factors and whether conventional spacing factors are applicable to concrete containing HRWRAs.

THE PROBLEM

The commonly used test for resistance to freezing and thawing is the ASTM Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, Designation C 666 (*40*). There are two permissible options: Procedure A, freezing and thawing in water; and Procedure B, freezing in air and thawing in water. For each procedure the equipment must be capable of a complete cycle within the range of 2 to 5 hours. Specimens are stored in water from the time of their removal from their molds until exposure to the freezing-and-thawing cycle, and the normal age at the beginning of the exposure is 14 days. The condition of specimens during exposure is monitored by dynamic tests for resonant frequency, from which the dynamic modulus of elasticity may be calculated. The durability factor is the ratio of the dynamic modulus of elasticity after 300 cycles to the initial, expressed as a percent. Although the test is severe, concrete specimens having an adequate air-void spacing factor and containing sound aggregates regularly produce durability factors near 100; the test has proved useful in evaluating the susceptibility of aggregates to D-cracking. The bubble-spacing factor of 0.2 mm usually accepted as desirable was established primarily from empirical data from this test, although theoretical considerations based on cement paste permeability and strength confirm the order of magnitude for this parameter.

As early as 1955, Powers (*41*) complained that the test was too severe to be of practical value. His complaint was two-fold: no drying of specimens is permitted in Procedure A and only a limited amount in Procedure B, and the rate of freezing is many times that typically occurring in nature. Virtually all concrete subject to freezing undergoes some drying. Most concrete that does not dry is concrete that is permanently far enough under water to benefit from the insulating effects of water or ice, and such concrete is protected from freezing. The rapid rate of freezing in the freezing-and-thawing test departs from nature in two ways. The rate at which ice forms determines the rate at which water will be forced through the capillaries and thus determines the pressures that will be built up in a given distance of capillary. On the other hand, the speed of testing minimizes the time at which the concrete is held below freezing and thus greatly limits the opportunity for osmotic accretion to take place.

Powers proposed an alternative test. He proposed that specimens be conditioned to the moisture content the pertinent field concrete could be expected to have attained at the start of the freezing season, then stored in water and periodically subjected to a slow freezing cycle. If the length of the specimen decreased linearly down to a temperature of 15°F (−9.4°C), it was deemed to be not critically saturated and thus immune to damage from freezing at that rate. If in the freezing range the length departed from the straight line in an expansive direction (see Figure 9), this undesirable dilation was evidence of critical saturation and vulnerability to freezing. If the specimen remained in water storage for a length of time equal to the freezing season at the site without undergoing dilation, it could be considered durable for use at that site. In principle, only one cycle need be run: that at the end of the freezing season. In practice it has been found that some dilation occurs in any concrete containing freezable water and that "critical dilation" may be defined as the dilation, at critical saturation, that cannot be elastically accommodated by the concrete.

Shortly after it was proposed, the test was implemented by the California Division of Highways (*42*) to evaluate aggregates for a major highway construction project. They placed concrete slabs of the same thickness as the prototype pavement at the site of the project and measured their moisture content at the start of the freezing season. Then specimens conditioned to the

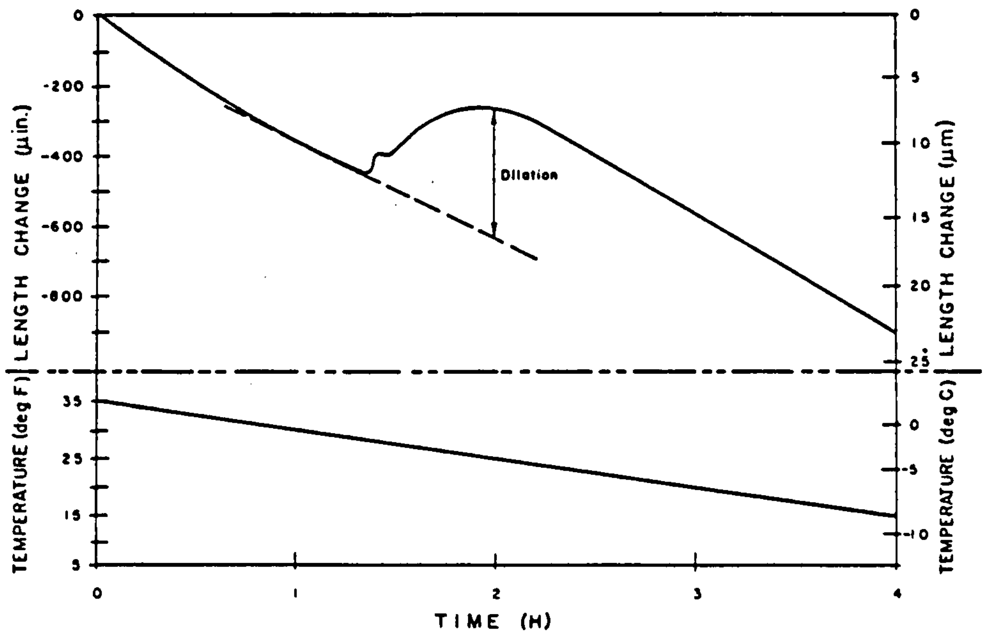

FIGURE 9 Typical length change and temperature curves in dilation test (from Ref. *41*).

same moisture content were subject to the dilation test. This approach permitted the use of aggregates that would have been rejected by approaches then in use at the Division of Highways. Performance of the prototype has verified the correctness of the decision.

The dilation test was standardized by ASTM in 1971 as Standard Test Method for Critical Dilation of Concrete Specimens Subjected to Freezing, Designation C 671 (*43*). The method requires a cycle every two weeks and considers critical dilation to have been attained when the dilation of one cycle is double that of the preceding cycle. The standard does not specify a curing cycle before testing but leaves the matter open to permit specimen conditioning that matches the anticipated condition of the prototype. In fact, ASTM Standard Practice for Evaluation of Frost Resistance of Coarse Aggregates in Air-entrained Concrete by Critical Dilation Procedures, Designation C 682 (*44*), gives guidance on specimen conditioning. Although the method is much less energy intensive than the conventional freezing-and-thawing test, it requires more sophisticated instrumentation. In the absence of commercial equipment, the test at this time is relatively expensive and it has received little use. It may, however, be necessary to employ it to resolve the anomalies surrounding the durability of high-strength concrete.

Two other factors must be kept in mind when analyzing results from freezing-and-thawing tests. The first is the reproducibility of the method itself. Although ASTM Test Method C 666 contains voluminous data *only* on within-laboratory precision, the subcommittee having jurisdiction over the method has taken the position that, because the method is used for comparative testing within a laboratory, it is the within-laboratory precision that is important; and it has made no attempt to evaluate the between-laboratory precision. The data (*45*) show very good precision when the durability factor is near 0 or 100 (standard deviation of 1 to 2) but quite poor precision for intermediate results (15 and 20 in the range 50–70 for Procedures A and B, respectively). It would be instructive to know the relative severity of various organizations' apparatus. The method permits a length of cycle of from 2 to 5 hours. The permissible distribution of time between freezing and thawing results in a permitted ratio of freezing rates greater than 2.5:1. The Corps of Engineers, which frequently reports relatively low durability factors, uses a 2-hour cycle. Most commercial apparatus is close to the upper end of the permitted cycle time to minimize refrigeration capacity, although there are examples of apparatus throughout the permitted range. These possible differences in severity may be contributing to some of the confusion in the literature.

The second factor to be considered is the choice of aggregate used in tests of concrete. The most frequent non-research use of freezing-and-thawing tests is the evaluation of aggregates. Aggregates to be evaluated are mixed with cement pastes of proportions known to produce good durability and tested in the freezing-and-thawing apparatus. Poor aggregates produce low durability factors in spite of the durable paste. If any research program includes nondurable aggregates, misleading conclusions could be drawn.

Available Dilation Data for High-Strength Concrete

Little information exists in the literature on dilation data pertinent to this study. The extensive study by Larson and Cady (*46*) was directed to the evaluation of coarse aggregate. Buck (*47*) worked with mortars of three water-cement ratios (0.4, 0.6, and 0.8 by mass) and four levels of air entrainment including non-air entrained mortars. He performed both C 666 and C 671 tests. He found air entrainment to be needed in all cases with the higher water-cement ratios requiring the highest air contents. Mortars with durability factors as low as 11 were shown to have some frost resistance by the dilation test. Recent work by Ragan

(*48*) on roller-compacted concrete with a low water-cement ratio indicates the usefulness of the method. Specimens from several projects were subjected to both conventional freezing-and-thawing tests and dilation tests. No HRWRA or silica fume was used; some concretes contained fly ash. Water-cement ratios as low as 0.30 by mass were obtained by the use of zero-slump concrete, which is the normal consistency for the roller-compacted system of placement. Table 3 contains a summary of pertinent data. It is seen that the data support the commonly assumed relationship between spacing factor and durability factor, although from these data one might set the limiting value for spacing factor at 0.25 mm rather than 0.2 mm. With spacing factors of 0.25 mm or less all durability factors were at least 75 by Procedure A. At higher spacing factors durability factors as low as 8 were measured. However, only one of the concretes had failed the ASTM dilation criterion of a doubling of the dilation between consecutive cycles at the age of 20 weeks, the latest age for which data were available. The duration of 20 weeks exceeds the length of the freezing season at most locations in the temperate zone. Thus, it is verified that for high-strength concrete, as well as for lower-strength concrete, the conventional freezing-and-thawing test may be too severe from a practical point of view.

The following review of the durability literature will not attempt to include all of the data that tend to lend support to one side or the other of the need-for-air-content-in-high-strength-concrete controversy but will confine itself to those papers that seem to shed some light on resolving the matter.

CONCRETE CONTAINING HIGH-RANGE WATER-REDUCING ADMIXTURES

Although he did not use a dilation procedure, Sprinkel (*49*) reported on specimens from several concrete pavements and bridge-deck overlays in a study in which specimen conditioning before testing was a variable. Table 4 summarizes the freezing-and-thawing data. Testing was by ASTM C 666, Procedure A, except that the water in which the specimens were exposed contained 2 percent sodium chloride by mass. All specimens contained HRWRA except where noted. Where a range of time is given for the exposure condition, the results are averages for that period. All concretes containing HRWRA had water-cement ratios of 0.34 or 0.35 by mass. The results are explainable primarily in terms of exposure before freezing and only secondarily in terms of spacing factor. All the specimens that were continuously moist cured until tested performed poorly; their durability factors were below 50. Those cured in the field did much better. Those with spacing factors below 0.30 mm had durability factors of 70 or above. The two with spacing factors exceeding 0.30 had durability factors of 38 and 62. Drying helped greatly, but it did not eliminate the need for a reasonable air-void system in high-strength concretes containing HRWRA.

TABLE 4

DURABILITY OF HIGHWAY FIELD SAMPLES WITH AND WITHOUT A HIGH-RANGE WATER-REDUCING ADMIXTURE (FROM REF. *49*)

Project	Water-Cement Ratio by Mass	Spacing Factor (mm)	Durability Factor (%)	Curing Before Test
B602[a]	0.34	0.26	70	2-6 months, field
B603[a]	0.34	0.25	44	1 month, moist
I85A[a]	0.35	0.31	63	1 month, field
			8	2 weeks, moist
I85B[a]	0.35	0.36	38	1 month, field
			19	1 month, moist
B604[b]	0.43	0.20	90	3-7 months, field
B639[b]	0.43	0.12	98	1 month, field

[a]Naphthalene
[b]None

TABLE 3

RESULTS OF DURABILITY TESTS ON ROLLER-COMPACTED CONCRETE (FROM REF. *48*)

Water-Cement Ratio by Mass	Spacing Factor (mm)	Durability Factor (%)	Dilation Ratio at 20 Weeks[a]
0.33	0.51	8	2.07
0.31[b]	0.30	10	1.70
0.30	0.20	89	1.33
0.35	0.25	75	1.10
0.35	0.25	81	1.04
0.43[b]	0.25	84	1.08
0.43[b]	0.25	75	0.97
0.43[b]	0.25	82	0.94

[a]Ratio of last measured dilation to dilation on previous cycle.
[b]Concrete contains fly ash.

With specimens not containing HRWRA, a study conducted by Perenchio and Klieger (*50*) confirms the above observation. They made zero-slump concretes with water-cement ratios of 0.30, 0.35, and 0.40 by mass. Compressive strengths ranged up to 11,000 psi (76 MPa). Half were air entrained and half were not. Specimens were subjected to freezing and thawing after 28 days of moist curing and 14 days of air drying. Testing was not by ASTM C 666 but by a slower cycle at the rate of two cycles a day. Spacing factors for air-entrained concrete varied from 0.18 mm to 0.41 mm, although for non-air-entrained concrete they varied from 0.56 mm to 1.04 mm. The combination of aging to 42 days, which promoted a maximum of hydration and self-dessication, 14 days of drying, which continued the drying, and slow freezing cycle produced favorable conditions for all the specimens.

The realization that the whole theory of spacing factor was developed for relatively high water-cement ratios, which produce concretes that contain freezable water even at complete hydration, caused two groups of Japanese investigators to study whether in the high-strength range the spacing factor might be a function of water-cement ratio. Both used HRWRA in their investigations.

Okada et al. (*28*) tested air-entrained concretes having water-cement ratios from 0.25 to 0.55 by ASTM C 666, Procedure A, and continued testing for 1,000 cycles. The results are plotted in Figures 10 and 11 for 300 and 1,000 cycles, respectively, where specimens with durability factors exceeding 90 are plotted as open circles and those with lower durabilities as solid squares. Required spacing factor is seen to increase as the water-cement ratio decreases. It may also be seen that the curves are essentially horizontal at an ordinate near 0.2 mm for water-cement ratios above 0.50. Thus the practice of using a constant spacing factor for the higher water-cement ratios appears to be valid. Because of the particular form of equation chosen to represent the curve that divides the two regions, the curve appears to approach a vertical asymptote at a water-cement ratio of 0.36. It could be inferred that below this water-cement ratio there is no requirement for spacing factor. However, the authors had previously concluded that some air entrainment is required and offer Figure 12 as evidence. The figure includes data on non-air-entrained concrete from seven sources. Although there are conflicting data at very low water-cement ratios, two sources indicate durability factors below 50 for water-cement ratios between 0.25 and 0.30. In one case the strength exceeds 13,000 psi (90 MPa). In keeping with this observation, their water-cement ratio-spacing factor curves should probably be drawn so that finite spacing factors are required throughout the range of water-cement ratios from 0.25 to 0.55. Although the authors recommend some entrained air in all high-strength concrete, they also present the very positive observation that when HRWRAs are used, air may be entrained with no sacrifice of strength. Their finding is that a volume of air decreases strength only half as much as an equal volume of water. Thus, entrained air may be compensated for by decreasing water through the use of an HRWRA. Figure 13 demonstrates how strength may be maintained as air is added, even at strengths of 15,000 psi (103 MPa). Although the curves show the expected decrease in strength when air content is increased at a given water-cement ratio, they demonstrate that, with no loss of workability, strength lost by introduction of air may be regained by a modest reduction of water-cement ratio.

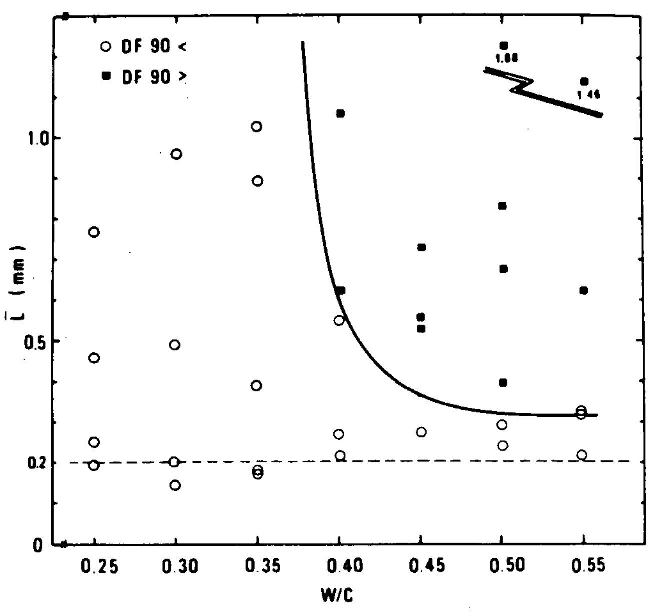

FIGURE 10 Relation of durability, water-cement ratio, and spacing factor at 300 freeze-thaw cycles (from Ref. *28*).

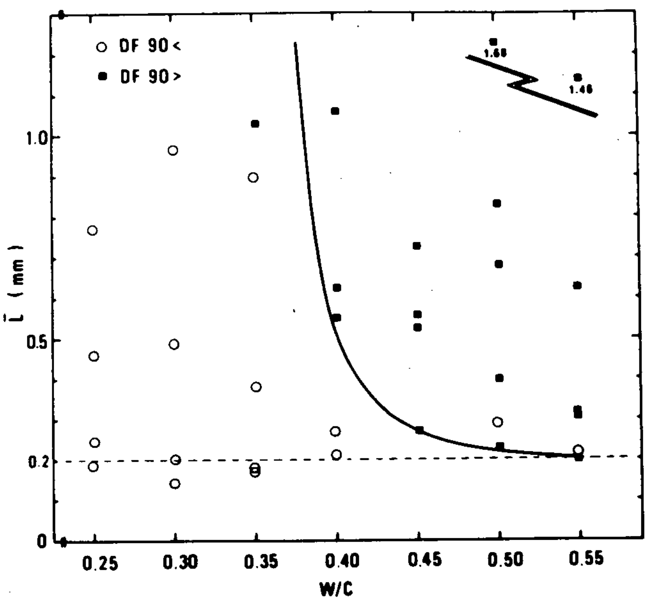

FIGURE 11 Relation of durability, water-cement ratio, and spacing factor at 1000 freeze-thaw cycles (from Ref. *28*).

Kobayashi et al. (*27*) performed a similar experiment with similar results. Their results are shown in Figure 14 where durability factor is plotted against spacing factor for various water-cement ratios. Not shown on this plot are the results for a water-cement ratio of 0.27, but based on the available two data points it would form a curve parallel to the existing curves. These authors also believe that some air entrainment is necessary, although they speculate that at water-cement ratios of 0.25 and below air entrainment might not be necessary. However, their single data point for a water-cement ratio of 0.25, which demonstrates a durability factor of 98 for a spacing factor of 1.523 mm, fits in the family of curves in Figure 14. There is nothing in the authors' data to suggest that durability factor for this low water-cement ratio is not a function of spacing factor. Their estimates of required spacing factors are not greatly different from those of Okada et al. (*28*) except for the very low water-cement ratios. The values they scale from the curves for a durability factor of 95 are 0.27 mm for a water-cement ratio of 0.55 and 0.38 mm for a water-cement ratio of 0.42, which are about halfway between the values for 300 and 1,000 cycles indicated by Okada et al. for a durability factor of 90. For a water-cement ratio of 0.32, Kobayashi et al. indicate a required spacing factor of 0.44 mm, which is in the area not well defined by Okada et al. Although the authors do not attempt to estimate a spacing factor for a water-cement ratio of 0.27, their data can reasonably be extrapolated to a value of about 0.75 mm. Plotting the two points for a water-cement ratio of 0.27 and the single point for the water-cement ratio of 0.25 would have been useful to demonstrate that the curves come closer together as the water-cement ratio increases. This would have permitted the observation that a nearly constant spacing factor requirement exists for concretes in what has been considered in the past to be the normal range.

CONCRETE CONTAINING SILICA FUME

The literature contains more speculation than actual data to show that properly proportioned non-air-entrained concrete containing silica fume should be capable of resisting freezing and thawing. Nevertheless, there is evidence that durable concrete without air has been produced. Sorensen (*51*) tested non-air-entrained concretes with and without silica fume by RILEM Recommendation CDC 2 (*52*), which is similar to the ASTM Standard Test Method C 672 for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals (*53*). The method calls for 14 days of drying following 14 days of moist curing. Concrete with a water-cement ratio of 0.38 by mass and 10 percent silica fume had no scaling, although scaling was evident on slabs of the same water-cement ratio without silica fume, on slabs with 10 percent silica fume and water-cement ratios of 0.45 and 0.55, and on slabs at all water-cement ratios tested with 20 or 40 percent silica fume. Perhaps the most convincing evidence of durable non-air-entrained concrete is provided by Saucier (*54*). A study of high-strength concrete included a non-air-entrained concrete with a water-cement ratio of 0.24 by mass, 15 percent silica fume, and an HRWRA. The concrete had a slump of 9 in., an air content of 0.8 percent, a bubble spacing factor of 0.33 mm, and a strength of 16,590 psi (114 MPa) at 31 days. It was tested by ASTM C 666, Procedure A, except that the specimens were inundated for 28 days, rather than 14, before test. The durability factor was 95. It should be noted that the compressive strength increased to 18,390 psi (127 MPa) at 154 days. Thus, the concrete cannot be said to have been completely free of freezable water at the time it entered the freezer, but apparently the water content was so low that no cavity was critically saturated.

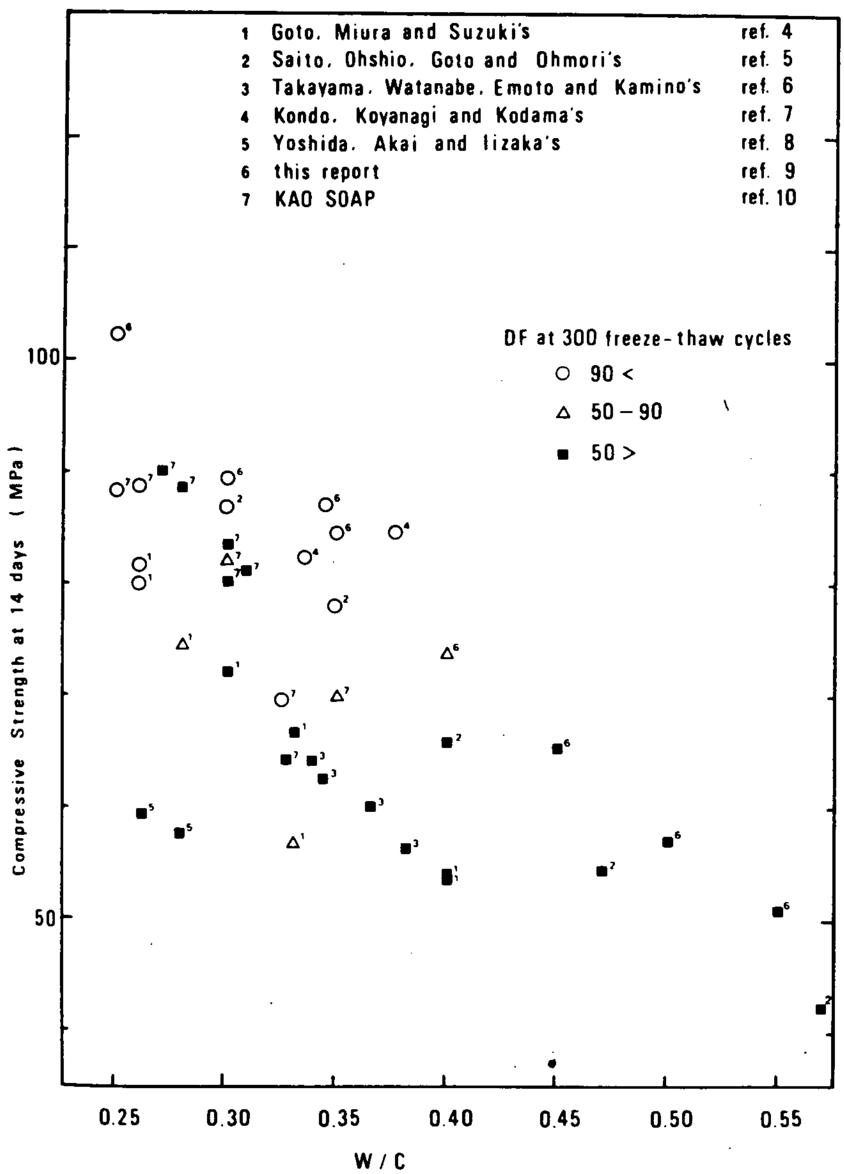

FIGURE 12 Durability as a function of water-cement ratio and 14-day compressive strength (from Ref. *28*).

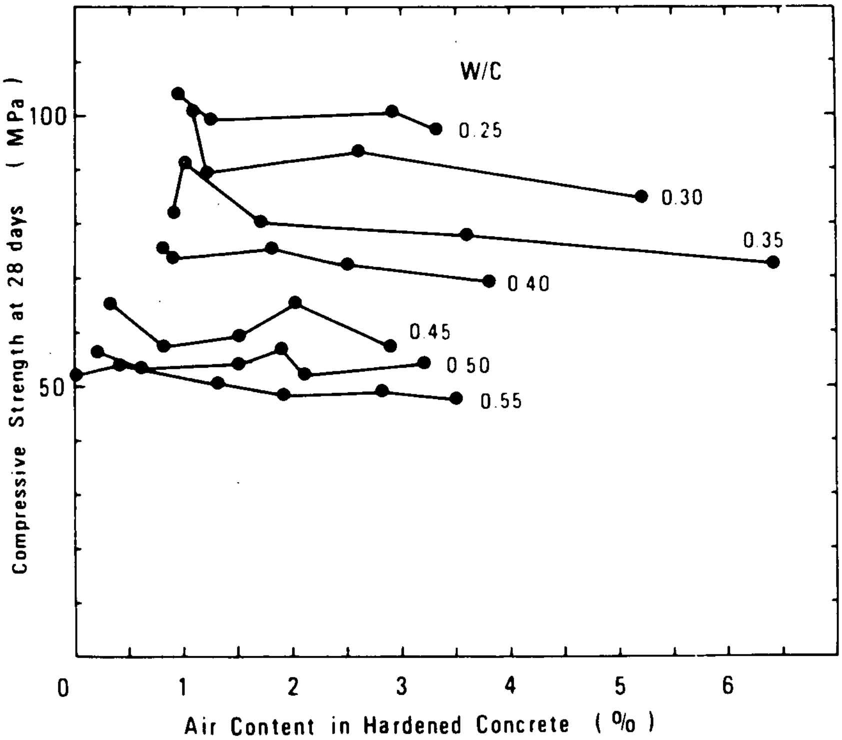

FIGURE 13 Effect of air content in hardened concrete on 28-day compressive strength (from Ref. *28*).

On the other hand, Malhotra (*55*) conducted an extensive series of tests on concretes with and without silica fume tested in strict accordance with ASTM C 666, both Procedures A and B. Water-cement ratios ranged from 0.40 to 0.60 by mass and silica fume replacements from 0 to 30. Both air-entrained and non-air-entrained concretes were included. All the air-entrained concretes were durable except for the combination of a water-cement ratio of 0.42 with 30 percent silica fume, for which the durability factors by Procedure A and Procedure B were 2 and 7, respectively. All the spacing factors for air-entrained concrete were below 0.15 mm with the same exception. For that concrete the spacing factor was 0.569 mm. It proved difficult to entrain air in the concrete containing 30 percent silica fume. Only 4.8 percent air could be achieved as compared with the nominal 6 percent achieved in the other concretes. This finding agrees with that of Sorensen that high replacements of silica fume do not promote durability. Data for non-air-entrained concrete are summarized in Table 5. It may be seen that none were durable. The highest durability factor by either procedure for concrete without silica fume is 11, and the highest for concrete containing silica fume is 6. Spacing factors were not determined.

Although they produced a consistent set of data, the relevance of the Malhotra findings to the current stuay may be questioned because they did not include very-high-strength concrete. The lowest water-cement ratio was 0.40 by mass and the highest compressive strength 9,820 psi (68 MPa) at 28 days. To answer this question his laboratory performed additional tests (*56*) at lower water-cement ratios. Although the limestone coarse aggregate used in the initial tests does not appear to be at issue because of the high durabilities obtained with air-entrained con-

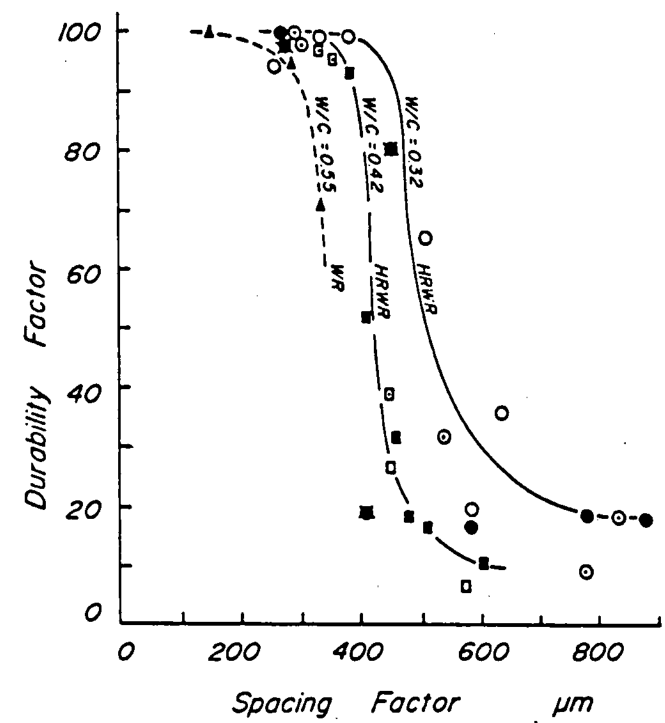

FIGURE 14 Relationship between air-void spacing factor and durability factor in concrete containing high-range water-reducing admixture (from Ref. *27*).

TABLE 5

SUMMARY OF DURABILITY DATA FOR NON-AIR-ENTRAINED CONCRETE (FROM REF. *55*)

Water-Cement Ratio by Mass	Silica Fume (% of mass of Cement)	28-Day Compressive Strength (psi)	Durability Factor ASTM C 660 (%) Procedure A	Procedure B
0.60	0	4,950	11	8
0.60	5	5,690	6	6
0.60	10	6,030	2	3
0.60	15	5,710	1	3
0.50	0	5,550	1	2
0.50	5	5,890	1	4
0.50	10	7,110	2	5
0.50	15	7,310	1	4
0.40	0	6,180	1	4
0.40	5	6,410	1	6
0.40	10	7,280	1	1
0.40	15	7,890	2	3
0.40	30	9,820	1	2

cretes, a portion of the new tests were with a natural gravel to allay any fears of an aggregate effect. The results have not yet been published, but they were presented at the Transportation Research Board 65th Annual Meeting in January 1986 and are reprinted here with permission. Water-cement ratios varied from 0.25 to 0.36 by mass and 28-day compressive strengths from 7,470 to 10,500 psi (51 to 72 MPa) for non-air-entrained concrete without silica fume and from 8,900 to 12,630 psi (61 to 87 MPa) for non-air entrained concrete containing silica fume. The durability data are summarized in Table 6. The non-air-entrained concrete continued to be nondurable, and spacing factors were in the order of 1 mm. It may also be noted that at the lower water-cement ratios, the air-entrained concretes containing silica fume were nondurable with the durability decreasing as the quantity of silica fume increased. The difficulty of entraining air in the low-water high silica fume concrete is indicated by the spacing factors. All are excessive by normal criteria, and for concretes with 20 percent silica fume they are either marginal or excessive by the criteria proposed by Kobayashi et al. (*27*).

SUMMARY

Because much of the evaluation of concrete in this synthesis is based on ASTM test methods, it might be well to review the

TABLE 6

DURABILITY FACTORS AFTER VARIOUS CYCLES OF FREEZING AND THAWING AND AIR-VOID PARAMETERS OF HARDENED CONCRETE FOR LOW (w/c+sf) RATIO CONCRETE (FROM REF. *56*)

	Mix No.	W/(C+SF)	% SF Re-placement	Air %	Freezing and Thawing Cycles	Durability Factor	Air-Void Parameters of Hardened Concrete: Voids in Concrete %	Specific Surface mm^{-1}	Spacing Factor mm
Non Air-Entrained	1	0.35	0	2.0	66	6	1.2	8.7	0.912
	2	0.35	10	1.8	70	6	1.4	5.4	1.506
	3	0.35	20	1.2	70	10	1.1	6.6	1.428
	7	0.30	0	1.9	67	12	2.8	6.7	0.907
	8	0.30	10	1.3	67	3	1.1	8.6	1.047
	9	0.30	20	1.1	70	3			
	13	0.25	0	2.0	89	11			
	14	0.25	10	1.3	89	5			
	15	0.25	20	1.5	89	8			
	16	0.25	0	1.8	79	3			
	17	0.25	10	1.5	79	2			
	18	0.25	20	1.8	79	2			
	19*	0.25	0	2.0	47	6			
	20*	0.25	10	1.6	47	7			
	21*	0.25	20	1.8	47	2			
	22	0.25	0	2.2	70	4			
	23	0.25	10	1.8	70	3			
	24	0.25	20	2.0	70	3			
Air-Entrained	4	0.35	0	5.4	302	97	7.2	14.9	0.230
	5	0.36	10	5.6	265	59	5.5	15.9	0.269
	6	0.36	20	4.9	203	36	4.3	10.2	0.502
	10	0.30	0	3.7	300	99	6.7	13.9	0.267
	11	0.30	10	4.2	170	33	5.4	12.8	0.325
	12	0.32	20	4.5	138	16	5.6	10.6	0.428

* Gravelstone coarse aggregate

intended and potential uses of these methods. ASTM C 666 is entitled "Resistance of Concrete to Rapid Freezing and Thawing." It is the most widely used test for frost resistance. In practice it is used primarily to evaluate aggregates since the required properties for pastes in concretes of normal strength were determined long ago. ASTM C 682 is entitled "Evaluation of Frost Resistance of Coarse Aggregates in Air-Entrained Concrete by Critical Dilation Procedures." Its title and scope recognize that the principal use of such tests is aggregate evaluation. However, the test is equally suitable to evaluating paste properties and, by giving guidance on conditioning procedures, is ideally suited to evaluating all aspects of concrete subjected to different environments. ASTM C 671, "Critical Dilation of Concrete Specimens Subjected to Freezing," is the test method on which the evaluation in C 682 is based. ASTM C 672, "Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals," makes possible an evaluation of that aspect of frost resistance that manifests itself as scaling on pavement surfaces when deicing chemicals are applied in cold weather.

When specimens are tested in strict compliance with ASTM C 666, including curing conditions, the preponderance of evidence is that the concrete needs to be air-entrained with a reasonable spacing factor. The data that exist for concrete subjected to ASTM C 672 and similar scaling tests suggest that this observation may be extended to those tests. Non-air-entrained concretes that have proved durable in laboratory testing have benefitted either from a longer period of hydration or a period of drying before being tested by ASTM C 666, or they have been tested by ASTM C 671 after being conditioned to the moisture content of the prototype for which the information is desired. Available data confirm the need for a spacing factor of about 0.2 mm for low and medium strength concrete to satisfy the requirements of ASTM C 666, but they suggest that below a water-cement ratio of 0.50 by mass the required spacing factor is a function of water-cement ratio. Thus, the required spacing factor becomes larger as the water-cement ratio decreases. Concrete containing silica fume appears capable of developing a pore structure, an absence of freezable water, and an immunity from resaturation from the environment that render it immune to freezing and thawing, but it cannot do so in 14 days. It is also apparent that at early ages high replacement quantities of silica fume are incompatible with durability. This may simply be a time problem in that the greater time required for the reaction of the larger amounts of silica fume may merely delay the age at which durability is achieved.

ASTM C 666 is a good test for judging the inherent frost resistance under severe conditions of a specimen of concrete and can be used empirically to screen aggregates for D-cracking potential. The ambient conditions in the test are more severe than in most field exposures. It is an extremely severe test because of the young age-at-test, the lack of a drying period, and the very rapid cooling cycle. The critical dilation test, ASTM C 671, may offer a more realistic alternative, yet one that still protects the owner of the concrete structure. In exposures where air is required, there is evidence that the introduction of air can be compensated for by the reduction of water with no loss in strength.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

Conventional theories on hydration state that concrete with a water-cement ratio exceeding 0.38 by mass may hydrate completely in a sufficiently moist environment and that after hydration there will be excess capillary space in the cement paste that may be occupied by freezable water. At any time when the concrete is less than completely hydrated, either because it is too young for hydration to have been completed or because it has been in an environment too dry to support continued hydration, it contains more capacity for freezable water than at complete hydration. If in such concrete the capillaries are more than 91 percent filled with water, the concrete will be resistant to rapid freezing and thawing only if the concrete contains a system of entrained air bubbles with a spacing factor not exceeding 0.2 mm.

When the water-cement ratio is below 0.38 the theories recognize two alternative means of obtaining frost resistance: (a) a complete absence of capacity for freezable water, and (b) a cement paste of such low permeability that once dried through self-dessication the paste may not again be critically saturated by outside moisture. The cement cannot be completely hydrated in such concretes. Space for depositing hydration products will be depleted before the cement is depleted. Alternative (a) cannot be obtained unless water is forced in under conditions of high hydrostatic pressure. As self-dessication brings the hydration process to an end before all the space is filled, the extremely low permeability of the hydrated paste may make penetration of additional water for hydration from the outside unlikely unless it is forced in at great pressure. But if water for hydration cannot enter the concrete, neither can water that might damage the concrete by freezing. Conversely, if water for freezing can penetrate to the interior of the concrete, that water is available to continue hydration until all the space for freezable water has disappeared.

Nothing reviewed in the literature disproves these theories. Two papers establish refined spacing factors for high-strength concrete. All high-strength concretes were durable when they had a reasonable spacing factor or when the period of hydration or the ambient exposure before freezing were such that they provided a high probability that no pore large enough to contain water freezable at normal winter conditions was critically saturated. What is apparent in the literature, and should have been apparent for a long time, is that the conventional freezing-and-thawing test, ASTM C 666, is an extremely severe test and represents conditions almost never duplicated in nature. An alternative test for critical dilation, ASTM C 671, which can be realistically tailored to any ambient condition, is available. Although it is a less energy-intensive test than ASTM C 666, it requires more sophisticated instrumentation. In the absence of commercial equipment, the test at this time is relatively expensive and has received little use. In addition, almost all the data in the literature with which an investigator wishes to compare results are in the form of C 666 durability factors, and C 666 provides very conservative results. If a concrete can yield a high durability factor after surviving 300 C 666 cycles, it can almost certainly handle anything in nature. There are only a few natural exposures where the C 666 exposure approaches reality. If concrete is placed late in the fall and is exposed to freezing at a young age before any drying has occurred, it is in a critical exposure. Perhaps the most critical freezing exposure a concrete can sustain routinely is in a tidal zone in freezing weather. When the water level falls, the concrete in the zone is immediately exposed to subfreezing temperature in a nearly saturated condition. For most exposures, however, a more realistic test criterion seems to be in order.

The principal effect of HRWRAs is to extend practical concrete technology into a range of low water-cement ratios never before possible. In freshly mixed concrete where high strength is not sought, they make possible high-slump "flowing" concretes that may be placed with little vibration and little segregation. The only adverse effects before hardening are a propensity for slump loss and plastic shrinkage cracking. There is apparently also a viscosity effect that affects the ease with which a normal distribution of air voids can be mixed into the concrete when air-entraining admixtures are added. Thus, the only significant effect on hardened concrete is an air-void system that frequently has a larger spacing factor than its non-admixture counterpart. Otherwise, the pore structure and physical properties of a concrete containing an HRWRA are similar to those of a concrete without HRWRA at the same water-cement ratio. Whether the higher spacing factor inhibits durability depends on whether the concrete, if high strength, is rendered durable by factors not involving air entrainment or whether the spacing factor is within the more liberal limits apparently applicable to low water-cement ratio concretes.

In contrast to HRWRA, silica fume does appear to affect the pore structure. By its extreme fineness it promotes hydration at more reaction sites and produces a finer, more discontinuous pore system than concrete without silica fume. In addition, it participates in a pozzolanic reaction with the calcium hydroxide to produce more hydrated product and to convert the calcium hydroxide that preferentially deposits along the boundaries of fine aggregate particles from potential bond breaker to strong gel. The discontinuity of the pore system produces an extremely low permeability. In the case of the resistance to freezing this low permeability is a mixed blessing. Although it prevents the resaturation of concrete after it has dried, it makes movement of water through the paste during freezing (while it is still young enough to contain freezable water) so difficult that disruptive pressures are developed before water may be expelled into an air void. This is demonstrated in the data of Malhotra (*56*) and Saucier (*54*). After 14 days of water curing, the concrete was not resistant to freezing and thawing. After 28 days it was. A curing time of 14 days is simply not long enough for hydration and self-dessication to reduce the quantity of freezable water below critical saturation. That hydration continues for a considerable period of time, even for very low water-cement ratios, is illustrated by Saucier's data, which contain the highest strengths studied in this review. In a non-air-entrained concrete of interest there was a strength gain from 16,590 psi to 18,390 psi (114 to 127 MPa) between 31 and 154 days.

Entrained air and high strength are usually considered incompatible; hence the interest in eliminating or minimizing the air in high-strength concrete. The introduction of air makes possible the reduction of water with no change in workability. This fact is well known to producers of low-cement-content mass concrete who take advantage of the fact that in that type of concrete air entrainment permits such a large reduction of water that strength is actually increased when air is entrained. Previous findings have shown that in the high-strength range there is a net loss in strength when air is substituted for water. One reviewed paper says the HRWRAs have changed that. The reduction of water made possible by addition of an HRWRA makes it possible to add air without sacrificing strength. This conclusion should be further studied. It may be possible to have the best of both worlds.

CURRENT RESEARCH

Although it is not specifically directed at high-strength concrete, NCHRP Project 10-32, "Durability of In-Place Concrete Containing High-Range Water-Reducing Admixtures," has as its objective the assessment of the relationship between durability and air void characteristics of concrete placed with HRWRA. The research includes testing of cores from existing structures. It is expected that this project will be completed in 1987. Another research study, NCHRP Project 10-32A, "Durability Testing of High-Strength Concrete Containing High-Range Water-Reducing Admixtures," will investigate the significance of various concrete properties on the durability of high-strength concrete containing HRWRA and will compare the variability of durability factors calculated from various methods of testing concrete for freezing and thawing resistance. Research is expected to start late in 1987.

CONCLUSIONS

1. The standard test for freezing and thawing, ASTM C 666, particularly Procedure A, is a good test for judging the frost resistance of structural concrete under very severe conditions, and may be used empirically to screen aggregates for D-cracking potential.

2. Where a high durability factor by ASTM C 666 is the acceptance criterion, it is virtually impossible to consistently produce durable concrete without intentionally entrained air.

3. Where a more lenient criterion than a C 666 high durability factor is established, to take into account the fact that most concrete undergoes some drying before freezing and is usually more than two weeks old before the first freezing, compliance may be possible without intentionally entrained air for concrete with a low water-cement ratio and a prolonged period of hydration. A drying period is also realistic. Inclusion of silica fume produces a less permeable product, but it may require a longer time for reaction. There is even evidence that the 14 days of water curing in C 666 is at times inadequate for air-entrained concrete containing silica fume.

4. HRWRAs do not appreciably alter the pore structure of hardened concrete except that with some materials the air-void structure is altered. Their effect is principally to extend concrete technology into areas of lower water-cement ratios or into areas of greater workability.

5. Silica fume does alter the pore structure of concrete. It produces smaller pores and more discontinuous pores so that there is a marked reduction in permeability. Other pozzolans, which have a fineness comparable to that of cement, do not demonstrate this fine pore effect. They merely increase the hydrated product by reacting with calcium hydroxide crystals. All pozzolans have the potential advantage of increasing strength by replacing the calcium hydroxide that preferentially deposits along fine aggregate particles with gel structure.

6. Silica fume should not be used in large quantities when durability is important. Amounts in the range from 5 to 10 percent by mass of cement are optimum.

RECOMMENDATIONS

1. ASTM C 666 should be modified or replaced by a more realistic standard for judging the acceptability of structural concrete for field applications. At the very least the curing conditions in C 666 should be relaxed to permit a reduction of freezable water to a value more in keeping with practice. The most promising choice as a replacement is the critical dilation test in ASTM C 671. The continued use of the very stringent requirements of C 666, particularly Procedure A, is uneconomical. Although an examination of field data was not a part of this review, there are many examples of field repair procedures, among them certain cement-latex formulations, that serve well in the field but cannot yield a high durability factor when tested by C 666. Continued use of the method reduces the confidence of practitioners in laboratory testing. For certain very severe exposures C 666 might still be useful.

2. Bubble-spacing factors for high-strength concrete should be established. For severe applications where C 666 is applicable, the increase in permissible spacing factors to values above 0.2 mm for water-cement ratios below 0.50, reported herein, should be confirmed. Other spacing factors for less severe exposures should be developed. The combinations of exposures and water-cement ratios not requiring intentionally entrained air should be delineated.

3. The contention, reported herein, that air may be entrained in high-strength concrete without loss of strength should be confirmed.

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APPENDIX

PORE STRUCTURE OF CEMENT PASTE CONTAINING SILICA FUME

In their study of the effect of silica fume on pore structure Sellevold et al. (*32*) determined pore structure by three methods: mercury intrusion, water sorption, and low-temperature calorimetry. In the figures given below, the pastes are represented by a three-digit code in which the first digit represents water-cement ratio and the second and third represent silica fume content, except for the designation followed by a C, which represents an addition of calcium carbonate rather than silica fume. There are a few pastes indicated by a suffix R that contain silica fume as a replacement rather than an addition; in these cases the amount of cement replaced was three times the amount of the silica fume added. There is also one paste, labeled C-S, that contains calcium hydroxide rather than portland cement.

MERCURY POROSIMETRY

Figures A-1 and A-2 show mercury intrusion results after two months of hydration. The ordinate is the percent of total porosity accessible to mercury. It may be seen that increasing silica fume leads to finer pores and a smaller pore volume accessible to mercury, that replacing cement on a three-for-one basis produces a moderate reduction in porosity, and that the inert filler produces results intermediate between those for straight portland cement and an equal silica fume addition. The latter observation is made by noting that the curve for 612 c in Figure A-1 falls between the curves for 600 and 612. Thus, silica fume is seen to have a significant effect on the pore-size distribution, and it may be deduced that the effect is partly caused by the particle size of the silica fume and partly by pozzolanic reaction.

WATER SORPTION

Figure A-3 presents the first desorption isotherm for disc samples and the first adsorption isotherm for both disc and powder samples for several specimens with a water-cement ratio of 0.60. The two types of specimens agree very well. For both desorption and adsorption the greater the silica fume content the greater the water retention at every relative humidity. This denotes a greater internal surface for the higher additions of silica fume and may be interpreted as evidence of smaller but more numerous pores.

LOW-TEMPERATURE CALORIMETRY

To obtain porosity data directly applicable to field performance, the authors lowered the temperature to well below the normal freezing point and noted the amount of water frozen in the pores as a function of temperature. Figure A-4 presents the results for virgin specimens with a water-cement ratio of 0.60. The area under the curve is a measure of water frozen. It may be seen that the paste without silica fume has a very large amount

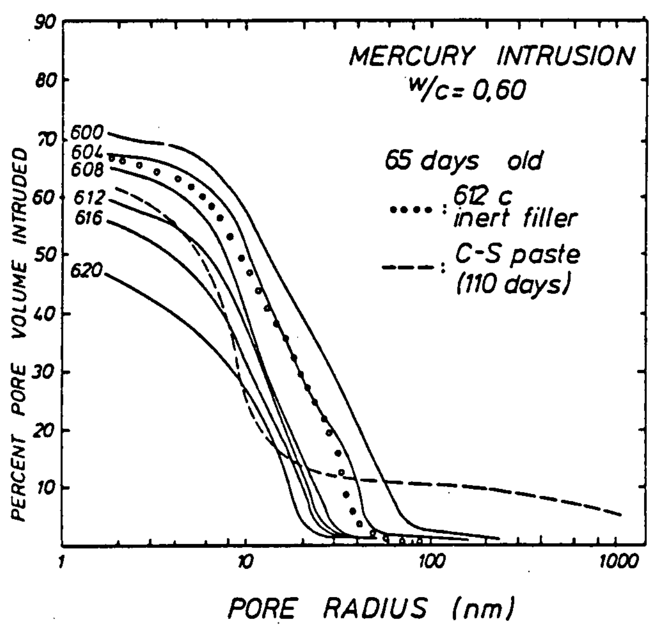

FIGURE A-1 Porosity by mercury intrusion in mature pastes with different amounts of silica fume added (from Ref. *32*).

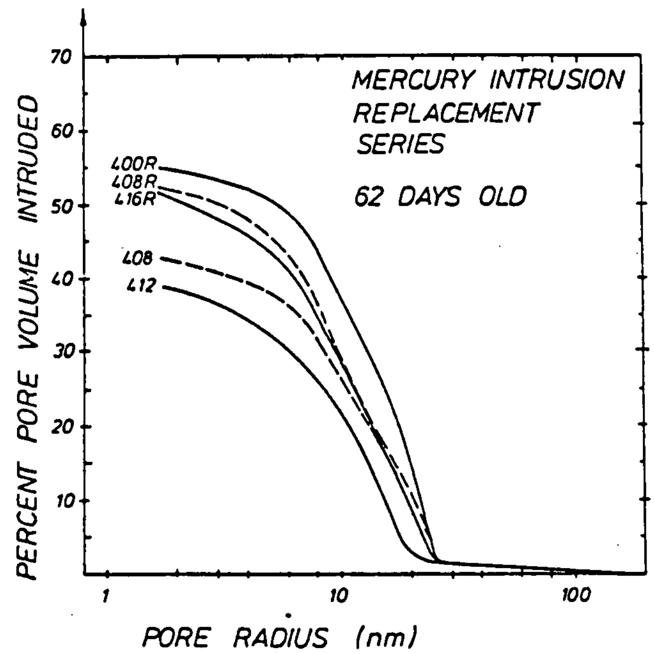

FIGURE A-2 Porosity by mercury intrusion in mature pastes with silica fume both as addition and as cement replacement (from Ref. *32*).

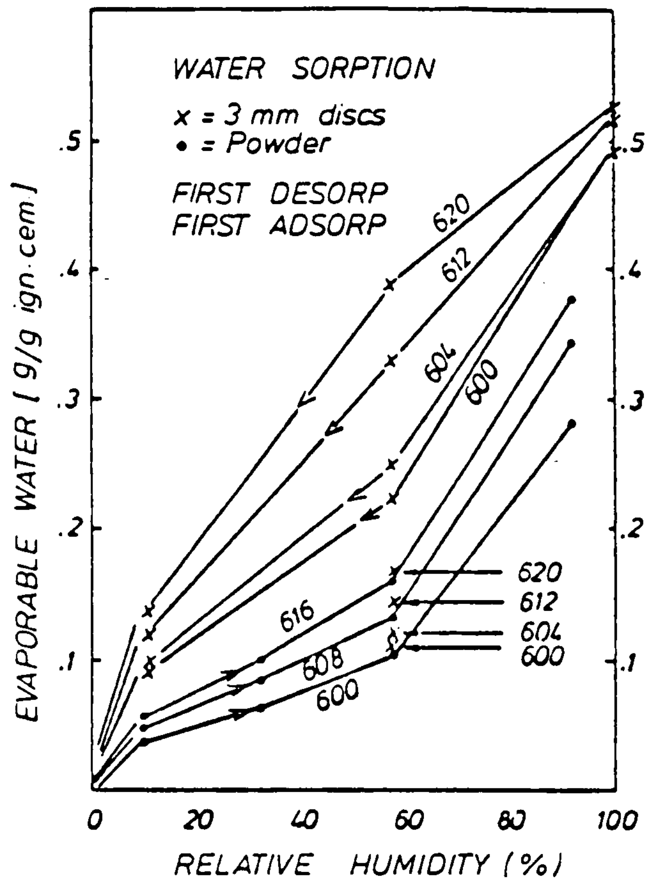

FIGURE A-3 Water sorption in disc and powder specimens (from Ref. *32*).

of water frozen at about −5°C (23°F). The addition of silica fume reduces the temperature for significant freezing to −20° or −30°C (−4° or −22°F). These data speak well for the pore structure of concrete containing silica fume. However, the picture is not so optimistic when the specimens are dried and

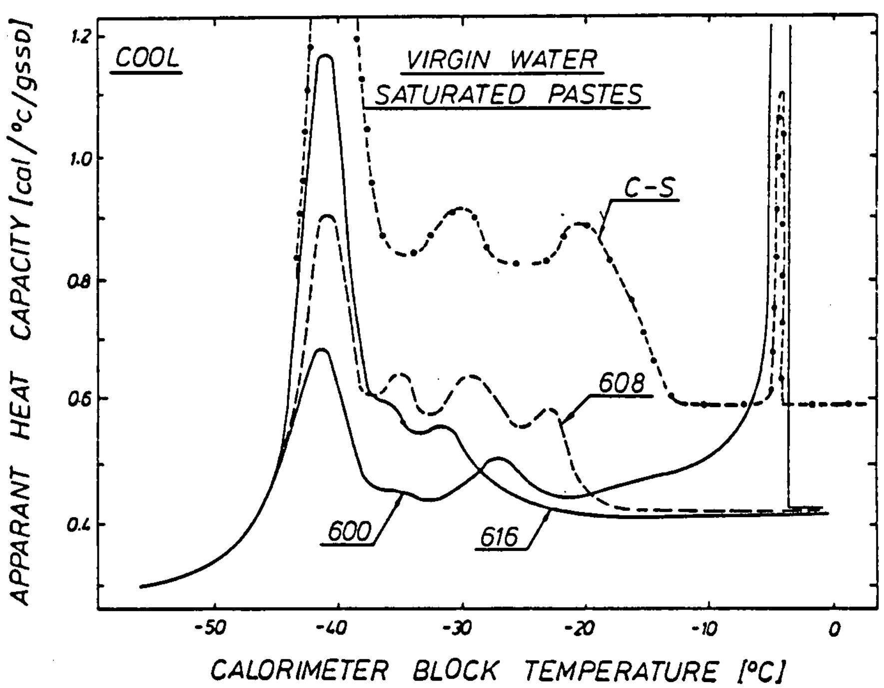

FIGURE A-4 Low temperature calorimetry; heat flow during cooling for virgin water-saturated pastes (from Ref. *32*).

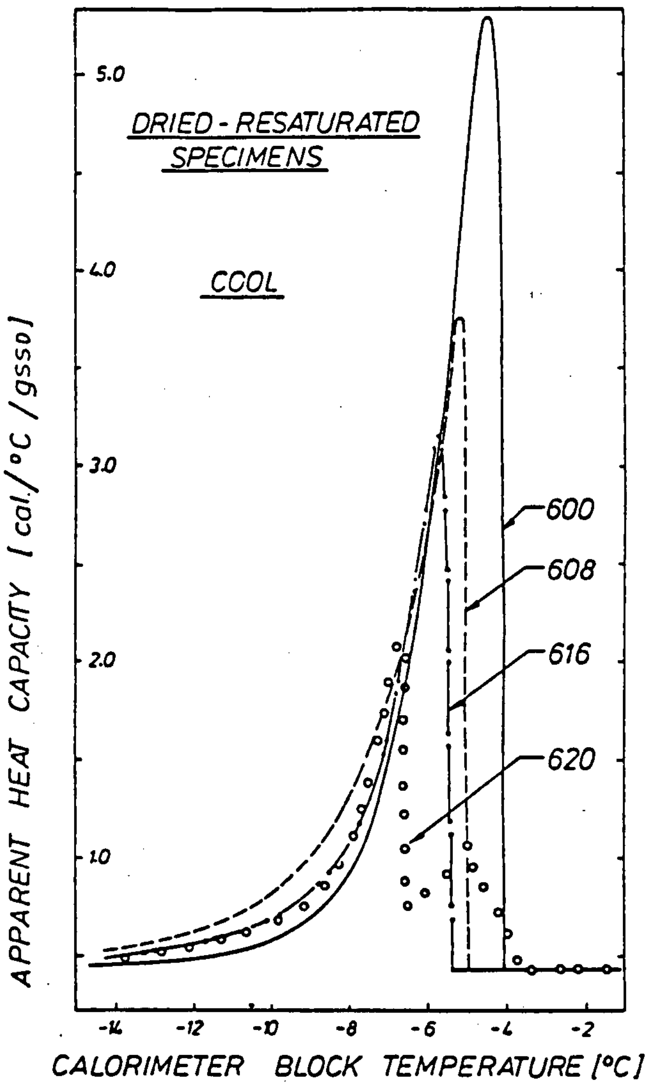

FIGURE A-5 Low temperature calorimetry; heat flow during cooling for dried resaturated pastes (from Ref. *32*).

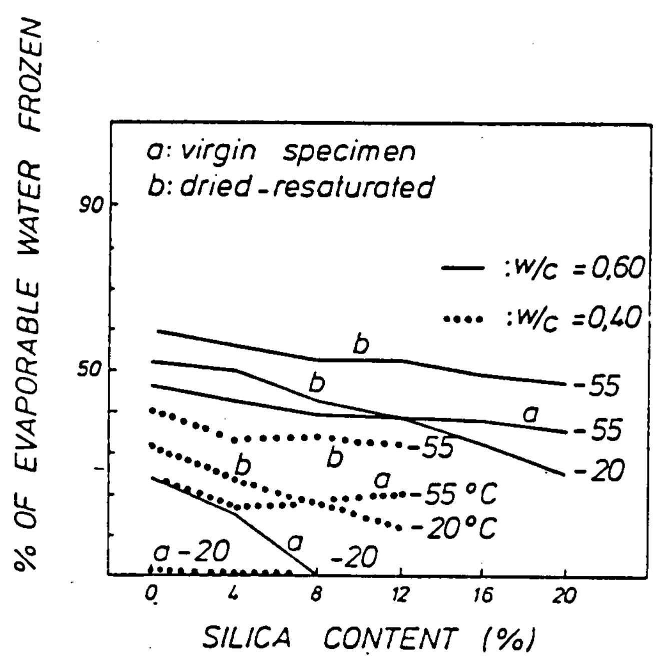

FIGURE A-6 Ice formed during cooling to −20°C and −55°C for mature water-saturated pastes with different silica fume contents (from Ref. *32*).

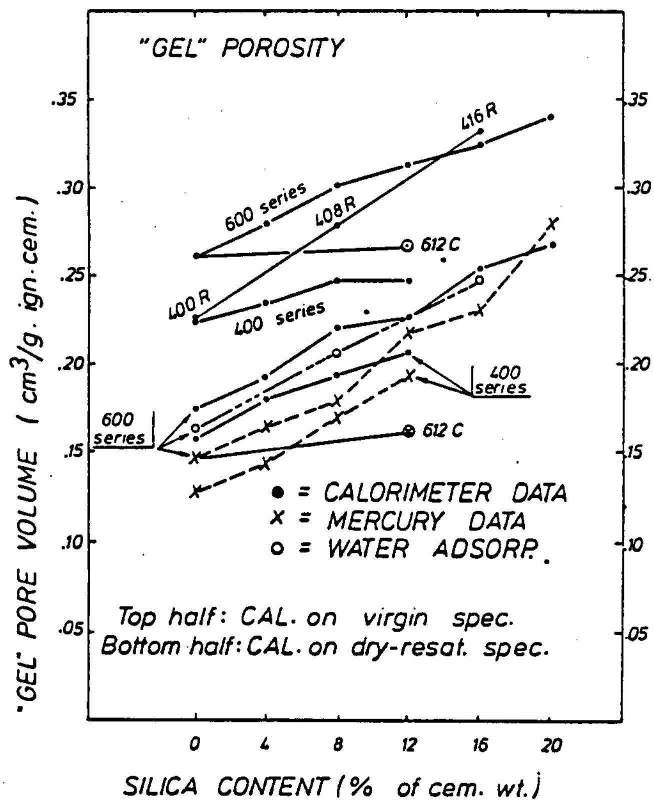

FIGURE A-7 Calculated gel porosities based on different experimental methods for mature pastes with different silica fume contents (from Ref. *32*).

resaturated. These data are presented in Figure A-5. Although increasing additions of silica fume depress the freezing point, there is significant freezing even with 20 percent silica fume at −7°C (19°F). The authors attribute this effect to the fact that "the first drying of a paste opens up and increases the continuity of the pore structure"(*32*). Figure A-6 shows data on ice formation at −20° and −55°C (−4° and −67°F) for water-cement ratios of both 0.40 and 0.60. Although dried and resaturated specimens consistently contain more ice than virgin specimens, for both temperatures the amount of water frozen decreases as the water-cement ratio decreases and as the silica fume content increases. That the silica fume has an effect beyond the creation of more hydrated product may be seen by examining the resaturated curve for a temperature of −20°C, which is probably the most pertinent for practical considerations, at a water-cement ratio of 0.60. For the paste with 20 percent silica fume the water-cementitious material ratio is 0.50, but the ice formed is less than that for a water-cement ratio of 0.40 without silica fume. By extrapolation it appears possible to find a condition with no freezable water at −20°C.

COMPARISON OF POROSITY EVALUATIONS

Having made three independent evaluations of porosity, the authors compared the results by making a determination of the quantity of "gel" pores by each method. Their definition of gel pores is not quite the same as that of Powers (*1*). Powers considered the gel porosity as the inherent internal porosity in each unit of hydrated product, as distinguished from the capillary porosity, which is the space between the units of hydrated product. Without ready means to measure pore-size distribution, he inferred from physical behavior that the gel pores were much smaller than the capillary pores. It is now known that there is a continuous gradation of pore sizes with the smaller capillary pores approaching the gel pores in size. The authors define gel pores on the basis of size or performance without regard to their origin. They define gel pores as (a) those too small to be intruded by mercury at a pressure of 345 MPa (corresponding to a pore radius of 1.27 nm), (b) the volume equal to three times the volume of water needed to cover all internal surfaces with one monolayer of water molecules, as calculated by the BET equation, and (c) the volume in which water will not freeze at −55°C. All the results are plotted in Figure A-7. There are two sets of points for the calorimetry determinations to include both virgin specimens and resaturated specimens. Although the results do not coincide, the curves are generally parallel, indicating that there is a consistent increase in "gel" porosity as silica fume is added. It may also be seen by an examination of the data for paste 612 c that the inert fine material, while decreasing the size of capillary pores, has no effect on gel pores.

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