



The effect of prestress on concrete durability
by Michael J Gonsior

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Civil Engineering
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Abstract:

The primary purpose of this study was to investigate the effect of prestress upon the durability of concrete. Small pretensioned concrete slabs, at stress levels of zero, 500, and 1200 psi., were fabricated from non-air-entrained concrete made with Type II cement. Half of these slabs were steam cured; the remaining slabs, were cured in a moist, room temperature environment. These slabs were subjected to a freeze-thaw environment, half with water ponded on their top surfaces and the remaining specimens with a CaCl_2 solution in contact with their top surfaces. At frequent intervals the natural frequencies of transverse flexural vibration, weights, and lengths of the slabs were measured. Evaluations of the degree of surface scaling were also made.

Duplicates of these slabs were fabricated for an additional study to determine the effects of prestress, curing procedure, and type of solution upon the permeability, or absorption characteristics of concrete.

Tall glass standpipes were sealed to the surfaces of these slabs and filled with water or CaCl_2 solution. Absorption rates were determined by periodically measuring the quantities of liquid necessary to maintain a constant level in the standpipes.

From statistical and qualitative interpretations of the data from these studies it was concluded that prestressing slightly improves the durability of concrete. It was also concluded that steam cured concretes are less durable, more susceptible to scaling damage, and possibly more permeable than concretes cured in a moist, room temperature environment.

The extremely deleterious surface effects of salt solutions upon concrete, in a freeze-thaw environment, were also observed; although the slabs ponded with CaCl_2 solution exhibited only slightly greater durability losses than slabs ponded with water.

The only important conclusion drawn from the permeability study was that concrete absorbs CaCl_2 solution at a rate which does not differ significantly from that at which it absorbs water.

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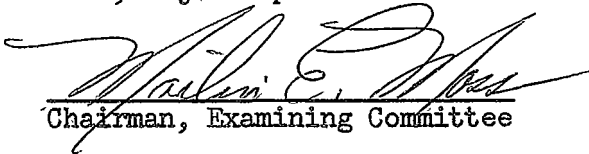
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ABSTRACT

The primary purpose of this study was to investigate the effect of prestress upon the durability of concrete. Small pretensioned concrete slabs, at stress levels of zero, 500, and 1200 psi., were fabricated from non-air-entrained concrete made with Type II cement. Half of these slabs were steam cured; the remaining slabs were cured in a moist, room temperature environment. These slabs were subjected to a freeze-thaw environment, half with water ponded on their top surfaces and the remaining specimens with a CaCl_2 solution in contact with their top surfaces. At frequent intervals the natural frequencies of transverse flexural vibration, weights, and lengths of the slabs were measured. Evaluations of the degree of surface scaling were also made.

Duplicates of these slabs were fabricated for an additional study to determine the effects of prestress, curing procedure, and type of solution upon the permeability, or absorption characteristics of concrete. Tall glass standpipes were sealed to the surfaces of these slabs and filled with water or CaCl_2 solution. Absorption rates were determined by periodically measuring the quantities of liquid necessary to maintain a constant level in the standpipes.

From statistical and qualitative interpretations of the data from these studies it was concluded that prestressing slightly improves the durability of concrete. It was also concluded that steam cured concretes are less durable, more susceptible to scaling damage, and possibly more permeable than concretes cured in a moist, room temperature environment. The extremely deleterious surface effects of salt solutions upon concrete, in a freeze-thaw environment, were also observed; although the slabs ponded with CaCl_2 solution exhibited only slightly greater durability losses than slabs ponded with water.

The only important conclusion drawn from the permeability study was that concrete absorbs CaCl_2 solution at a rate which does not differ significantly from that at which it absorbs water.

CHAPTER I
INTRODUCTION

Concrete durability

The importance and versatility of portland cement concrete as a construction material is well recognized. The annual world-wide consumption of concrete is exceeded in quantity by few other materials. Yet, despite its wide usage, it is one of the least understood materials at our disposal. It has been only in the past few decades that a concentrated scientific study of this material has been attempted, and the time for reasonably accurate prediction of the behavior of concrete in all structural and environmental situations is still in the future.

Perhaps the most serious disadvantage of concrete is its lack of durability in many common environments. As with all materials, there are certain environments which are deleterious to the appearance and structural utility of concrete. Nearly everyone is aware of the damage that results when rock salt is used to remove ice from the surface of concrete. Also evident is the severe damage to concrete coastal structures caused by salt corrosion and alternate wetting and drying between the tide lines. These are just two of the many examples of conditions which cause unsightly, dangerous, and costly damage to portland cement concrete.

Of particular interest is the progressive deterioration that occurs when concrete is subjected to repeated cycles of freezing and thawing in the presence of de-icing salts. The exact mechanism of this type of

destruction is not completely understood, but it is generally conceived to be a physical mechanism.

Concrete is a relatively porous mass, with part of its porosity attributable to capillary channels, or voids. These channels, if continuous, readily allow the penetration of water into the concrete mass. When frozen, this interior water expands, thereby exerting pressure on the capillary walls. If these pressures are sufficiently great, cracking of the concrete will occur. The newly formed cracks allow further penetration of water into the concrete mass after thawing, and further freezing and thawing causes the damage to continue until the concrete is so weakened as to result in the loosening of sizeable pieces of the material. If the penetrating moisture is salt-laden, then additional pressures might be created by the growth of salt crystals in the voids.

Concrete protection

Perhaps the most effective means for improving the durability of concrete in a freeze-thaw environment is air-entrainment. Air-entrained concrete contains innumerable minute air bubbles uniformly distributed throughout the cement paste. Entrainment of air can be effected by additions interground with the portland cement during manufacture or with admixtures added during the mixing of the concrete. The entrained air reduces the destructive effects of freeze-thaw action by providing readily accessible chambers into which the liquid under pressure may escape, and thereby alleviates the pressure on the capillary walls caused by the ice and salt-crystal expansions.

Generally high strength concrete will be more durable than low strength concrete. This can be rationalized by considering the relationship between strength and the W/C (water/cement) ratio of concrete, which has been fairly well established to be that strength is inversely proportional to the W/C ratio, if all other factors remain unchanged. Since a reduction in the W/C ratio will produce a less porous concrete, hence a concrete which is probably less permeable, the general strength-durability relationship seems reasonable.

Certain admixtures such as silicone-water solutions tend to improve the durability of concrete in freeze-thaw environments. Here the effect is similar to most water-reducing admixtures, in that the desired workability of the concrete can generally be achieved with a reduced W/C ratio. It is also noteworthy that air-entrainment usually improves the workability of concrete, thereby allowing a reduction in the W/C ratio.

Surface treatments, such as certain resins and bituminous tar products, will often serve to protect concrete from the destructive effects of freeze-thaw action. These are primarily barriers to prevent ingress of liquids and do not cause basic structural alterations of the concrete.

All of these practices result in concrete which is more durable. The improved durability would seem to lend support to the concept that freeze-thaw destruction results from expansion due to ice and salt-crystal formation in the pores, since the reduced permeability resulting from these practices would decrease the effects of such a physical mechanism.

Purpose of study

Although the aforementioned practices, accompanied by stricter field inspection of concrete mixing and placement, have helped to lengthen the maintenance-free life of many concrete highway structures, the lack of durability of concrete still remains a serious weakness. The tremendous annual cost for repair of frost damage to our highway systems, as well as the discomfort to motorists, is sufficient cause for concentrated efforts to find better ways for preventing its occurrence.

That freeze-thaw destruction in the presence of de-icing salt solutions is primarily a mechanical rather than chemical action is supported by the methods employed for reducing its effects. It would appear that any practice which would reduce the permeability of concrete would improve its durability. Alternatively, any method which would increase the tensile strength, or expansion resistance, of concrete should also improve its durability.

Considering the behavior of concrete under compressive loading, and more importantly the creep of concrete under sustained load, we may hypothesize that prestressing might reduce the permeability of concrete by reducing the average capillary cross-sectional area through distortion, and thereby increase its durability. In addition, the uni-directional restraint against destructive expansion, or increased effective tensile strength, should also help to improve the durability of prestressed concrete.

Therefore, the primary purpose of this study is to determine the effect of prestressing on the durability of portland cement concrete.

Nature of investigation

Small pretensioned slabs were fabricated using carefully controlled, non-air-entrained concrete. Air-entrainment was intentionally omitted in an attempt to accelerate the destructive effects of freeze-thaw action. The levels of prestress chosen were zero, 500, and 1200 p.s.i.

In order to simulate actual field conditions, mortar dikes were attached around the peripheries of the top surfaces of the slabs to retain ponded solutions. These slabs were also used to study the effect, if any, of prestress on the scaling resistance of concrete.

The measured parameters for the durability study were the natural frequency of transverse vibration, weight, and length changes. For the scaling resistance study, the weight of material loosened from the top surface was the measured index.

Duplicate slabs were cast to determine the effect of prestress on the permeability of concrete. These slabs had standpipes sealed to their top surfaces to provide a means for the determination of rate of fluid ingress under a two-foot pressure head.

Since steam curing is the predominant practice in most prestressing operations, half of the slabs were steam cured to study this effect on the durability, permeability, and scaling resistance of prestressed and non-stressed concrete.

CHAPTER II
REVIEW OF LITERATURE

The hydration of portland cement

The chemical and physical transformations which occur when water and portland cement are combined are highly complex and not fully understood. However, basic scientific investigations in this area, with the aid of such refined techniques as X-ray diffraction analysis and electron microscopy, have greatly aided the understanding and explanation of the many complex phenomena existing in the hydration process. A thorough review and discussion of the work which has been accomplished in this area is beyond the scope of this paper; however, a brief discussion of the hydration process, as it is understood at present, seems necessary in order to better understand the porous structure of the hydrated product.

Four compounds are generally regarded to be the main constituents of portland cement. These compounds, or phases, are identified in Table I, along with their compound compositions, accepted abbreviations, and average weight percentages as calculated by the Bogue* method for a typical Type I, or standard, cement (1).**

* A method devised by R. H. Bogue, circa 1930, by which the amounts of the compounds in a cement can be calculated if the elements are known from a quantitative chemical analysis.

** Underlined numbers in parentheses refer to references listed in the section LITERATURE CITED, beginning on page 213.

TABLE I

MAJOR CONSTITUENTS OF PORTLAND CEMENT

Phase	Compound composition	Abbreviation	Weight content
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2$	C_3S	48 %
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2$	C_2S	27 %
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	C_3A	12 %
Tetracalcium aluminoferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	C_4AF	8 %

In addition to these major phases, there exist other compounds in portland cement, such as MgO , TiO_2 , Mn_2O_3 , K_2O , and Na_2O , which amount to only a few per cent of the weight of the cement. CaSO_4 , in the form of gypsum, is also added to the cement during manufacture, primarily for the purpose of preventing "flash setting" of the cement.

The manufacturing processes whereby these compounds are produced and combined in the desired proportions, are described by many authors (1, 2, 5, 14) and will not be further discussed in this paper.

The word "compound" is usually reserved for pure substances which have definite formulas. Since the four constituents listed in Table I usually contain relatively large quantities of dissolved impurities, their composition formulas are not quite correct, so most researchers prefer to call them phases. The relative amounts of these phases are dependent upon the proportioning of the raw materials from which the cement is manufactured, and portland cements have been classified into basic different types depending upon the relative amounts of these major phases and of

the other minor compounds in the cement.

When water in the correct proportions is mixed with portland cement, a plastic cohesive mass is formed composed of aqueous solution, a little powdered gypsum, and particles of cement which lie in the size range between 1/2 micron and 75 microns (3). These particles immediately begin to be transformed by reaction with the water to form new compounds approximately as shown in Figure 1 (4).

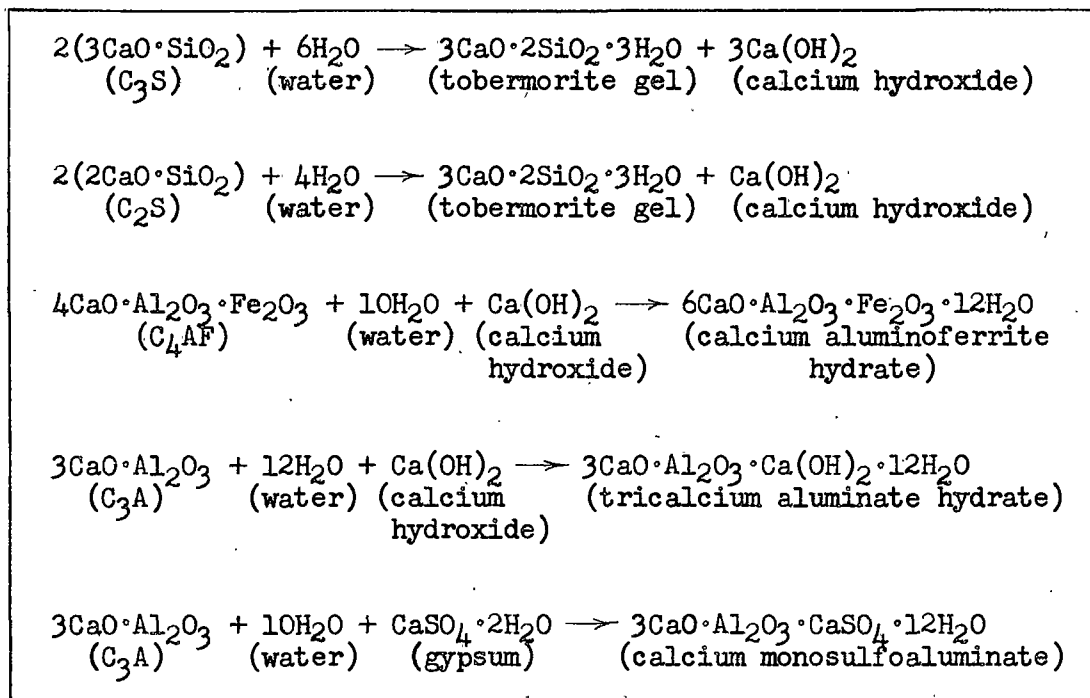


Fig. 1. Portland cement hydration reactions (4).

It should be understood that the reactions described in Figure 1 are probably not stoichiometric equations, but serve only as a guide to visualize the transformations that occur in the hydration process. These reactions will be discussed briefly before proceeding to a discussion of the physical characteristics of their combined mass.

The reaction of tricalcium aluminate with water and calcium hydroxide is quite violent, and leads to a high heat production and rapid stiffening of the cement paste, which is called flash set. If unchecked, this reaction is very undesirable. In order to retard this reaction, gypsum is usually interground with the cement clinker during manufacture, and when water is added to the cement, the C_3A and gypsum combine to form insoluble calcium monosulfoaluminate. It has been theorized that the calcium monosulfoaluminate forms a coating over the exposed C_3A particles, and thus hinders the rapid hydration of the C_3A .

The tetracalcium aluminoferrite is a relatively unimportant phase in portland cement. It is the iron bearing phase which imparts the characteristic gray color to portland cement, and in its absence the cement will be white. However, both C_3A and C_4AF are useful in the manufacture of portland cement, since they act as a flux and therefore reduce the clinker burning temperature, facilitating the combination of lime and silica (5). It should be noted that C_4AF also may react with gypsum to form calcium sulfoferrite, which may accelerate the hydration of the two silicate phases. (One can appreciate the reasons for careful control of the gypsum content in portland cement, since it can behave as an accelerator as well as a retarder.)

The two silicate phases, C_3S and C_2S , are the most important constituents of portland cement, and the behavior of these two phases alone is reported to be similar to that of portland cement (5). Together they constitute about 75 per cent of portland cement, by weight. It is generally accepted that these two compounds form the same products when combined with

water, these being crystalline calcium hydroxide and a calcium silicate hydrate known as tobermorite gel, so called because its composition and crystal structure resemble that of the natural mineral tobermorite. In a fully hydrated cement, tobermorite gel constitutes about 50 per cent, by weight, and is the most important cementitious material in the cement. About 25 per cent, by weight, of a fully hydrated cement is composed of calcium hydroxide.

The term "cement gel" has been used in describing that part of hydrated cement which is responsible for "internal surface" and porosity (4). Powers (6) has given a figure of $650 \text{ m.}^2/\text{cm.}^3$, or $250 \text{ m.}^2/\text{gm.}$, for the specific surface of the tobermorite, and approximately 87 angstroms as the size of the gel particle, expressed as the diameter of an equivalent sphere. This diameter corresponds to about 15 "diameters" of a calcium silicate molecule. Values for specific surface and gel-particle size have been obtained from adsorption and porosity measurements. Thus the sizes of the hydrated particles are so small that hardened pastes are colloidal systems, and the term "gel" depicts a finely divided, cohesive mass.

It is known that in the hydration process, there is a doubling of the volume of solids without a significant change in the paste volume. The hydrated cement is bonded to the unhydrated cement grains, but the mechanism whereby the structure growth takes place is not certain. There are several possible explanations compatible with observed heat gain periods, X-ray diffraction evidence, differential volume measurements, and absorbed water computations. Perhaps the hydration product forms

an enclosure, or shell, around each cement grain, and the dissolving interior silicates permeate outward through the layer of hydrate to precipitate on the exterior surface. Alternatively the shells may grow from the interior by continued reaction between the remaining unhydrated grain and water which penetrates the surrounding enclosure, the shells ceasing to expand at points of contact with other shells and subsequently distorting into available voids where there are no growth restrictions. Otherwise, the process may be one in which the silicates go into solution, and are precipitated throughout the entire paste mass when the solution becomes saturated.

Regardless of the exact mechanism of formation, the terms "colloidal system" and "gel" appear to be quite accurate in describing the cementitious hydration product. The bonding forces responsible for cementing action probably are due to physical attraction, or van der Waals' forces, between the individual gel particles, and between the gel particles and the aggregate surfaces. In addition, there may be chemical bonding, or cross-linking, between the gel surfaces. It may be noted that calcium hydroxide exerts a stronger attractive force per unit area than does the tobermorite gel, but the specific surface area of the most finely divided calcium hydroxide is only about one-tenth that of tobermorite gel (4), and thus the calcium hydroxide is a less important cementing material than is the tobermorite gel.

Finally, we arrive at a consideration of the paste structure as a whole, and patterns into which the hydrated particles become oriented. One very simple model (3) of the paste cross-section may be thought of as

the classical bubble model, with each bubble representing a gel particle. The bubbles, or spheres, are very closely packed, and the interstitial voids represent the paste voids which are called gel pores. In addition, there are large channels, or capillary voids in hardened paste, and these may be visualized in cross-section by considering that several of the bubbles in a few randomly scattered, irregularly shaped areas have burst. Considering that the specific surface of the paste proper may be about $650 \text{ m}^2/\text{cm}^3$, this means that the gel particles, represented by the bubble spheres, would average about 90\AA in diameter (5, 6). However, the gel particles are by no means spherical; rather they are mostly fibrous and platy, so the bubble model is of little more than academic interest.

The electron microscope has been the chief tool for observing the hydration structures, and some works contain many fine illustrations of these structures (7, 8, 9). The results of such electron optical studies have been interpreted (4) to show that the gel particles tend to form in the following shapes: 1.) clusters of rod-like fibers, 2.) rolls, or tubes, made up of very thin sheets only a few molecules thick, and 3.) nearly flat, but more generally crumpled sheets -- again, very thin. The sketches in Figure 2, on page 25, better illustrate these three formations. The gel fibers, rolls, and sheets, along with the microscopic calcium hydroxide crystals, apparently form an intricate network containing other amorphous materials and void spaces.

The permeability of concrete

As mentioned previously, the fresh cement paste is a fluid mass of

aqueous solution, cement grains, and some entrapped air bubbles introduced in the mixing process. When fully hydrated, the hydration products occupy a volume which is greater than that of the original solid volume by a factor of about 2.1 (10). In actuality, a portland cement never really becomes fully hydrated, but there is still approximately a doubling of solid volume under normal hydration circumstances. Thus as the hydration process continues, that volume of the paste occupied by water is gradually reduced as the hydration products are formed. When the hydration is essentially complete, there usually will remain water-filled voids which have not been filled with hydration products. These voids are termed "capillary voids" and are the primary reason for the permeability characteristics of concrete.

Ideally, one would desire an end product of the highest possible density, with no capillary voids. This is possible, providing the hydration is continued to completion, and the W/C ratio is not in excess of about 0.35, by weight (5, 10). However, in normal concreting practice, the W/C ratio is seldom, if ever, as low as 0.4, and is usually greater than 0.5. Thus, under most circumstances, there remain capillary voids in the matrix of cured, in-service concrete.

The porosity of the gel proper is about 28 per cent, but the mean "diameter" of these gel pores is in the range of only 15\AA to 25\AA (5, 11). The mobility of water in such small spaces would be quite unlike that of free water, so the contribution of the gel pores to the concrete permeability is negligible. Powers (12) has given a value of 7×10^{-14} cm./sec. as the approximate permeability of the gel pores. He explains that this

is only about one-twentieth to one-hundredth of the permeability of the paste as a whole. Therefore, the permeability of concrete is generally considered to be controlled by the capillary porosity of the cement paste. The volume of capillary voids may be as low as zero per cent or as high as 40 per cent of the paste volume (5), depending primarily on the W/C ratio, and the degree of hydration.

The capillary pores form a randomly distributed system throughout the paste, and though they vary in shape of cross-section, their "diameter" has been estimated to be in the range of 0.0005 to 0.00005 inch (11). This system may or may not be continuous, again depending upon the W/C ratio and degree of hydration. In a fresh paste, the water system is continuous throughout the mass, but as hydration proceeds the system becomes segmented and gradually constricted. If the W/C ratio is low enough, and the degree of maturity sufficiently large, the capillary channels may become completely "plugged" or segmented by the gel products. Estimates for the time required for the capillary channels to become discontinuous and segmented into capillary cavities, for various water/cement ratios, have been made for an ordinary Type I cement under standard laboratory conditions (10). These estimates are given in Table II.

The permeability of any cement paste will decrease with maturity, but if the W/C ratio is too large, discontinuity of capillary pores may never be achieved. As will be discussed later, the degree of continuity or discontinuity of the capillary pores in cement paste is an important factor in the durability of concrete.

TABLE II

CURING TIME REQUIRED FOR CAPILLARY DISCONTINUITY (10)

W/C ratio by weight	Time required
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
> 0.70	impossible

It should be mentioned that the porosity of concrete is not due entirely to the matrix, or paste, since the aggregate is also porous. In fact, the aggregate in a concrete may often be even more permeable than the paste. However, since each aggregate particle is coated entirely with a layer of paste, the permeability of the concrete is usually considered to be dependent upon the characteristics of the paste alone.

Concrete deterioration

Causative factors

The various organic and inorganic compounds which can cause destruction of concrete by chemical attack of the cement paste are too numerous for complete discussion. The effects of chemical agents on portland cement are not of immediate interest, except in cases where the destructive effects are magnified due to penetration into the concrete through the paste capillaries. More extensive discussions of chemical attack on concrete appear in references 2, 13, and 14. Usually, the chemicals to which concrete may be exposed can be anticipated, which is fortunate since

concrete is quite easily destroyed by so many, particularly in industrial situations.

Of the more common forms of chemical attack, only the effects of leaching, sulfate solutions, sea water, alkali-aggregate reaction, and natural slightly acidic waters will be considered in this discussion, since the permeability of concrete can be an important factor in reducing or amplifying these effects. It is realized that no concrete can resist the attack of many chemicals, particularly strong acids, since such chemicals destroy the paste by compound breakdown and separation; so the density and permeability of the concrete are of no consequence under such conditions.

Leaching of compounds out of cement paste occurs when water percolates through cracks, through poorly compacted concrete, or along poorly made joints. Usually, it is the readily soluble calcium hydroxide which is dissolved and removed by the water. Ordinarily the most harmful aspect of such a process is that it mars the appearance of exposed concrete surfaces by depositing white calcium carbonate, and sometimes calcium sulfate. However, the same process conceivably can occur in reasonably "good" concrete by water migration through the capillaries, with resulting channel enlargement.

Certain ground waters are essentially sulfate solutions, and these sulfates cause destructive expansion of concrete by reacting with calcium hydroxide and with the tricalcium aluminate hydrate. The reaction products are gypsum and calcium sulfoaluminate, which have considerably greater volume than the original compounds. Of course, such reactions would occur

at any exposed concrete surfaces, but the destructive effects would be considerably more serious in the event of deep penetration of the concrete by the sulfates.

Sea water contains other salts as well as sulfates. The sulfates attack the cement compounds as described above; however, failure arising from attack by sea water is not preceded by the large expansions noted in attack of sulfate-bearing ground waters. This is presumed to be because gypsum and calcium sulfoaluminate are much more soluble in chloride solutions (14), and thus the sea water leaches out these products before expansion occurs to any degree. However, salt solutions penetrate and rise in concrete structures by capillary action, and drying at or near the tide line causes crystallization to take place. This crystallization causes expansive pressures which are deleterious to concrete, and will be discussed more thoroughly in a later section.

The active silica compounds of certain aggregates will react with the alkalis, notably Na_2O and K_2O , in cement to form an alkali-silicate gel. This results in destructive expansion in the regions of the aggregate surfaces. This gel is of the "unlimited swelling" type (6), and when it absorbs water, significant pressures are developed. This reaction does not occur in dry concrete (14), and since a continuous supply of water increases its destructive effects it is apparent that the permeability of the concrete is an important factor in this type of attack.

Naturally occurring acidic waters are obviously harmful to concrete; however, most such waters are only very slightly acidic, and the damage is not so serious as might be expected. There are indications that such

waters may corrode the surface mortar of the concrete, and then the action stops or at least subsides (13). This may be because the reaction products tend to block the pores, preventing further ingress and attack. However, the dissolved paste may be carried away by moving water, leaving additional exposed surface on which the acid can act. A highly permeable concrete would undoubtedly be more rapidly destroyed by this type of attack, since more cement surface area would be exposed to the aggressive solution.

One other type of attack which might be considered to be in the realm of chemical deterioration of concrete would be that of corrosion of reinforcing steel in the concrete. Usually portland cement concrete provides good protection of embedded reinforcing steel against corrosion. This protective value may be ascribed to its high alkalinity and relatively high electrical resistivity in atmospheric exposure (13). However if cracks should develop, or if the capillary permeability of the concrete is too large, the ingress of moisture and air can cause steel corrosion, resulting in destructive expansion due to the increase in volume of the steel oxidation products. In addition, the absorption of salts which might exist in the penetrating moisture can lead to anodic and cathodic areas in the concrete. The resulting electrolytic action can cause an accumulation of corrosion products on the steel, with a consequent rupture of the adjacent concrete, as well as a reduction of the steel cross-sectional area. Of course, cracks which extend to considerable depths into the concrete can be caused by many factors, not the least of which is the destruction promoted by an initial high capillary permeability.

It is also pertinent to note that, in the absence of cracks, a highly permeable concrete will be able to contain more water than will a more dense material. This greater water content means that the electrical resistivity of the concrete will be reduced, which can result in galvanic corrosion of the reinforcement.

Thus, we can observe many forms of concrete deterioration which we might classify as being the result of chemical attack on concrete. All of these are, to a degree, affected by the permeability of the concrete, the intensity of attack generally being increasingly dependent upon the permeability.

In the realm of physical, or mechanical destruction of concrete, we may certainly consider excessive loading, impact, and surface wear or abrasion. However, these are directly controllable by the users and can be accounted for during the design of the structure. These conditions will not be considered further in this paper.

One type of mechanical deterioration which is exceedingly important and difficult to control, however, is that of frost action against concrete. As saturated concrete is frozen, the water in the capillary pores freezes and expansion takes place. If the stresses developed by this expansion exceed the tensile strength of the concrete, damage will occur resulting in cracking and spalling. This type of destruction, as well as that occurring as a result of de-icing salts on the concrete, will be discussed later.

Protective measures

A few of the ways in which concrete can be damaged have been discussed, and now consideration will be given to some measures which can be taken to prevent, or at least hinder, these destructive mechanisms. One obvious protective measure against all of these destructive causes is complete enclosure of the concrete in an impenetrable shield. Surface treatments with bituminous or rubber products, resins, and other agents have been employed successfully, and such treatments are probably the only effective means for protecting concrete which may be exposed to harsh chemicals, such as strong acids. However, complete surface sealing can be expensive and often impossible where concrete is cast in situ.

The resistance of concrete to the attack of slightly acidic solutions can be improved by allowing the concrete to dry in air before exposure (5). The $\text{Ca}(\text{OH})_2$ in the cement reacts with CO_2 in the air to form a surface film of CaCO_3 , which blocks the surface pores and reduces the permeability. Air drying is usually practicable only with pre-cast concrete members. For cast-in-place structures it is best to exercise careful control of the concrete mixing and placement so that a high quality, low permeability concrete will result.

Where the concrete is to be exposed to sulfate-bearing waters, it is possible to reduce the damaging effects by using a cement which is low in C_3A content, thus providing less reactant. Also, replacement of some of the cement by pozzolanic materials is helpful, since these combine with, and effectively fix or stabilize, some of the free, or readily soluble $\text{Ca}(\text{OH})_2$. However, the permeability of the concrete is a most impor-

tant determinant of the seriousness of sulfate attack, and the greater the permeability the more vulnerable will be the concrete.

At this point, it might be noted that steam curing of concrete is beneficial in that it increases the resistance to sulfate attack, and practically eliminates leaching and efflorescence (2). More will be said about steam curing in a later section.

In general, the best protection for concrete against sea water attack is to assure that the concrete is of low permeability and high density. Also, it is important that the reinforcement in coastal structures be covered by sufficient depth of concrete to prevent ready access of the corrosive liquids to the steel.

Control of the destructive effects of alkali-aggregate reactivity is generally achieved by limiting the alkali content of the cement, and/or by rejecting those types of aggregate which are potentially reactive with the alkalies in cement. Also, the addition of finely ground siliceous, or pozzolanic materials to the concrete can reduce the expansion by reacting initially with the alkalies, thereby reducing the quantity of alkaline materials available for reaction with the larger aggregate particles after hardening. As has been noted, however, impermeability is a highly important criterion for the resistance of concrete to this type of deterioration.

Leaching is entirely dependent upon the permeability of the concrete; and in the absence of cracks and poor compaction, the seriousness of this type of damage is primarily dependent on the capillary characteristics of the concrete. Thus, good construction practices and mix proportions are

imperative for prevention of this phenomenon.

Therefore, the importance of low permeability of concrete can not be too strongly emphasized as a factor for improvement of durability under most common natural conditions. The use of surface treatments and coatings, as well as other procedures which effectively plug the capillary pores, has already been indicated as being practical. Also, the importance of good compaction and the lowest possible W/C ratio consistent with adequate workability has been emphasized. Certain water-reducing admixtures are marketed which allow the reduction of water content in concrete without reducing the workability. Any such admixtures which allow a reduction in the W/C ratio are beneficial to the durability of concrete, providing no adverse reactions or shrinking and swelling characteristics are induced by the use of such materials.

For resistance to frost action on concrete, again low permeability is the most important single factor, in that it affects the degree of concrete saturation. In addition, the degree of aggregate saturation is important (15), since a highly saturated aggregate particle will expand upon freezing, and tend to destroy the surrounding matrix. In general, dry aggregate will result in a more frost resistant concrete.

Perhaps the most effective means for improving the freeze-thaw durability of portland cement concrete is air-entrainment. There are many compounds, notably natural resins, tallows, and sulfonated soaps or oils, which will cause billions of minute bubbles to be distributed throughout the concrete mass when added to the fresh concrete during the mixing process. Other materials interground with the cement clinker

during manufacture will accomplish the same effect. In addition, gas-forming agents, such as aluminum or zinc powder, and hydrogen peroxide, can also cause nearly the same effect.

The primary reason for the beneficial effect of air-entrainment is that the water under pressure in the capillary voids is afforded a much shorter path to other voids which can accommodate the excess moisture. This factor will be elaborated in the following section. An additional important benefit of air-entrainment is that of allowing a reduction in the W/C ratio. The tiny bubbles retain their sphericity, effectively replacing some of the fine sand particles, and thereby reducing the water demand. They are also rather like a lubricant between the solid particles of the fresh concrete, allowing the particles to glide past each other more readily, thus causing an increase in workability. The reduced W/C ratio, as has already been indicated, causes a reduced permeability in the mature paste.

Of course, any surface treatments or coatings which effect a reduction in the permeability of concrete will generally improve its frost resistance.

Thus, the effect of permeability on the ability of concrete to resist many ordinary destruction mechanisms is quite pronounced. Usually, any material or procedure whereby the ingress of moisture can be hindered or prevented will result in a concrete better able to withstand many types of chemical and/or physical attack.

Freeze-thaw and related modes of destruction

A few statements have been made concerning frost action upon concrete. As the concrete is frozen, moisture in the voids will begin to freeze and expand. Freezing will occur first at the exposed concrete surface, and then proceed slowly inward. Thus ice formed in the pores at the surface will block the pores, and the rate at which the water will be displaced by the advancing ice will depend upon the rate of freezing and the degree of saturation. The hydraulic pressure developed will depend upon the length and size of the capillary channel and the permeability of the paste between the capillary and another void that can accommodate the excess water (16). The pressures developed can be quite large, since water undergoes a volume increase of about 9 per cent when frozen.

Freezing of the water in the gel pores is quite unlikely under most natural circumstances, since these pores are so small that the formation of ice nuclei would probably not occur above about -78°C (17). However, movement of water in and out of the gel pores has been theorized as an important factor in the damaging effects of shrinking and swelling of the cement paste (4). In light of the observed physical forms of the hydrated gel products, this movement might occur as shown in the sketches of Figure 2 (4).

From entropy considerations, Powers (17) has suggested that, with a fall in the temperature of the capillary water and ice, the gel water acquires an energy potential enabling it to move into the capillary pores containing ice. Thus the ice can grow and cause further expansion.

