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THE DURABILITY OF CONCRETE UNDER FROST ACTION

BY

ANALYZED

E. G. SWENSON

JUNE 1955

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Technical Paper No. 26
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Division of Building Research

Ottawa
June 1955

PREFACE

This paper, which is the result of a literature search carried out as the initial phase of a program of studies on the durability of concrete, deals with a subject which is of unusual interest to this Division. Durability is an important requirement in all building materials and particularly so in the case of the principal structural materials such as concrete. Durability under freezing conditions is of particular concern in Canadian building.

This review serves to emphasize the very important role played by water in the deterioration of concrete and the need for a still more intimate knowledge of its action. Much of the present knowledge obtained from a study of concrete can be used to advantage also in studies of other materials.

Ottawa,
April, 1955.

Robert F. Legget,
Director.

THE DURABILITY OF CONCRETE UNDER FROST ACTION

by E. G. Swenson

Adequate durability under conditions of service is one major requirement common to all building materials. Since the service life required is seldom less than twenty, and frequently more than fifty years, the evaluation of durability becomes a very slow process, unless accelerated laboratory methods can be found. Much attention has therefore been given to the development of such methods, and much information is available in the literature.

Ultimately, it may be possible to predict the durability of a material under a given set of conditions. This will require, however, that the factors involved, and their functional relationship to durability are known, and that all pertinent coefficients have been evaluated. The present position falls far short of this, with evaluation being carried out in most cases by noting certain changes in a material as it is subjected to conditions intended to simulate in an accelerated fashion the deteriorating influences to be found in service.

The present empirical methods of laboratory evaluation pose at least three major considerations. There must first exist some suitable method of evaluating the progress of deterioration. This is still a subject of much debate and there are several methods in current use. Loss of dynamic modulus is now growing in acceptance as an index of deterioration in freeze-thaw testing. The selection of the proper exposure factors and the ways in which these are to be incorporated in a laboratory test have not as yet been resolved. There are four distinctly different sets of test conditions in current use in testing for durability under freeze-thaw conditions alone. Finally, it must be possible to relate the performance of the material in the test with that to be expected in the field.

The major problem lies in the proper interpretation of the results, whatever the method used. It is most important that the phenomena that occur in the field be recognized and understood. Water plays a very important role in almost all forms of breakdown of materials, especially in the case of deterioration under freeze-thaw action. A study of durability may therefore be regarded fundamentally as a study of the action of water in materials.

1. THE PHYSICAL STRUCTURE OF CONCRETE

1.1 Properties of Hardened Cement Paste

The major chemical constituents of portland cement are silica, alumina, lime, and iron oxide. In properly clinkered cement they are present as the chemical compounds: tricalcium and dicalcium silicates, tricalcium aluminate and tetracalcium alumino-ferrite. The chemical reactions between

water and these compounds involve hydrolysis and hydration, the mixture of products consisting principally of hydrated silicates and aluminates of calcium. These products are largely colloidal and retain their colloidal properties after the cement-water paste has hardened. Dispersed throughout this gel are microcrystals of calcium hydroxide (a product of hydrolysis), small crystals of the sulpho-aluminates of calcium, crystals of hydrated calcium silicates, and bodies of unhydrated cement particles.

Tricalcium silicate and tricalcium aluminate are responsible for setting and early hardening. The tricalcium aluminate contributes very little to the subsequent hardening of the paste. The dicalcium silicate reacts more slowly and is responsible for the later gain in strength and hardness. The iron compound appears to play no significant role in the hardening of cement paste. The gypsum interground with the cement acts as a retarder to regulate the initial setting of the cement. As in most chemical reactions, the setting and hardening of the paste are accelerated by an increase in temperature and by the addition of catalysts.

Any colloidal gel is a metastable system chemically, and can be induced to change over to the more stable crystalline form. Under ordinary conditions, this change is exceedingly slow in the case of cement gel. Microscopic evidence indicates that after twenty years there has been a considerable conversion from the colloidal to the microcrystalline state in hardened cement paste (1). This change is accelerated to some extent by a higher initial water-cement ratio; it is brought about rapidly by high-pressure steam curing, the products, however, being somewhat different.

During the initial stages of gel formation the paste undergoes an expansion due to the absorption of water, a characteristic of all hydrophilic colloids. This is followed by contraction or shrinkage through loss of water by hydration and evaporation. The initial drying shrinkage is largely irreversible (2) and is of the order of 0.05 to 0.06 per cent for concrete exposed for six months to dry air. Concrete containing sandstones that exhibit a high degree of moisture movement themselves may shrink twice as much as those containing limestones (3). Shrinkage is many times greater for neat cement paste than for concrete. Expansion on subsequent wetting of well-cured concrete is only about one-half of the initial drying shrinkage. This small reversible volume change varies with the degree of hydration and increases with cement content and water-cement ratio.

During drying shrinkage, local tensile stresses are set up which produce microcracking in the paste. This appears to be a direct result of the restraint to shrinkage contributed primarily by the coarse aggregate. The majority of these microcracks are probably healed by continued hydration (autogenous healing), the degree to which this is achieved depending on the water available and the original fineness of the cement. It is to be expected that the less finely ground cements would provide greater reserve for this action.

The specific surface of hardened cement paste is of the order of 2 by 10⁶ square centimetres per gram of cement (4). This is roughly about twenty times that of high-pressure steam-cured paste in which much of the paste gel has been converted to the microcrystalline state.

1.2 Types of Voids

(a) Gel pores. - Hydrogels which are partially dried develop a system of pores which are characteristic of the particular material. In hardened cement paste these ultra-fine pores are characteristic of the type of cement and their number is proportional to the amount of cement hydrated. The very large specific surface of cement paste is determined by its system of gel pores. They are estimated to be about eight times the size of a water molecule, or about 30 Å in diameter (4). The actual gel particle itself is about 100 Å in diameter (51).

(b) Capillary pores. - These consist of scattered submicroscopic channels and cavities, some isolated, some interconnected. The chief contributors to the formation of capillary pores are, (a) microcracking resulting from shrinkage stresses set up in the hardening paste, (b) the original water content of the paste and (c) degree of curing received. An excess of mixing water accumulates in small spaces which gradually empty through continued hydration and evaporation, leaving a more or less connected capillary system.

Capillary pores are largely responsible for the permeability of cement paste. Their size ranges from about 200 Å to about 800 Å in diameter (4). Unlike the gel pores, the capillary pores gradually diminish in size and number as they become filled with the products of continued hydration and salts of crystallization.

(c) Macropores. - The mortar paste in concrete contains larger voids which result from a number of causes. Relatively large water pockets may occur which eventually empty during drying. Accidentally entrapped air usually accounts for 1 to 2 per cent of the voids volume in concrete. Fissures occur on the underside of large aggregate due to a combination of settling and local bleeding. Vertical channels are formed as a result of compaction particularly in wet mixes. These are especially dangerous in sidewalks and pavements since they permit ready absorption of water.

Purposely entrained air may be classified as a macropore system. These pores are essentially isolated from each other and are of the order of 0.01 inch in diameter (5).

In general macropores are large enough to remain essentially unaffected throughout the life of the concrete.

(d) Pore system of aggregate. - The aggregate used in concrete is almost always a heterogeneous mixture of rock and mineral types. Certain quarried rock, however, such as limestone, may be very homogeneous. The pore system of the aggregate as a whole is at least as varied as that occurring in the cement paste. It consists

of gas bubbles found in glassy lavas, plane fissures and ramifying passageways. These voids in rock may be empty, partially or completely filled with chemically precipitated minerals such as quartz, or insoluble residues such as clays (6). Generally speaking, porosity may range from very low values as in dense limestones to very high values as in the case of some sandstones. Of special importance to the durability of concrete is the relative size of the continuous voids in aggregate and hardened cement paste.

1.3 Porosity of Concrete

In an average mix (1:6) with a water-cement ratio of 0.60, the water voids make up about 12 per cent of the volume of the concrete or about $6\frac{1}{2}$ per cent on a weight basis. In terms of paste alone this is approximately 40 per cent by volume. In over-sanded or high-slump concrete this value may go as high as 20 to 25 per cent of the volume of the concrete.

The paste porosity of concrete decreases with age due to the deposition of the products of continued hydration. In general, porosity increases with increasing water-cement ratio, and with decreasing cement content. Well-graded aggregate and proper compaction techniques tend to reduce porosity.

2. MOISTURE MOVEMENT IN CONCRETE

2.1 How the Water is Physically "Held"

(a) Theoretical aspects.- Although many of the hydrated compounds in set cement are known to exhibit step-wise vapour-pressure -- water content relationships, experimental curves are essentially smooth. This has been attributed to a merging of curves for the several hydrates present (2) but is probably due to the characteristic behaviour of colloidal hydrates. The calcium sulpho-aluminates are definite salt hydrates. In any case, the chemically bound water is bound very firmly and the hydrates exhibit extremely low vapour pressures.

The physically held water in a porous system like concrete is not all free water in the strict sense of the word. It is bound more or less strongly by certain forces determined by surface attraction and capillary phenomena. The theories advanced to explain physically bound water in a porous solid are based largely on data obtained from highly uniform materials, and depend on whether the capillary system or the intrinsic structure of the material is the predominating factor (2).

Where importance is attached to capillary structure, the capillary-condensation theory has been used in explaining physically bound water. The vapour pressure of a porous solid is determined by the capillary pore diameter at which the liquid meniscus occurs and the corresponding curvature of the meniscus (2). The smaller the pore diameter, the greater the curvature, the lower the vapour

pressure and the more strongly is the water held. The origin of the forces responsible for the curvature are attributed to the inequality of the cohesive and adhesive attractions between molecules at the liquid-solid interfaces (7). Adhesive forces affect the angle of contact, influencing the wetting process. The cohesion forces determine curvature through surface tension.

In more modern theories, the concept of surface absorption is applied to physically held water at low relative humidities; capillary water can exist only at high relative humidities.

The surface of a solid is an asymmetrical environment in which there is an uneven electron density distribution (8) due to the phenomenon of polarization. Anionic atoms, such as the oxygen atom, are highly polarizable while cations are polarized to a lesser extent. A rearrangement occurs in an attempt to decrease the intensity of the unbalanced surface forces. The degree to which this is accomplished determines the "reactivity" of the surface. The surface exposed immediately on fracture is nascent, or very reactive, and undergoes rearrangement to lower the surface energy.

According to the same concept water surfaces exhibit the same phenomenon. In water this is referred to as the "Helmholtz double layer"; i.e., an outside layer of polarizable oxygen and a second layer of non-polarizable hydrogen. The water at the surface therefore has a different atomic structure than water within the liquid body (8). There is consequently a certain reactivity at a water surface as in the case of a solid surface.

The nature of the water film adsorbed on a solid surface has been explained by the monomolecular concept of Langmuir and, more recently, by the B.E.T. multimolecular theory. The latter postulates a succession of layers of water molecules with affinity decreasing with increasing distance from the solid surface. On the average these forces are of a lesser order than chemical forces involved in hydrates but they extend over greater distances. These forces of adsorption, often referred to as van der Waals forces, produce, during condensation of moisture, a total heat made up of heat of liquefaction plus a heat of interaction or adsorption which may be greater by 65 per cent than the former (4). The amount of water adsorbed is proportional to the surface energy of the solid, the area of the solid, and the temperature and vapour pressure of the gas.

The phenomenon of surface adsorption is accompanied by a "compression" effect of the water. This can be determined experimentally through property changes such as decrease in specific volume. In hardened cement paste the specific volume of gel water averages about 0.90 (4) and is probably much lower than this for the first few layers. It may be noted here that exerting an external pressure on water lowers its specific volume and raises the vapour pressure, but the compression effect of adsorbed water produces a lower specific volume and lowers the vapour pressure. Thermodynamically, adsorbed water possesses lower free energy, or exists at lower energy levels than ordinary water and has, in effect, lost its original identity.

The significance of these adsorptive forces in concrete may be better grasped when one considers the relatively large surface area of hardened cement paste gel. It is estimated that 1 gram of hardened cement paste has a surface area of the order of two million square centimetres (4).

Theories involving solid solution, which is the normal phenomenon occurring in the swelling of a gel, and hydration-dehydration theories that are related to the variation of chemical bond strength of the complex cement hydrates, cannot be completely ignored. Whether the water in these states is subject to the ordinary adsorption and desorption behaviour in concrete has not been clearly demonstrated. When one considers that water in concrete may be "held" by capillary action, surface adsorption, solution, and hydration (9), it is not surprising that the mechanisms involved in moisture movement and frost action are far from being understood.

(b) Classification of Physically Bound Water.- In concrete the pores in the cement paste and the aggregate may be classified as gel pores, capillaries, macropores, and aggregate pores, the latter comprising all of the first three types.

A sharp distinction between the physically bound water in each of the three types of pores is not practical since removal by drying does not completely empty one type of pore before the others are affected. Capillaries, for example, contain a small proportion of water which is more strongly bound than some of the gel water, and macropores contain a very small quantity of strongly adsorbed water. Still it is convenient to classify water as gel water, capillary water and macropore water. Water in macropores, however, may be considered as free water since the surface forces are relatively insignificant.

Powers (4) has used a convenient but arbitrary method of distinguishing evaporable water and non-evaporable water by means of a desiccant, a mixture of two hydrates of magnesium perchlorate at 23°C. This is equivalent to drying to a vapour pressure of 4×10^{-4} mm. of Hg and is not quite as desiccating as the usual drying at 105°C. The non-evaporable water is largely combined chemically but would also include some strongly absorbed water, particularly in gel pores. The evaporable water would be largely physically held water but probably also includes some water from the less stable hydrates such as the calcium sulpho-aluminates.

2.2 Factors Involved in Moisture Distribution

(a) General Aspects.- The relative amounts of physically held water in gel pores, capillaries, and macropores at a given temperature and a fixed relative humidity, is determined by their respective affinities for water. From earlier considerations it was indicated that several types of forces are responsible for this affinity and that more than one is present in each type of pore. For example, in capillaries surface adsorptive forces are present as well as capillarity. The relative binding power of capillarity and surface

adsorption is difficult to assess. It is questionable whether a distinction should be made at all since the forces of capillarity are related to surface phenomena. In hardened cement paste the heterogeneous nature of the surface would tend to magnify variations in surface effects in the gel pores and the smaller capillaries. Furthermore capillarity would be affected by dissolved salts such as the alkali sulphates and the lime released through hydration. Any distinction made between capillary and gel water is therefore rather arbitrary.

In hardened cement paste of low original water-cement ratio, properly compacted and cured, by far the greatest proportion of surface area is in the gel structure and it is therefore reasonable to assume that on the average gel water is more strongly held than capillary water. As the capillary diameter decreases the capillary forces increase so that, under drying conditions, some of the more loosely bound gel water can be lost before all the capillary water is removed.

(b) Desorption and adsorption effects.- If a completely saturated sample of concrete is exposed to progressively lower relative humidities at a constant temperature the physically held water is gradually lost through evaporation. Macropores would be the first to lose water followed by the water in the largest capillaries where the menisci would recede to regions of smaller diameter. At some relative humidity below saturation the macropores would become completely empty except for a thin film of adsorbed water on the surfaces. In the larger capillaries the menisci would have receded to positions where the surface curvature corresponds to equilibrium vapour pressure conditions (6). Under these conditions only the most loosely held gel water is lost.

As the relative humidity is further lowered some of the larger capillaries empty while the water in the smaller capillaries evaporates until equilibrium is again reached. The adsorption forces in the gel pores prevent the same rate of loss as in the capillaries. At this point then, there is no water in the macropores and by far the larger proportion is in the gel pores. Eventually a point is reached when the capillaries are, for all practical purposes, emptied and the water held is entirely in gel pores except for highly adsorbed surface films in capillaries and macropores. In hardened cement paste this condition is obtained at a relative humidity of about 45 per cent (4). Further drying results in water loss from gel pores.

From actual data on a cement paste ($w/c = 0.59$) wet-cured for six months (4), the proportionate loss of water by the pores when the relative humidity is decreased from 100 per cent to 80 per cent was found to be about 40 per cent decrease in gel water and 80 per cent decrease in capillary water. At the same time the total water loss was 56 per cent. At a relative humidity below 45 per cent essentially all the water is held in the gel pores.

It is important to note as evidence supporting this that shrinkage of hardened cement paste during desorption is not noticeable until the aqueous vapour pressure drops considerably below 50 per cent of the saturation pressure. Thus shrinkage is associated with loss of gel water as in the case of any hydrophilic colloid. Freyssinet (10)

however, attributes shrinkage of concrete to the increase in tension of the water held in its capillaries as drying proceeds, thus inducing a compressive stress in the solid which produces elastic deformation. More recent theories favour the concept that adsorbed water is under compression which induces a tension in the solid resulting in expansion (2). As drying proceeds this compressive stress is reduced, the tension in the solid is reduced, and shrinkage occurs.

In the reverse phenomenon of adsorption, the water is adsorbed on the dry surfaces of the solid, the first stage being the monomolecular layer of Langmuir, followed by multimolecular adsorption of the B.E.T. theory, up to about 45 per cent relative humidity where capillary condensation starts.

As for other porous materials, hardened cement paste exhibits adsorption-desorption hysteresis. That is, under the same conditions of temperature and relative humidity, the water lost on drying is always less than the water gained on wetting. One explanation is that during adsorption the vapour does not completely wet the surface of the solid whereas desorption corresponds to complete wetting (11). Actually this implies that sorption curves do not represent true equilibrium conditions. According to another concept (12) crevices in the solid that are too narrow to accommodate the adsorbed film are forced open by the solid-to-liquid attraction, thus tending to force the solid units apart. The resulting swelling exposes more surface on which more liquid can be adsorbed. Once spread apart the crevice walls are beyond each other's range of attraction, hence the desorption curve would not follow the adsorption curve. The hysteresis occurring in the cement paste is common to other porous materials.

When a concrete specimen is placed in water the initial rapid intake of water does not result in expansion. It is proportional to the permeability and is dependent on capillarity. The subsequent slower intake is associated with surface adsorption of water in the gel and is related to expansion. The former depends on the coefficient of permeability, the latter depends on the coefficient of diffusivity.

(c) Effect of hydration.- Continued hydration of the cement in concrete increases the gel content and at the same time reduces the capillarity by filling of capillaries with the products of hydration. The total water held at saturation increases with the length of curing period but the evaporable water content decreases (4). If the original water-cement ratio is sufficiently low and the curing conditions favourable, the capillarity will be reduced to a negligible amount. This so-called "self-desiccation", however, is offset to a greater or lesser extent by the formation of new capillary systems through microcracking caused by restrained shrinkage. The coarse aggregate in concrete tends to reduce shrinkage but the stresses consequent to this restraining action of the aggregate produce microcracking. This phenomenon is markedly affected by the type of aggregate and by the water-cement ratio. If the latter is high the shrinkage and cracking incidence is high. Thus the capillary system

in concrete is likely to be changing constantly, increasing with drying and decreasing during reasonably long periods when moisture is accessible for further hydration.

The effect of increasing water-cement ratio on the susceptibility of concrete to freezing and thawing has been well established.

The influence of aggregate, particularly coarse aggregate, has often been noted and explained solely on the basis of absorption properties, degree of saturation, and differences in thermal coefficients of expansion of paste and aggregate. The additional possibility that the shrinkage restraint contributed by aggregate will produce a certain degree of microcracking and thereby increase capillarity has not received due attention.

The redistribution of moisture in concrete which is subjected to load appears to play a definite part in creep phenomena. A continuous load sets up localized stresses and deformations which result in a corresponding redistribution of moisture. Continued hydration would tend to stabilize these deformations and elastic recovery would not be complete (13, 49).

(d) Effect of temperature changes.- The magnitude and causes of moisture-volume changes in cement paste and in concrete are recognized. The variations in thermal expansion characteristics of aggregates are also well known. The magnitude of thermal expansion of cement paste and of concrete, however, varies with the moisture conditions within the material; this phenomenon has only recently been investigated (16).

The apparent coefficient of thermal expansion is at a minimum for a completely saturated sample of hardened cement paste, and also for one which is "bone dry". It is therefore the true kinetic thermal coefficient. Up to a relative humidity of about 40 per cent the apparent coefficient is only slightly higher than the true coefficient, the difference being attributed to adsorbed water alone. Above 40 per cent relative humidity, water menisci are formed which are affected by changes in temperature in such a way as to increase considerably the value of the apparent coefficient of thermal expansion. The maximum apparent thermal coefficient appears to be at 60 to 70 per cent relative humidity for concrete and hardened cement paste (16). The maximum for cement paste is higher than for concrete and the variation is much greater. This is to be expected of the gel structure of the paste. It is surprising that this relatively large effect of moisture condition on the thermal coefficient of expansion has received little or no attention as a factor in freeze-thaw durability studies of concrete.

(e) The concept of suction.- The nature of the forces by which moisture is held or retained against gravity in a porous material such as concrete may be considered collectively as moisture-retaining or suction properties of the material (14). The pressure of held water is always less than that of the atmosphere, the magnitude of this pressure deficiency being referred to as moisture suction or suction (14). The magnitude of suction at the air-water interfaces in capillaries, for example, is indicated by the radii of the menisci (24). A reduction in moisture content is therefore accompanied by an

increase in suction (15).

The suction of a comparatively dry porous material may be very high, in some cases exceeding 10,000 lb. per square inch while in a completely saturated sample the suction is zero. Table I, taken from a research paper on the moisture held in soils (15), illustrates the magnitude of suction forces operating in a dry or semi-dry porous material.

TABLE 1

The pF Scale in Terms of the Equivalent Negative Hydraulic Head, the Suction in lb./sq. in. and Relative Humidity

pf	Equivalent Negative Hydraulic Head		Suction (lb./sq. in.)	Relative Humidity %
	cm.	ft.		
0	1	3.28×10^{-2}	1.42×10^{-2}	--
1	10	3.28×10^{-1}	1.42×10^{-1}	--
2	102	3.28	1.42	99.99
3	103	3.2×10	1.42×10	99.92
4	104	3.28×10^2	1.42×10^2	99.27
5	105	3.28×10^3	1.42×10^3	93.00
6	106	3.28×10^4	1.42×10^4	48.43
7	107	3.28×10^5	1.42×10^5	0.07
	oven dry			

Since suction may be a combination of forces such as capillarity, surface adsorption, and solution, it is clear that moisture content is not uniquely related to suction. One material may have a higher suction than another material even though both contain the same quantity of water.

When two porous materials are placed in intimate contact, equilibrium moisture conditions require that suction pressures equalize, but the moisture contents of the two materials at equilibrium may be quite different. The suction forces operating between aggregate and cement paste in concrete would therefore affect the original water contents in each, and would have a direct bearing on durability. Large voids in the aggregate will be drained by smaller voids in the paste and stone, and the reverse will also take place (6). The moisture content of many aggregates when freshly quarried may be as high or higher than that obtained by vacuum saturation methods (20). The application of the suction concept to the study of the factors which affect freeze-thaw durability of concrete should prove fruitful.

2.3 Thermal Actuation of Moisture Transmission

Temperature gradients set up in concrete exposed to freezing and thawing cycles may result in a net transfer of moisture from warm regions to cold regions. The extent to which this occurs and the mechanisms involved may be of fundamental significance in the interpretation of test and field data.

In hygroscopic materials there is a much more intimate relation between water and the material during moisture transmission than is the case in pure diffusion (17). The permeability of hygroscopic materials to water vapour bears no direct relationship to their permeability to air. Winterkorn (18) has summarized the theoretical concepts that may be applied to moisture movement through porous solid systems subjected to a thermic potential or to a water-vapour concentration potential:

- (i) Diffusion of water vapour through a pore space under concentration or partial pressure potential;
- (ii) Diffusion of water in solid solution as observed for hydrophilic membranes separating chambers of different water-vapour pressures;
- (iii) Movement as capillary water due to difference in surface tension at different temperatures;
- (iv) Flow of moisture in the film phase along the internal surfaces of the porous system due to change in water affinity with change in temperature.

It is highly probable that the solid solution concept does not apply to concrete because of the inorganic nature of the materials involved. In the case of soil, it has been asserted that vapour diffusion plays only a small part in the observed moisture flow through a temperature gradient (19). Moisture transmission by capillarity is considered to be the main driving force by several research workers on soils (21, 23). More recently the film phase theory has been favoured and has been confirmed as applying to soil systems providing soils possess greater affinity for water at low than at high temperatures (22).

One of the main arguments for the film phase mechanism as against vapour diffusion lies in the difference in energy requirement. The heat of evaporation (or condensation) for vapour diffusion transfer requires much more energy than that for film flow. For a given thermal potential the optimum water transfer occurs at a moisture content that corresponds very closely to that required for a degree of compaction which provides the greatest lubrication value of water.

Winterkorn has developed the analogy between electro-osmosis and thermo-osmosis and, as part of the former theory, he notes that liquids like water, with little or no electrical conductivity, possess the greatest efficiency in moisture transfer in soils. The dissolved ions, like Na^+ , K^+ and Ca^{++} , have the greatest effects in retarding the transfer (18). Since the water in hardened cement paste contains relatively high concentrations of one or more of these ions, the rates of moisture transfer in concrete may be considerably affected.

Winterkorn also has shown (18) that in a saturated capillary system electro-osmotic permeability is a function of porosity and the physico-chemical inter-relationship between solid and liquid, and is not dependent on the size of pores. The electrical character of thermo-osmosis has been shown (18) and the concepts derived for electro-osmosis may be applied in a general way to thermal actuation of moisture transmission. Smith (21) and Bouyoucos (19) pointed out that in soils of low moisture contents the transfer of moisture increased with increase in moisture content up to a maximum. At moisture contents greater than this "thermal critical moisture content" the thermal transfer decreased as the moisture content increased. Transfer, therefore, at very low and at very high moisture contents was negligible.

While Bouyoucos concluded that vapour transfer in soils is negligible, W.O. Smith maintained that capillarity by itself does not appear capable of producing thermal transfer of moisture under ordinary temperature gradients. The latter, therefore, postulated a theory that vapour condensation serves as a trigger to start the process of coalescing of adjacent small globules of water. These are drawn towards cold regions through non-equilibrium conditions of temperature. This mechanism would start only if the water bodies in the capillaries are close together, a condition prevailing at higher moisture contents and agreeing in general with the maximum moisture transfer at the "thermal critical moisture content".

Johansson (23) believes that moisture transmission through a temperature gradient in building materials is by both vapour diffusion and capillarity, and that the latter occurs only as "localized capillarity" through condensation at one end and evaporation at the other. The rate of diffusion increases with moisture content for the larger pores and decreases with moisture content with smaller pores. As a result of an increased moisture ratio in the cold side, water is drawn back towards the warm side by a "moisture-equalizing" capillarity. Johansson uses this phenomenon to explain the gradual slope of the moisture distribution curve. The assumption is that if no reverse flow mechanism occurred, the moisture would build up on the cold side to saturation values. A phenomenon similar to this has been observed in other materials (25). The moisture-equalizing capillarity is almost negligible at low moisture ratios and becomes important only at higher moisture ratios.

Assuming that moisture transmission in concrete is essentially of the same character as that for soils, bricks, and other porous solid materials, the relatively low rate due to vapour diffusion for the dry solid, compared with high transmission rates due to a combination of vapour diffusion and capillarity for the wet solid, become very significant. The effect of age, curing conditions, water-cement ratio and other factors that affect the pore structure of cement paste should have a direct effect on moisture transmission through a temperature gradient. Although the problem is a complex one for concrete, preliminary research has yielded some promising results (45, 50).

2.4 Relation to Durability of Concrete

Whether the concrete which is subjected to freezing and thawing is a relatively small laboratory specimen or is part of a structure, temperature gradients are always produced under cycling conditions. These may cause a movement of moisture from warm regions to cold regions. The effect of this in the destruction of the material has not been established. The theories outlined suggest that the rate of moisture flow is affected by capillarity at higher moisture contents. The capillary system in hardened cement paste varies greatly with water-cement ratio, curing conditions, degree of hydration and probably with factors which involve shrinkage. For this reason it is highly probable that the rate of moisture transmission may also vary greatly.

Since the lowering of water vapour pressure is followed by a lowering of the freezing point of water, the phenomena of capillarity and adsorption will directly affect the durability of concrete. The distribution of water in the various pore systems will determine the amount of freezable water. The relative water contents and suction pressures of aggregate and hardened cement paste will influence the amount of freezable water in concrete.

3. CONCRETE DETERIORATION DUE TO FREEZING AND THAWING

3.1 Evaluation of Durability to Freezing and Thawing

When concrete is subjected to cycles of freezing and thawing, particularly at early ages, a progressive deterioration occurs which causes the rock-like material to become soft and crumbly. In general two types of destructive action are recognized (34). The first occurs with the richer, more impermeable concretes, and involves a gradual loss in strength and modulus of elasticity but with little or no spalling and weight loss. The processes of destruction appear to penetrate the whole specimen. The second type occurs with lean, permeable concretes and involves surface spalling with a consequent loss in weight. The inner core of the concrete remains essentially intact and the strength loss may be relatively small unless the specimen is subjected to prolonged cycling action in the presence of water. Intermediate cases involving both these types of destruction are common.

The methods used to determine the loss in durability to freezing and thawing are varied, but are usually based on the following, either singly or in combination: loss in compressive strength, loss in weight, reduction in modulus of elasticity, expansion, and visual and microscopic examination. A more recent development, in which the deterioration of concrete is related to the modulus of elasticity as determined by the rate at which sound pulses travel through it, promises to be an extremely useful tool both in the field and laboratory (26). Early indication of failure appears to be most reliably determined by length change (27). Loss in weight is probably the least reliable method, not only because of its dependence on spalling but also because of the effects of handling specimens. Reduction in compressive strength and modulus of elasticity are most commonly used, but neither method distinguishes between the two general types of destruction outlined above.

3.2 Factors Which Influence Durability

(a) Aggregate. - The most common type of destruction is the breakdown of the bond at the interface of the aggregate and the paste, or in the paste itself. This is associated with aggregate which is less porous than the cement paste (28). Water-logged porous aggregate causes a rapid breakdown of concrete, the aggregate itself failing before the paste (34). Aggregate with a coefficient of thermal expansion considerably greater or less than that of the paste will produce a concrete with lowered resistance to freezing and thawing (29, 39).

The degree of saturation of aggregate incorporated in concrete affects the quantity of freezable water present. Saturated aggregates cause a much more rapid deterioration in concrete than partially dried aggregates (30). The interchange of water between the aggregate and cement paste, as governed by their respective water contents and suction characteristics, may have an important bearing on durability (6).

(b) Mortar saturation and curing methods. - The durability of concrete appears in general to increase with decrease in water-cement ratio and with the length of curing period and age. An excess of water in a mix is retained for a considerable period and is largely freezable water. Although an excess of water may be lost at later ages, the capillary system developed in a mix of high water-cement ratio is susceptible to a high degree of water absorption. Specimens of low water-cement ratio absorb very little water during thawing periods and generally fail only through disintegration of the aggregate. Those with a high initial water-cement ratio have a higher degree of absorption and usually fail through mortar disintegration (32, 34).

Continuously moist-cured concrete is less durable than concrete which is moist-cured for a short period and then allowed to dry out (31). This, of course, applies only to periods of short duration. In general, durability increases with an increase in the period of moist-curing. Even intermediate drying periods increase durability by reducing the degree of mortar saturation.

For any given curing condition the older the specimen the less the destructive effect of freezing and thawing, due to self-desiccation resulting from continued hydration. There appears to exist an optimum curing temperature and an optimum degree of hydration to produce maximum durability of concrete (37).

Concrete subjected to freezing and thawing when the paste-plus-air component has a degree of saturation of 0.91 or greater will deteriorate rapidly. Below this value deterioration is much slower and probably is affected by a variety of factors such as expansion of inferior aggregate, differential thermal expansion of components, hydraulic pressure from resistance to flow of water, non-uniform distribution of freezable water, or adverse chemical reactions (35).

(c) Cement. - Variations in durability due to differences in cements are not usually of major importance but are measurable. Fineness appears to affect durability because of its influence on the water required. Fineness of 1,800 sq. cm. per gram (Wagner) is claimed to provide the highest durability (27). High early strength cements with fineness up to 2,400 sq. cm. per gram show the least resistance to freezing and thawing and the older cements (1200 to 1400) provided high durability. According to the same source, the types of cements (A.S.T.M. terminology) may be listed in order of increasing durability as follows: III, IV, I, II, V. Other factors which adversely affected durability are reported to be: high SO_3 content, high C_3A in older concrete, low $C_3S + C_3A$ in younger concrete, and freshly ground cement (27).

(d) Exposure conditions during freezing and thawing. - For any given temperature range an increase in the rate of freezing and thawing is followed by an increase in the rate of deterioration. For a constant thawing temperature, the lower the freezing temperature the quicker is the reduction in strength; for a given freezing temperature, the lower the thawing temperature, the quicker is the reduction in strength. It is claimed that a combination of low thawing temperature and low freezing temperature is the only way to distinguish intermediate quality aggregate from good and bad aggregate (31). The slowing up of deterioration with higher thawing temperatures is attributed to the longer time permitted for dehydration during cooling (31), and to autogenous healing at the higher temperatures (33).

Freezing in air and thawing in water is less destructive than freezing in water and thawing in water. Brine solutions are more destructive than water (34).

Specimens subjected to freezing and thawing until the modulus of elasticity was reduced by 70 per cent have shown complete recovery when stored in water for about one year. This has been attributed to autogenous healing (27).

Alternate cooling to 37°F. and warming to about 75°F. also results in deterioration of concrete (31), the greater the temperature range, the greater the effect. This is of particular significance in view of the possible connection between moisture movement and freezing and thawing.

(e) Air-entrainment.-- Properly entrained air in concrete increases its durability to a remarkable degree. Normal concrete contains about 1 to 2 per cent trapped air and fails in accelerated cycling tests at 10 to 50 cycles. Incorporation of 4 to 6 per cent entrained air in the same type of concrete increases the cycles required for failure to 100 to 300 on the average. Air-entrainment has the effect of reducing the degree of mortar saturation (35) and reduces the adverse effects of saturated aggregate (30) and high initial water-cement ratio (27). The efficiency of entrained air in increasing the resistance of concrete to freezing and thawing appears to depend on the air bubble spacing (5). The actual amount of air required for maximum resistance depends upon the paste content and the specific surface of the voids.

Entrained air reduces the durability of hardened neat cement pastes (36). This is attributed to the effects of adsorption of air on the finer fractions of cement particles. The fine fractions of sand also appear to retard air-entrainment. The optimum air-retention is obtained by sands between No. 30 and 50 sieves (36).

In addition to its inherent benefits, entrained air in concrete permits an appreciable reduction in mixing water for a given workability and may in this way also result in increased durability. Lean mixes benefit the most from air-entrainment.

3.3 Theories Advanced for the Destruction of Concrete by Freezing and Thawing

A study of the literature reveals that no completely satisfactory theory has been advanced to explain the mechanism by which concrete is destroyed by frost action. The most recent and exhaustive treatment has centred around the Powers hypothesis (34, 37). Powers distinguishes between two basic concepts: his own hydraulic pressure theory and the so-called Taber-Collins theory (38, 28).

The following is an outline only of the essential features of these concepts along with conclusions drawn from other sources. No attempt will be made to analyse critically the postulates made since further fundamental research is needed to clarify the nature of the processes involved.

The preceding treatment of the physics of concrete and of water in concrete is, it is suggested, necessary background for a critical examination of the mechanism of frost damage in concrete, as revealed by the major contributions to this field to date, as well as for further work.

(a) The Taber-Collins' hypothesis.- Collins (28) applied Taber's theory of ice lens formation in soils (38) to the freezing and thawing destruction of concrete. According to this concept cooling gradually progresses into concrete and when the freezing temperature is reached at a given plane the water freezes in the larger pores. The latent heat released maintains the temperature until all the water is frozen. The ice crystals formed tend to draw water from the warmer inner regions and grow until the hydrated paste is at least partially disrupted at this plane (providing enough water is present).

When the water supply for further crystal growth is exhausted, no more latent heat is released and the temperature then drops. Freezing of more water cannot now occur until the temperature has been reduced in regions where the larger pores still contain water. Thus ice lenses are formed at intervals determined by the rate of cooling and by the moisture available.

Planes of weakness in concrete subjected to freezing and thawing have been observed in the field and the laboratory (28, 37). In support of this hypothesis Collins found that water moved into a concrete specimen partly immersed in water and frozen from the top. Ice lenses have been found in pavement concrete destroyed by frost action.

(b) Powers' hydraulic pressure hypothesis.- According to Powers (34) the destruction of concrete by freezing and thawing cannot be attributed solely to direct crystal pressure resulting from ice formation. Even concrete with a moisture content considerably below the critical saturation value of about 0.90 will fail after successive cycles of freezing and thawing. Although concrete may have a high moisture content the adsorption and capillary forces are such that only part of the water is frozen at a given freezing temperature. This is illustrated by data in Table II (37).

TABLE II

Relation Between Temperature and the
Formation of Ice in Concrete

°C.	Amount of Ice Formed as % of Amount Formed at -15°C.
-0.25	21
-2.00	59
-4.00	70
-6.00	80
-8.00	86
-15.00	100

Powers' hydraulic pressure hypothesis for the destruction of concrete by freezing and thawing (34) may be summarized as follows:

- (i) Ice first forms at the cold surface, sealing off the interior of the specimen;
- (ii) Pressure exerted by expansion due to ice formation forces water inward to less saturated regions;
- (iii) In a fine-textured porous solid such as concrete, the relatively high resistance to flow of water sets up hydraulic gradients which exert pressure on the pore walls;
- (iv) This hydraulic pressure increases with increasing rates of freezing, degree of saturation, and fineness of pores;
- (v) When the hydraulic pressure exceeds the tensile strength of the solid, the pore walls are ruptured.

From experimental data on permeability and tensile strengths, along with certain assumptions, Powers has calculated the rate of flow of water which would develop sufficient pressure to disrupt cement paste. He concludes that his estimates are in good agreement with observed results.

During freezing, the resistance to flow of water increases with the distance from the surface. The point at which rupture occurs as a result of hydraulic pressure is called the critical depth of saturation. Crumbling or spalling begins at this point. For concrete of low permeability this critical depth may be so low that there is no evidence of spalling. The ultimate hydraulic pressures developed in such cases may, however, be very high and penetrate well into the concrete. For this reason the better quality concretes often show no spalling but a gradual deterioration takes place throughout the specimen. For more permeable concretes the critical depth may extend to several inches from the face and spalling results. The inner cores of such specimens may remain unaffected. Lean concretes of very high permeability may be practically immune to freezing and thawing because of the low resistance to flow of water, unless the moisture content is above the critical saturation value.

The hydraulic pressures, as calculated by Powers for a given set of conditions, drop very rapidly with a small drop in degree of saturation, Table III (34).

TABLE III

Relation Between Degree of Saturation and
Hydraulic Pressures Developed on Freezing

<u>Degree of Saturation</u>	<u>Hydraulic pressure developed on freezing under a given set of conditions</u>	<u>%</u>
1.00	taken as	100
0.99		86
0.98		68
0.97		56
--		--
--		--
--		--
0.917		0

It is evident that the self-desiccation resulting from continued hydration is therefore an extremely important factor in frost resistance.

During thawing, the ice within the specimen may melt before the surface ice is completely melted due to the lower melting point of the former. The negative pressure thus created will cause water to flow into this region and build up the moisture content. The thickness of the outside ice layer and the rate of thawing will, therefore, also affect the resistance to freezing and thawing. In addition to the dynamic concept of destruction by hydraulic pressure, Powers also recognizes that static pressures may produce the same result where escape of water is impossible through sealing by surface ice.

Entrained air increases the resistance of concrete by reducing the hydraulic pressures developed through freezing and thawing (5). Although nearly all concrete contains more than enough space to accommodate freezing expansion, the spacing of pores is such that destructive hydraulic pressures can develop in the paste.

As the spacing is reduced by air-entrainment the thicknesses of pore walls are reduced, thereby reducing the pressures which can be developed through resistance to flow of water. The actual porosity is, therefore, not related to durability; it is the proximity of air pockets which determines resistance. The spacing factor necessary to produce resistance to frost has been calculated by Powers to be in the order of 0.01 inch, the air requirement depending on the paste content (5).

More recent research by Powers (51), using more refined techniques, has extended the basic knowledge of cement-paste structure and its change in volume during freezing. His new findings are in essential agreement with his earlier work.

4. SOME FURTHER ASPECTS OF FROST ACTION

4.1 Effects of Frost Action on Building Stone

The extensive work of W.H. Thomas (40) indicates that frost action on various kinds of building stone is very similar to that on concrete. He attributes the destructive action in stone to expansion accompanying freezing but suggests that many cases of deterioration attributed to frost may be due primarily to the crystallization of salts in the pores, and that freezing merely completes the process. According to Thomas the high pressures developed are responsible for preventing a considerable proportion of the water from freezing. At some given temperature the pressure is relieved either by dilation or breakdown of the material or by the extrusion of ice. When stone is frozen slowly and maintained at the freezing point for a long period only small strains are developed although more of the water is frozen. This is attributed to extrusion of ice. A rapid rate of freezing does not allow this since a very much greater pressure is required to liquefy ice at a lower temperature. Conditions which prevent extrusion, such as the choking off of pores by deposition of salts, or by application of sealing materials such as waxes or paints, may increase the liability to damage by frost.

Thomas finds that, although one material may have a higher frost resistance than another at one rate of freezing, the reverse may be true at a different rate. Certain types of sandstone when frozen in semi-dry condition contract, and when frozen in saturated condition expand first, then contract if the freezing temperature is prolonged.

4.2 Effect of Frost Action on Soils

The exhaustive report of Beskow on frost action in soils (42) brings out a number of concepts which may have a bearing on frost deterioration of concrete. Since soil is generally an open system, the excess of water can escape the expansion effect accompanying the formation of ice. Only fine clays can be considered a closed system. The heaving that occurs in soil as a result of frost is due to water flow to the freezing zone. The mechanism is considered to be flow in the film phase. Frost heave appears to be independent of the rate of freezing and is actually a measure of the water sucked up. Grain size and pressure are the most important factors which influence heaving. Dissolved salts affect the adsorption film which in turn determines the flow of moisture and heave. Osmotic phenomena are thought to be responsible for this effect. Any method for reducing the thickness of water films would tend to reduce frost heaving. Among several substances found effective is calcium chloride.

The mechanism of frost action in concrete is probably intermediate between that for building stone and that for soils. The physical structure of closely packed, fine-textured soil is in general similar to that of concrete. The movement of water through temperature gradients may be expected to occur in the same way, and the modifying influence of dissolved salts is present in both cases. Beskow believes that ice crystallization in soil occurs at any small discontinuity of structure, such as a "crack, a flaw, or a contained foreign solid", since they represent a surface of weaker force of attraction for water. The resulting pressures widen the cracks. Crystal growth is caused by a reduction in the adsorption film adjacent to the ice crystal which increases the suction pressure, thus drawing more moisture from warmer regions.

Heaving action in soils appears to be analogous to spalling of some concrete. Beskow reports that maximum heaving occurs in a medium fine soil. Stiff clays are too impermeable to suck up water and very coarse soils do not heave. It may be noted here that the spalling of concrete occurs in cases of moderate permeability. A lesser order of heaving takes place in clay-free, fine silts due to the additive effects of small increments of expansion between particles although no ice stratification takes place. Dense concrete of low permeability tends to expand during freezing and thawing cycles.

Formation of ice crystals occurs only in soils during slow cooling. With greater rates of cooling ice crystals become less and less well defined. For a given rate of cooling, the finer the soil texture the less well defined is the ice crystal system. Pressure has the same effect as an increase in the rate of freezing by counteracting the formation of ice strata due to squeezing out of the adsorption film. This has a tendency to diminish the supply of available water for the freezing zone. Pressure in soil may be considered analogous to tensile strength in concrete. Examination of the Collins' and the Powers' hypotheses indicates a close similarity between their concepts and those outlined for soils.

In soils ice stratification and heave appear to occur at a definite critical grain size of 0.1 to 0.6 mm. with slow freezing. With rapid freezing the critical size appears to be 0.05 to 0.1 mm. The first evidence of frost heave begins with the fractions 0.01 to 0.005 mm. Assuming that grain size and pore size are roughly of the same order in soils and concrete it may be noted as significant that rocks of intermediate permeability are most susceptible to destruction by frost under natural conditions; more specifically, rocks with voids less than 0.005 mm. to 0.004 mm. in diameter drain effectively only at hydrostatic pressures in excess of the tensile strength of some rocks and concrete (6).

In materials such as concrete and soils, conductivity determines the temperature gradients established which, in turn, determine the rate and amount of moisture flow. The relatively high conductivity of dense concrete would therefore not be conducive to large temperature gradients and ice strata would not be expected

to form. For porous concrete the reverse would be true and reported data agree with this view (28).

Beskow also reports that freezing of water in soils often produces a conglomerate of ice crystals similar to hoarfrost, and that this formation is capable of producing very high pressures. The nature of the ice formed in dense concrete has apparently not been investigated although it may have a bearing on the destruction of concrete containing moisture below the critical saturation value.

4.3 Directional Freezing of Concrete

The actual conditions of freezing and thawing of a concrete structure may be quite different from those obtained during testing. One important distinction is that field concrete may be subjected to freezing from one side. Since this may result in moisture transmission, field performance may not correlate with laboratory results obtained by the conventional rapid cycling methods. An attempt to develop an accelerated test involving "primary directional" freezing has been reported by Bollen (41) to cause a much more rapid breakdown of concrete. Non-air-entrained concrete of good quality that may require 100 to 200 cycles to produce a required degree of deterioration by the normal rapid cycling is found to deteriorate to the same extent with only about 25 cycles by primary directional freezing and the usual thawing in water. Air-entrained concrete specimens, properly designed and fabricated, are just as durable under these conditions of test, however, as in conventional testing. Cylindrical specimens, frozen from one end by this method, failed by deterioration at different planes as reported for slow freezing (28).

5. SOME PROBLEMS REQUIRING FURTHER RESEARCH

The problem of evaluating the durability of concrete to freezing and thawing is a complex one, depending as it does on the particular combination of properties possessed in a given case. These properties in turn depend upon the nature of the materials used, proportioning, and mixing, placing and curing techniques. Finally the actual durability rating is likely to be dependent on the test conditions and the methods of test used.

Both the slow cycling and the rapid cycling methods of evaluating durability provide fairly good guidance in field work owing to the practice of fabricating test specimens from the same materials to be used on the job and using the same mix design. This procedure largely eliminates such variables as the paste properties of the cement, the thermal expansion and absorption characteristics of the aggregate, the water-cement ratio, and grading characteristics of the aggregate. Correlation between laboratory data and field performance is generally good.

Patent weaknesses still exist, however, particularly in the interpretation of data on concretes of intermediate and low durability. Some progress has been made in applying test data to distinguish good and bad aggregates, but aggregates that show good

durability under one set of test conditions, may show up poorly under another. It is also practically impossible to simulate field curing in the laboratory, a major weakness since durability rating is highly sensitive to prior conditioning of concrete. At best the current test methods distinguish the relative durability of concrete but often fail to predict the stability and life of concrete in a structure.

The mechanism of the failure of concrete caused by freezing and thawing is explained by the Powers hydraulic pressure hypothesis for moisture contents below the so-called critical value of 91 per cent of saturation (34). Above this value frost destruction is due to physical expansion resulting from the conversion of water into ice. However, certain independent phenomena may operate during freezing and thawing which may, to a greater or lesser extent, affect the durability of concrete. Considerable research would be required to separate these factors but, until this is done, the evaluation of durability will remain uncertain and arbitrary. These phenomena are:

- (a) Differential thermal volume change of aggregate and paste during freezing and thawing cycles (29, 39). There is at present sharp disagreement as to the effect of "thermal shock" in accelerated test methods;
- (b) Large effect of moisture condition on the apparent coefficient of thermal expansion (16). This is of particular significance in view of the current practices of freezing in either air medium or in water medium;
- (c) Deterioration of concrete occurring through cycling above the freezing point of water, which is slower but similar to deterioration due to freezing and thawing (31);
- (d) Deterioration of some concretes subjected to cycles of wetting and drying (43);
- (e) The breakdown of stone due to localized crystallization of salts (40), a factor which may operate in concrete;
- (f) The variation in the durability factor which may be obtained with minimum freezing temperatures in the "sensitive region" of 20 to 25°F. (44). Since this may be the case for a large proportion of the cycles in nature, it is of particular significance in evaluation studies.

The application of "moisture suction" concepts and techniques of measurement to the study of concrete (14, 15) should contribute greatly both to our fundamental and practical knowledge of its behaviour. Suction depends on the nature of the material and its moisture content. It is therefore affected by the size and distribution of pores, by admixtures, and by the aggregates present. It would determine the rate and amount of water absorbed during thawing. The

contribution of entrained air to high durability may be attributed to low moisture suction combined with a low ratio of moisture-content-to-voids-content, as well as to the "spacing factor" (5). The amount of "freezable water" present in concrete may be estimated from its suction characteristics. Knowledge of the variation of suction with temperature would be useful in estimating the change in moisture content during cycling. The effect of the initial moisture content of the aggregate on the durability of concrete has been roughly established (35) and good concreting practice requires pre-wetting of the aggregate before use. The relative suction characteristics of aggregate and cement paste and their ultimate effect on paste-aggregate bond will largely determine the durability of the concrete.

The extent to which thermo-osmosis occurs in concrete in the field and during testing may be an important factor affecting its durability (45). Practically all concrete elements in a structure are subject to temperature gradients and, during testing, this is particularly true of specimens subjected to rapid freeze-thaw cycling. Absorption of water during thawing may be considerably affected by temperature gradients. It is highly probable that this phenomenon is largely responsible for the considerable expulsion of water during freezing in air. "Primary directional" freezing appears to accelerate deterioration of concrete (41) and may be associated with moisture migration due to temperature gradients. The spalling and scaling of concrete surfaces may be promoted by this action. Of practical interest is the effectiveness of surface coatings such as cement-base paints, surface waterproofer, and silicones. Concrete research and testing can benefit greatly from the pioneer work in thermo-osmosis carried out in soil research.

Freezing and thawing tests on concrete are usually started at some arbitrary "age", often 28 days. This may not correspond with the real "maturity age" which is a function of temperature and time and depends on the degree of hydration (46, 47). The rate of hydration depends also on the fineness of the cement, water-cement ratio, and availability of moisture during curing. Since durability in general is affected by the degree of hydration the application of the concept of "maturity" in durability testing is necessary for accurate evaluation. Investigations are required into certain apparent anomalies that exist, such as the increase in durability obtained by intermediate drying periods during curing (31), the lower durability of the more finely ground high early strength cements (27), and the decrease in durability at later ages of concrete in which calcium chloride has been added as an accelerator (48).

The composition of portland cement has been modified to improve resistance to sulphate action and alkali-aggregate reaction, and to reduce heat evolution in mass concrete construction. The composition of cement as it affects frost resistance has not been investigated except for limited observations on the roles played by SO_3 , C_3A and C_2S contents (27). Evaluation studies to compare cements differing in compound composition should prove useful as a preliminary step in attacking the durability problem from the chemical point of view.

Of practical importance is the need for data on the dimensional changes occurring in concrete and mortars subjected to freezing and thawing, and the extent to which they contribute to cracking in monolithic and masonry elements. Modifications in design should be investigated so that a more extensive use of control joints is made in masonry wall construction. The durability and stability of concrete blocks made by the common dry-mix process, and the value of entrained air in such concrete, has not been sufficiently investigated. The intensive promotion of numerous cement-base paints and waterproofers and silicone coatings makes imperative the development of good testing methods for such materials. The problem of proper finishing of concrete surfaces exposed to frost action requires further research. Finally, there is urgent need in Canada for specifications and test methods designed to promote good concrete practice.

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