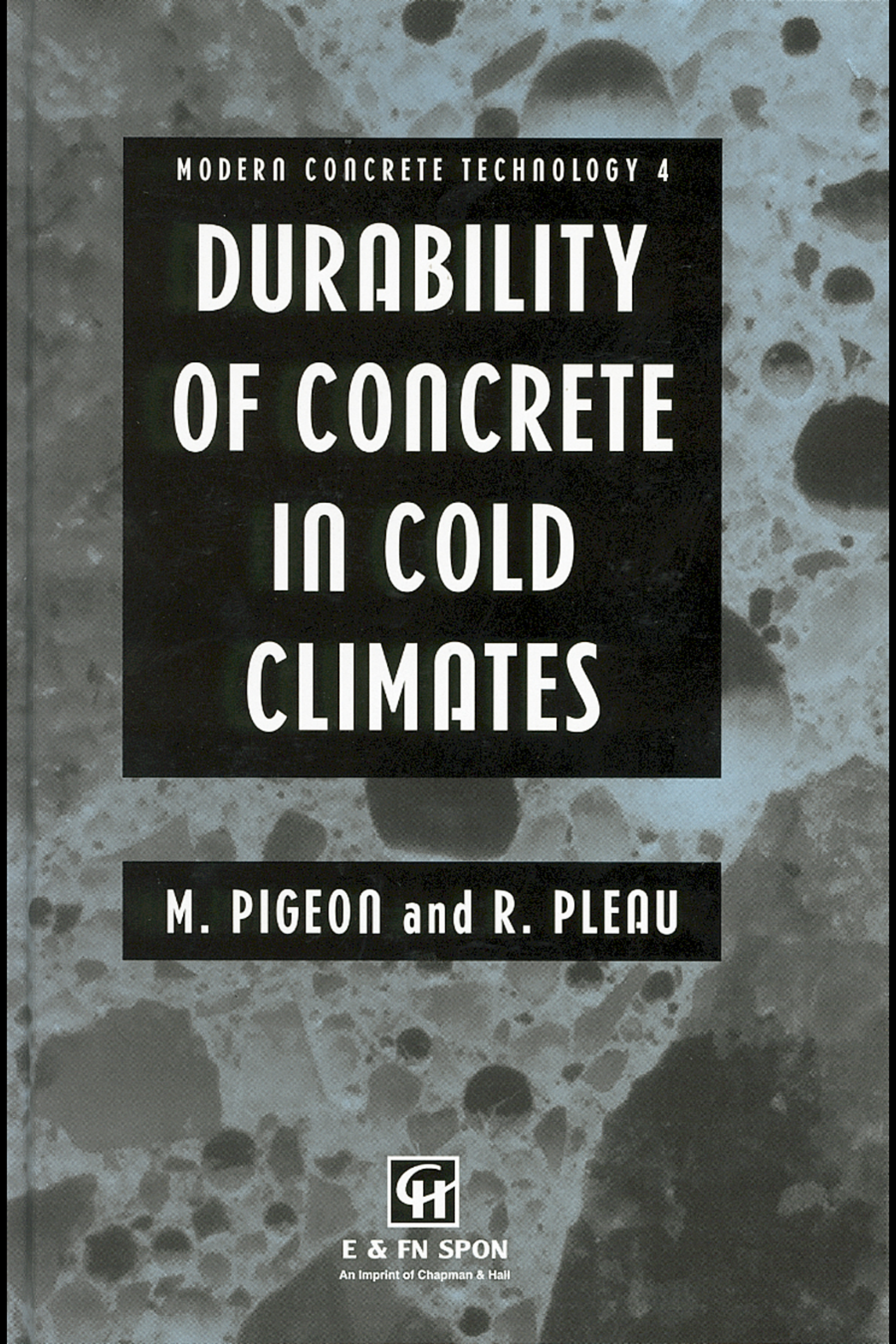

MODERN CONCRETE TECHNOLOGY 4

DURABILITY OF CONCRETE IN COLD CLIMATES

M. PIGEON and R. PLEAU

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Durability of Concrete in Cold Climates

Modern Concrete Technology Series

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Durability of Concrete in Cold Climates

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To Jack

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Series foreword

Plain concrete is a brittle material, with low tensile strength and strain capacities. Nonetheless, with appropriate modifications to the material, and with appropriate design and construction methodologies, it is being used in increasingly sophisticated applications. If properly designed, concrete structures can be produced to be durable over a wide range of environmental conditions, including hot and cold climates, as well as aggressive exposure conditions such as in marine and highly polluted industrial zones. Indeed, our understanding of cementitious systems has advanced to the point where these systems can often be ‘tailored’ for various applications where ordinary concretes are limited.

However, the results of the current research, which make these advances possible, are still either widely scattered in the journal literature, or mentioned only briefly in standard textbooks. Thus, they are often unavailable to the busy engineering professional. The purpose of the *Modern Concrete Technology Series* is to provide a series of volumes that each deal with a single topic of interest in some depth. Eventually, they will form a library of reference books covering all the major topics in modern concrete technology.

Recent advances in concrete technology have been obtained using the traditional materials science approach:

(1) characterization of the microstructure;
(2) relationships between the microstructure and engineering properties;
(3) relationships between the microstructural development and the processing techniques; and
(4) selection of materials and processing methods to achieve composites with the desired characteristics.

Accordingly, each book in the series will cover both the fundamental scientific principles, and the practical applications. Topics will be discussed in terms of the basic principles governing the behaviour of the various cement composites, thus providing the reader with information valuable for engineering design and construction, as well as a proper background for assessing future developments.

Durability of Concrete in Cold Climates, by Pigeon and Pleau, is a new addition to this series, dealing with a topic of vital interest for construction in cold climates, in view of the durability problems and rising maintenance and repair costs of concrete structures damaged in this environment. The book presents the essentials of the engineering approach required for the design of durable concrete in cold climates. Included in it is also a fundamental treatment of the causes of deterioration and the remedies, thus providing the necessary tools for the engineer to apply his judgement to deal with special cases, in addition to the more conventional engineering tools.

Arnon Bentur
Sidney Mindess

Preface

The authors of this book have been involved in research related to frost durability at Laval University for many years. During these years, many students obtained their MSc or PhD degree in this field of study. Clearly, without the knowledge and experience gained with them, without their hard and intelligent work, this book could not have existed. Research is a team effort, and collaborating with these students has brought invaluable benefits. Let each and every one of them be personally and sincerely thanked.

Michel Pigeon
Richard Pleau

Chapter 1
Introduction

Concrete is a porous material. As the cement and water it contains react to form a hardened paste binding together the coarse and the fine aggregates, voids are left in the originally water-filled space between the cement grains, which are not filled with the hydration products of the chemical reactions. These voids are known as capillary pores because they range in size from approximately 5 nm to 1 µm (and sometimes more) and capillary forces in such small volumes are very important.

The capillary pore volume in a hardened cement paste is a function of two basic parameters: the original water/cement ratio of the paste, and the degree of hydration of the cement. Table 1.1 gives the total approximate capillary porosities of Portland cement pastes as a function of the water/cement ratio and the degree of hydration. Thewater/cement ratio and the degree of hydration also have an influence on the average size of the capillary pores. The average size decreases significantly with the degree of hydration, and the number of very large pores also decreases significantly with lower water/cement ratios.

In addition to capillary pores, cement paste also contains a significant volume of smaller pores that Powers and Brownyard (1948) have called gel pores. The products of the hydration reactions between cement and water, the hydrates, have a very large specific surface area and this surface is necessarily covered with a few layers of adsorbed water. The gel pores correspond to the space occupied by this adsorbed water, which is bound to the solid surfaces of the hydrates by van der Waals forces and hydrogen bonds. Thus, contrary to the capillary porosity of the paste, the gel porosity of the hydrates is not a function of the water/cement ratio nor of the degree of hydration. The volume of the gel pores represents approximately 28% of the total volume of the hydration products (Neville, 1983). The word gel is used because some of the properties of the hydrates are similar to those of a gel.

Table 1.1 Capillary porosity as a function of the original water/cement ratio and the degree of hydration in an ordinary Portland cement paste.

Water/cement ratio (by mass)	Capillary porosity (% volume)	
	At 50% hydration	At 75% hydration
0.4	31	18
0.5	39	28
0.6	46	36

The aggregates, which normally represent about 75% of the volume of concrete, are also porous. These pores are generally of dimensions similar to those of the larger capillary pores, but the total porosity of aggregates is usually less than 5%. Since aggregates are normally made of natural rocks and since the properties of natural rocks are highly variable, the porosity of aggregates can cover a fairly wide range of sizes and the volume it occupies is variable.

Although concrete is made of aggregates bound together by hardened cement paste, the pore-size distribution of concrete cannot simply be estimated by adding up the pore-size distributions of the paste and the aggregates. The presence of the aggregates modifies the porosity of the paste. At the interface between the paste and the aggregate, there exists, at least for ordinary concretes, a transition zone in which the porosity is generally much higher than in the body of the paste (Maso, 1980).

Figure 1.1 shows the pore-size distribution of a 28-day old mortar made with normal Portland cement at a water/cement ratio of 0.5. This distribution, obtained with the use of the mercury intrusion porosimetry technique, shows that the pores of this mortar cover a very wide range of sizes, from more than 15 μm to less than 7.5 nm (these values correspond to the upper and lower limits for the particular instrument that was used). This technique does not allow the determination of the volume of gel pores, and the value of the total porosity measured in this way is often considered to correspond very roughly to the capillary porosity.

Unless the temperature is high or the relative humidity is very low, the gel pores are always filled with water because the forces which bind the water to the solid surfaces of the hydrates are relatively strong. The degree of saturation of the capillaries and of the aggregate pores, however, is largely dependent on the relative humidity of the atmosphere surrounding the concrete. The larger of these pores (particularly those close to the concrete

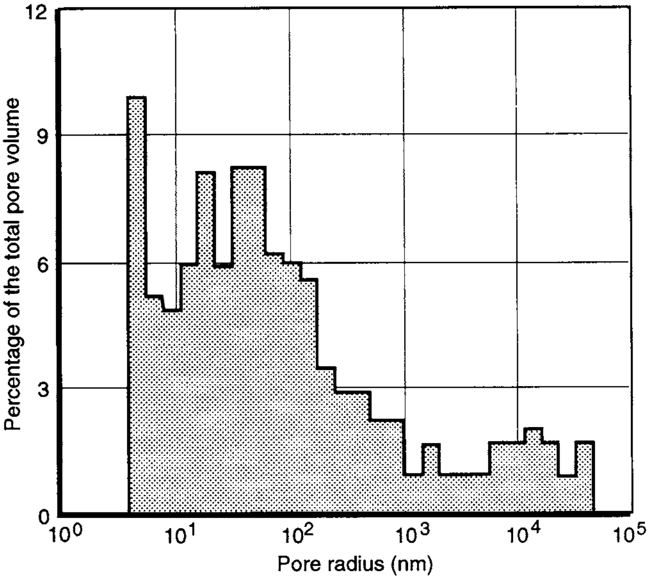

Figure 1.1 Pore-size distribution of a 28-day old mortar made with ordinary Portland cement at a water/cement ratio of 0.5.

surface) rapidly become empty if the relative humidity decreases significantly below 100%. However, due to the capillary forces, they tend to become filled with water again if moisture is available on the surface of the concrete. The relationship between the pore size and the relative humidity at which evaporation becomes possible is shown in Figure 1.2.

Water in any concrete pore can freeze, but the temperature at which this phenomenon becomes possible decreases with the size of the pore (Figure 1.3). In most settled areas throughout the world, winter temperatures rarely go below −40 °C, and, at such temperatures, gel pore water cannot freeze and ice can form in only part of the capillaries and aggregate pores.

When ice forms in any saturated pore, tensile stresses are generated in the paste because of the 9% increase in volume when water changes from the liquid to the solid state and because of the flow of water that is forced out of the pore. This, in a very general and simplified way, is the basic cause of damage to concrete due to frost. To prevent permanent damage from occurring, ways have to be found to ensure that these stresses or pressures will not be sufficiently important to cause cracking. One such way was found about 50 years ago in the United States and is called **air entrainment**.

When concrete is air entrained, which is achieved by incorporating into the mix an appropriate admixture, it contains a very large number of closely spaced air voids or bubbles. The spacing is typically of the order of 100 μm, and most bubbles range in size between 10 μm and 100 μm. Figure 1.4 shows a magnified view of a polished concrete section where the air voids in the paste surrounding the aggregate particles are clearly visible. Figure 1.5 indicates the approximate dimensions of the three basic categories of pores in concrete: gel pores, capillary pores and air voids.

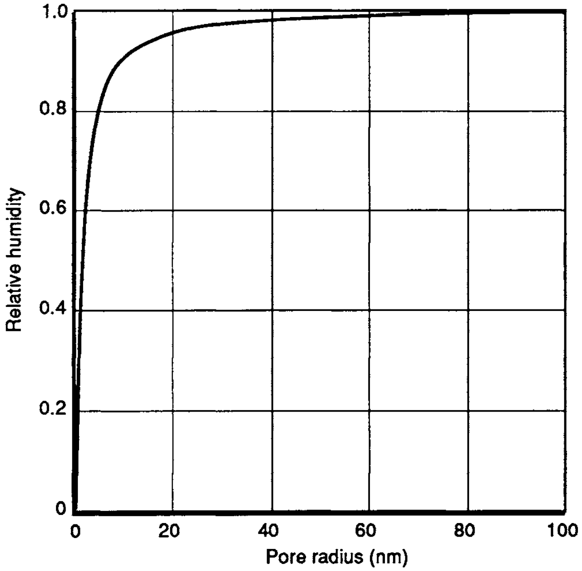

Figure 1.2 Relationship between the size of capillary pores and the relative humidity at which evaporation is possible.

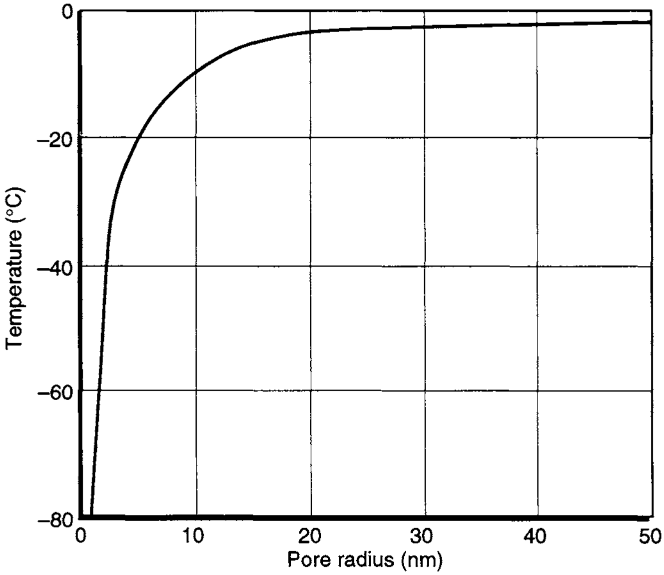

Figure 1.3 Relationship between the size of capillary pores and the temperature at which ice formation (from pure water) is possible inside these pores.

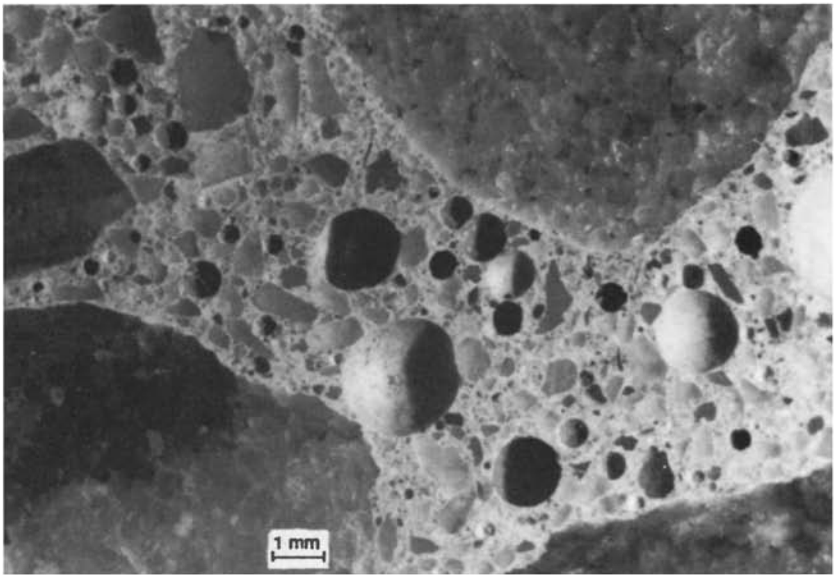

Figure 1.4 Typical air voids in an air-entrained concrete specimen examined under an optical microscope at an original magnification of 10×.

Water that is forced out of the capillaries by the pressure due to ice being formed (or by other thermodynamic phenomena) tends to flow through the porous paste to the nearest boundary. Air entrainment provides concrete with escape boundaries everywhere in the paste. If the air voids are sufficiently close, the pressure due to the flow does not cause any damage and, since these voids are almost never saturated, water can freeze in them without generating any significant internal pressures. Air entrainment also helps to reduce the pressures due to ice formation in aggregate pores but, as will be explained later, cannot protect concrete from the damage due to the freezing of certain types of frost-susceptible rocks.

Entraining air in concrete is carried out by using air-entraining admixtures. This simple statement suggests that entraining air in concrete is relatively easy; however, this is not always the case. Many parameters, such as the cement characteristics or the temperature of the mix, influence the characteristics of the entrained air-void system and a later chapter is therefore devoted to air entrainment.

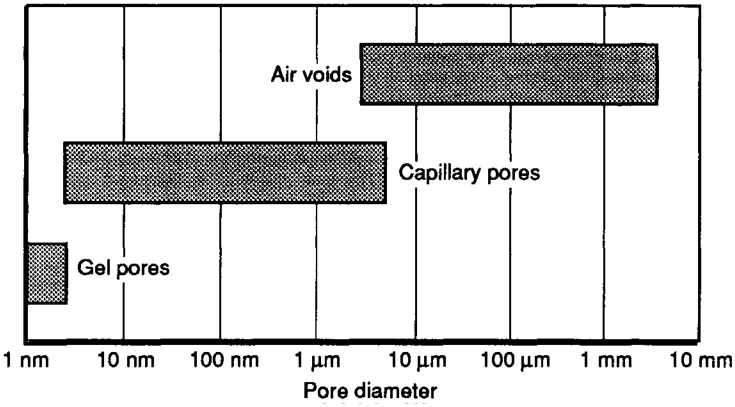

Figure 1.5 Range of pore sizes for the basic categories of pores in concrete.

Another method for reducing the risk of deterioration due to freezing and thawing cycles (besides keeping the concrete dry!) is obviously to reduce as much as possible the amount of freezable water present, i.e. the capillary porosity. This can be done by using mixtures with water/cement ratios that are as low as possible, since this reduces the space (between the cement grains) that is available for the products of hydration, and by keeping the concrete at 100% relative humidity for as long as possible, to promote hydration which further reduces capillary porosity. The use of superplasticizers now allows the manufacture of concretes with very low water/cement ratios (around 0.25), very little capillary porosity, and very high strengths. Do these concretes need air entrainment as protection against freezing and thawing cycles? This topic is discussed in Chapter 5, which deals with the influence of materials and mix composition.

Very often, when concrete is damaged by freezing and thawing cycles, the use of de-icer salts is associated with at least part of the damage. The use of such salts, as people living in the northern cities of North America are well aware, increases the damage arising from frost action. Some of the basic causes of this phenomenon are explained in the chapter on theories of frost action and de-icer salt scaling mechanisms. However, it should be noted that, in the vast majority of cases, salts are associated with surface damage (scaling) only. (Salts are of course also associated with the corrosion of the reinforcing steel in concrete, but steel corrosion is a very different as well as very complex problem that is beyond the scope of this book.) Surface damage is a form of deterioration that is different from the internal cracking and disruption that can be generated by freezing and thawing cycles. In fact, depending on the exposure conditions, one form of deterioration can occur independently of the other. Scaling is perhaps the most evident, as well as the most common, form of frost damage (Figure 1.6). It is generally associated with the use of salts but can also occur when concrete simply freezes in water. It is much more difficult to prevent than internal cracking and its causes are not that well known. Casting and curing procedures are more relevant to scaling resistance than to the resistance to freezing and thawing cycles.

Some types of concrete, collectively known as **dry concretes,** have an internal structure that is quite different from that of normal concretes. Roller-compacted concrete, used for building dams and also, in certain parts of the world, for constructing pavements, is one example of dry concrete. Because the mix in these concretes contains less cement and water (i.e. less paste) than normal mixes, and because pressure is utilized to put them into place, they contain a relatively large number of irregularly shaped compaction voids (Marchand *et al.,* 1990) which may or may not be interconnected, and the paste in these concretes tends to have less homogeneity than that in conventional concretes. Entraining air in dry concrete, although very difficult, is possible if certain special techniques are used but, because of the different internal structure of this type of concrete, it is not clear at the present time if entrained air voids can offer dry concretes satisfactory protection against freezing and thawing cycles and particularly against scaling due to the combined action of frost and de-icer salts. A short chapter at the end of this book presents the available information on the frost durability of dry concretes.

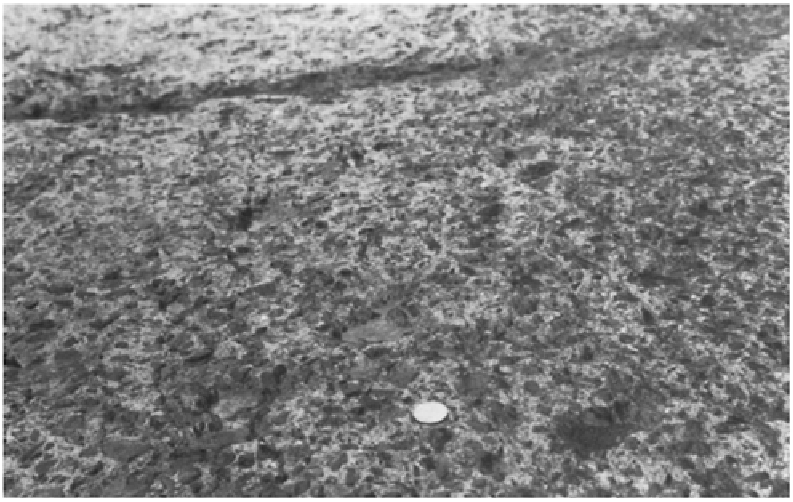

Figure 1.6 Severe surface scaling on a section of a sidewalk due to freezing in the presence of de-icer salts.

Standardized laboratory tests to evaluate the durability of concrete have been in use for a long time. It is not evident, however, that these tests are representative of the extremely variable exposure conditions to which concrete can be subjected in the field. Most of these tests are considered to be accelerated tests, but in many cases they do more than accelerate concrete deterioration: they amplify it. It is thus considered necessary in such a book on the frost resistance of concrete, not only to describe and discuss the significance of the various laboratory tests now in use, but also to provide information on the actual field performance of concretes of known composition (case histories). The book also contains recommendations on how to make durable concrete.

The durability of concrete repairs, although an important topic in many countries in which a large number of concrete structures exposed to severe winter conditions have to be repaired, is not covered. This is because the durability of repairs is mostly dependent on shrinkage-generated stresses at the interface between the repair material and the repaired structure, and not on particular phenomena related to frost action at this interface. The concretes that are used as repair materials must of course be frost resistant, and the principles described in this book should generally be applicable to the concretes that are used for repairs.

Engineers should not only know what to do, but also why it should be done. They must understand the basic principles that underlie their technical decisions and, in particular, must be aware of the limitations of this knowledge. This is why the fundamental phenomena related to the action of frost on concrete and the known de-icer salt scaling mechanisms are explained at the beginning of the book. The extent to which these theories and basic mechanisms are valid and applicable to concrete is also discussed. In spite of all the research carried out over the last 50 years, there remain many unresolved issues and the areas in which research is required are described. Such fundamental knowledge is necessary to ensure that engineers can find solutions that are appropriate to the type of problem (and type of concrete) they are faced with, and that they are able to take the correct technical decisions when faced with new problems (or new types of concrete).

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Chapter 2
Theories of Frost Action and De-icer Salt Scaling Mechanisms

Many theories have been put forward in the last 50 years to explain the action of frost on hardened cement paste and concrete. At first, the obvious ‘milk bottle’ explanation was given. If any pore in concrete is saturated, the expansion of water on freezing forces the pore to expand and cracking occurs, just as a milk bottle left at the front door by the milkman at four o’clock in the morning on a cold winter day will freeze and break. It was, of course, soon recognized that this explanation was not entirely satisfactory (although it certainly applies to at least part of what happens when concrete freezes), and other theories were put forward. The most well known of these is the ice lens formation theory (Collins, 1944). This theory, which explains the gradual formation of ice lenses perpendicular to the direction of the heat flow in porous materials with little cohesion, could of course only be applicable to very young pastes and could not explain fundamentally the importance of air voids that had just been recognized.

A few years after Collins’ publication, Powers (1945, 1949) presented his hydraulic pressure theory that explained the role of air voids and, in the decade that followed, he gradually developed (with Helmuth) the osmotic pressure theory (Powers and Helmuth, 1953; Powers, 1975). Together with the theory later put forward by Litvan (1972, 1973, 1975, 1980), these are the only relatively complete theoretical explanations of the mechanisms causing damage to concrete during freezing. Many other researchers of course, particularly Fagerlund in Sweden and Sellevold in Denmark and Norway, have studied various fundamental aspects of the problem. What constitutes a theory is obviously debatable, but the only theories described in this chapter are those by Powers, Powers and Helmuth, and Litvan. Some of the fundamental work done by Fagerlund and Sellevold, as well as by many others, is described in the following chapter.

2.1 THEORIES OF FROST ACTION

The importance of air entrainment as a protection against freezing and thawing cycles having been clearly demonstrated, Powers, working in the laboratories of the Portland Cement Association in the United States, attempted to calculate precisely the amount of air required to protect concrete against frost damage. In a paper published in 1949 entitled The Air Requirement of Frost-Resistant Concrete’, he developed a series of equations relating the spacing of air voids to the properties of the paste and to the freezing rate, i.e. the rate at which the temperature decreases.

Powers’ equations are based on a relatively simple mechanism. When the temperature decreases below 0 °C, water begins to freeze in the capillaries, which causes an increase in volume. Since water in the pores contains dissolved chemicals (mostly alkalies), the formation of ice increases only gradually as the temperature decreases. If the paste is saturated, the capillary pores are full and a certain amount of water is forced out because the pores cannot expand. This water must move towards the only available places in which it can freeze without causing any damage, i.e. the air voids. It must therefore travel through a porous body, the cement paste, which has a certain permeability. Darcy's law of water flow through porous bodies can be used to calculate the pressure required for a certain amount of water to travel a certain distance in a given time. If the pressure exceeds the tensile strength of the paste, for instance because the distance the water must travel is too long, or because the freezing rate (which determines the quantity of water that is forced out of the pores per, unit time) is too high, the paste breaks in tension.

Considering a single air bubble of radius r_b surrounded by a shell of paste of thickness L which he called the 'sphere of influence' of the bubble (Figure 2.1), Powers calculated the maximum value L_{max} of this shell (which represents the maximum distance that water must travel through the paste) above which the hydraulic pressures generated by the flow are sufficient to cause cracking of the paste. For a saturated paste, where capillary pores are small in comparison to the size of air voids and are well distributed in the paste,

$$\frac{L_{\text{max}}^3}{r_b} + \frac{3L_{\text{max}}^3}{2} = \frac{K\,T}{U\,R} \times (\text{constant}) \tag{2.1}$$

where L is the thickness of the shell of paste surrounding the air void, i.e. the thickness of the sphere of influence, r_b is the radius of the bubble, K is the permeability coefficient of the paste, T is the tensile strength of the paste, U is the quantity of water that freezes per degree of temperature drop, and R is the freezing rate.

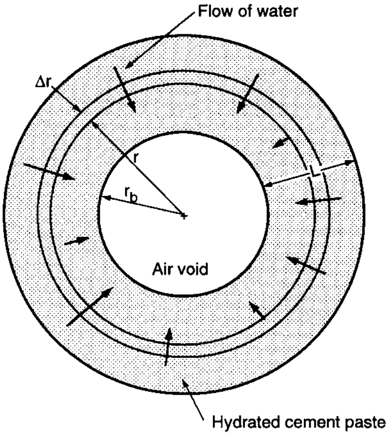

Figure 2.1 Air void surrounded by its sphere of influence of hardended cement paste (after Powers, 1949).

Equation (2.1) shows that the maximum thickness of the sphere of influence around an air void decreases as the freezing rate increases, and that it increases with the tensile strength and the permeability of the paste. When the permeability is high, the pressures are lower and the maximum thickness can increase. This equation also takes into account the amount of freezable water in the paste, i.e. the porosity of the paste. If the water/cement ratio is high, the porosity and the amount of freezable water increase; the quantity of water forced out of the capillaries therefore increases and the maximum thickness must be reduced.

The maximum thickness of the sphere of influence of the air bubble, as is clear from the equations just described, is not a function of the minimum temperature that is attained during freezing. Powers simply made the assumption that the amount of freezable water increases linearly with the decrease in temperature. Since the hydraulic pressure is a function of the amount of water forced out of the capillary pores per unit time, the freezing rate is important but the minimum temperature does not influence the phenomenon.

Theoretically, since Powers considered only a single air bubble surrounded by a shell of paste to develop his equations, his theory is only applicable to pastes where all air voids are of the same size and are equally spaced. Of course, in real pastes, the spacing as well as the diameter of the bubbles (and thus the thickness L of the sphere of influence) are variable. L_{max} must therefore be considered as a limiting value which must not be exceeded anywhere in the paste.

In his paper, Powers also explained how to estimate the average value of L for all air voids in the paste, i.e. the average value of the maximum distance that water must travel to reach an air void. He called this average value $\overline{L}$, which represents very approximately the average half-distance between two adjacent air-void walls for all air voids in the paste. Powers' method to measure and calculate $\overline{L}$ was adopted by the American Society for Testing and Materials (ASTM) and is described in ASTM Standard C 457: *Microscopical Determination of Air Void Content and Parameters of the Air Void System in Hardened Concrete* (Chapter 4).

On the basis of the results of laboratory tests carried out by Gonnerman (1944), Powers estimated that the maximum value of $\overline{L}$ for a saturated paste is of the order of 250 µm when the freezing rate is 11 °C/h. This value represents approximately the lower limit of the range of values he obtained with his equations for pastes of various properties. He wrote:

> *...it is tentatively concluded that paving type concrete should withstand the particular freezing and thawing test used in this laboratory if the spacing is not over 0.01 in (250 µm) for voids of the usual specific surface.*

Powers also calculated the maximum value of $\overline{L}$ for different freezing rates, assuming the value of 250 µm at 11 °C/h was correct, and assuming that his equations could apply to $\overline{L}_{max}$ as well as L_{max}.

This theory developed by Powers, called the **hydraulic pressure theory,** is the only one that establishes mathematical relationships between the paste properties, the freezing rate and the spacing of air voids. Unfortunately most researchers, including Powers himself, now consider that this theory is invalid because numerous experiments have shown that water tends to travel to, and not from, capillary pores where ice is forming. This theory, however, can explain the results of tests carried out very recently on the influence of the freezing rate. It is thus probable, even if the basic mechanism appears to be incorrect, that it takes into account the most relevant parameters and that a good part of it is correct. It is evident that, in order to avoid damage to the paste, water must move to the air voids to freeze, and that this movement necessarily implies that internal hydraulic pressures are generated. It is also evident that air voids must be sufficiently close to offer an adequate protection against the action of frost. In the authors' opinion, the advantage of this theory is mainly that it focuses on the most important parameter as regards resistance to freezing and thawing cycles, namely the spacing of air voids.

It was at the beginning of the 1950s, a few years after his famous 1949 paper, that Powers, working with Helmuth, discovered the important fact that during freezing water tends to move towards the capillary pores where ice is forming, and that this creates shrinkage in the paste. They also then realized, and this was later confirmed by others, that the temperature at which ice can form decreases with the size of the pores. The results of their experiments also showed that the amount of ice that forms in the capillaries during freezing is much smaller than would be indicated by the basic laws of thermodynamics. Because of surface tension and other phenomena, water in the capillary pores tends to become supercooled, and water in the gel pores simply cannot freeze because it is adsorbed on the solid surfaces of the calcium silicate hydrates (CSH). Powers and Helmuth (1953) therefore suggested a new hypothesis, different from the hydraulic pressure theory, to explain the action of frost.

If the temperature of a saturated cement paste is slightly above 0 °C, water in the capillary pores can be considered to be in thermodynamic equilibrium with water in the gel pores. If the temperature of this paste decreases sufficiently below 0 °C, so that ice begins to form in a number of capillary pores, this equilibrium is broken because, at a given temperature, the free energy of ice is lower than that of liquid water. The liquid water in the gel pores thus acquires a potential energy that forces it towards the capillary pores where ice has started to form. The movement of water away from the gel pores creates shrinkage in the paste. When this water reaches the capillary pores, it freezes and the ice crystals increase in size. The growth of the ice crystals creates pressure on the unfrozen film of water between the ice crystals and the solid walls of the pores. If, for various reasons, the pressure becomes too great before the system has time to reestablish equilibrium, permanent damage occurs because the pores cannot expand significantly. Of course, time is important in this sort of problem because the growth of ice crystals takes time. It must also be noted that, if the temperature stops falling, the phenomenon can still carry on for a certain amount of time, since equilibrium cannot be reestablished at once.

The preceding hypothesis put forward by Powers and Helmuth did not take into account the known fact that water in the pores of cement paste is not pure but contains dissolved chemicals (mainly the alkalies Na_2O and K_2O). They therefore modified this theory of frost action, based on thermodynamic considerations. This modified version is known as the **osmotic pressure theory** (Powers, 1975).

Figure 2.2 represents schematically saturated cement paste between two air voids. On this figure a certain number of pores (filled with water) are shown. Their size is greatly exaggerated to facilitate the demonstration. If the temperature decreases below 0 °C in such a paste, water does not freeze immediately, first because of the presence of dissolved chemicals which reduces the temperature at which ice formation is possible, but also

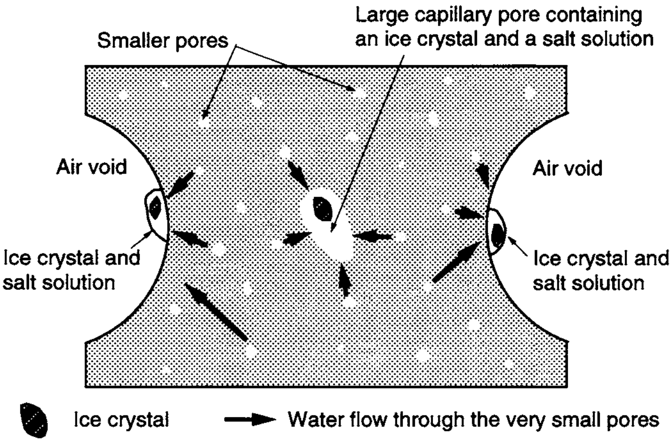

Figure 2.2 Schematic illustration of the osomotic pressure theory (note that the size of the pores is greatly exaggerated).

because of the relatively small size of the pores where surface tension is very significant. When, for a given size of pore, the temperature reaches the value at which the formation of ice is possible, not all the water in the pore freezes because of the dissolved chemicals. As ice forms, the concentration of dissolved chemicals in the unfrozen water increases. Ice stops forming when the concentration becomes such that the melting point of the solution becomes equal to the value of the temperature. There is, in other words, equilibrium between the ice and the solution in the pore at that temperature.

Since the formation of ice causes an increase in the chemical concentration of the pore water solution, the equilibrium is broken between this pore water solution and that in the smaller pores (including the gel pores) where ice has not formed and where the concentration has not increased. Due to an osmotic phenomenon, water in the smaller pores is attracted to that in the larger pores where ice has formed, in order to reestablish equilibrium between the concentrations. If the paste is saturated, internal pressures obviously start building up as soon as ice starts forming. The osmotic pressure due to the movement of water increases the internal stresses in the paste, and these stresses are further increased by the fact that, as water arrives in the pore where ice has formed, more ice can form because the concentration of the solution decreases.

As the temperature continues to decrease, the phenomenon becomes more pronounced because there are additional pores in which ice can form (frost, in other words, reaches smaller and smaller pores), but there is always a reservoir of water that cannot freeze and where the concentration stays constant, i.e. in the gel pore water. More ice can also form in the capillary pores because the decrease in temperature increases the concentration at which equilibrium between ice and the solution exists.

According to Powers, the role of air voids is to compete with the capillary pores where ice is forming. Air voids normally contain a little water or moisture. Ice can therefore form on the walls of the air voids as is shown on Figure 2.2, and there as well the solution becomes more concentrated and attracts water from the smaller pores where ice has not formed. If the air voids are sufficiently closely spaced, they win this competition and the paste is protected from frost damage.

This model of frost action suggested by Powers and Helmuth can explain the results of many laboratory findings. It can explain, for instance, the shrinkage during freezing that many researchers have observed. It can also help to explain the effects of de-icer salts which, at moderate concentrations, increase the phenomenon of osmotic pressure. It does not, however, explain the influence of the freezing rate. On the contrary, the results of Powers' tests led him to believe that it was the length of the freezing period and not the freezing rate that was important, because long freezing periods promote ice-crystal growth.

The weakest point of this model is the explanation of the role of air voids. This explanation is simply not satisfactory. For instance, how can the air voids completely protect the paste, since there is always a region halfway between two air voids in which the capillary pores win the 'competition'? In addition, as was previously mentioned, a saturated paste must start to expand as soon as ice begins to form, the role of air voids being simply to prevent water from the smaller pores from amplifying the problem. It is true that in most practical cases the larger pores, which are the first in which ice begins to form, are rarely saturated because they are the first to lose part of their water as soon as the relative humidity becomes lower than 100%. However, for average size pores which are filled with water, the formation of ice necessarily creates an excess of water which must be expelled. This water must travel through the paste to reach an air void, otherwise large internal tensile stresses will be created and cracking is likely to occur. This mechanism is not included in the osmotic pressure theory.

More recently, Litvan, working at the National Research Council of Canada, published a series of papers (Litvan, 1972, 1973, 1975, 1980) in which he gradually developed a theory of frost action applicable to all porous bodies (including concrete).

The results of Litvan's experiments, and particularly of those carried out using differential thermal analysis, have convinced him that water in the capillary pores does not freeze *in situ* when the temperature of the paste decreases below 0 °C. This water is thus supercooled, which tends to cause drying of the paste because the vapour (or saturation) pressure over supercooled water is higher than that over ice.

Consider the phase diagram for water (Figure 2.3). For temperatures lower than 0 °C, there are two curves originating from the triple point: one corresponds to ice and one corresponds to supercooled water. The distance between these two curves increases as the temperature decreases according to the equation

$$\log\left(\frac{p_{ow}}{p_{oi}}\right) = \frac{-1.1489\ t}{(273.1 + t)} - 1.33 \times 10^{-5}\ t^2 + 9.084 \times 10^{-8}\ t^3 \qquad (2.2)$$

where t is the temperature in degrees Celcius, p_{ow} is the vapour pressure over liquid water and p_{oi} is the vapour pressure over ice.

Assume that the hardened cement paste is saturated. If the temperature decreases below 0 °C, the pressure of the water vapour over the bulk of the paste p necessarily corresponds to the vapour pressure over ice p_{oi} because, due to condensation, ice will form on all external

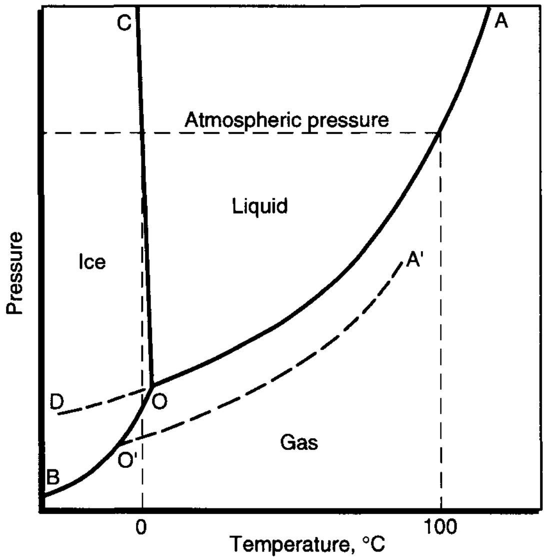

Figure 2.3 Pressure-temperature diagram for water: OB, ice-water vapour equilibrium curve; OD, Supercooled water-water vapour equilibrium curve; O, triple point for water O′A′. liquid water-water vapour equilibrium curve for water containing dissolved substances.

faces of the paste including the air-void walls. This will maintain the pressure p at this value because if it tends to increase, ice formation will reduce it. The relative humidity (p/p_{ow}) for supercooled water is thus equal to p_{oi}/p_{ow}. This value is lower than 100% and drying occurs. Litvan wrote:

> *Experiments indicated that not only the adsorbed water but also the capillaryheld liquid does not freeze in situ.... The fact that the adsorbate is in a liquid-like state and has a saturation pressure similar to that of undercooled bulk liquid while bulk ice has formed on the external surfaces, results in a non-equilibrium situation characterized by the vapour pressure difference. Equilibrium can be achieved by either solidification of the liquid in the pores, which apparently cannot occur, or by reduction of the vapour pressure of the adsorbate through desorption. When the adsorbate remaining in the pores has a vapour pressure equal to that of ice at a given temperature, equilibrium conditions have been restored.*

Frost action on saturated hardened cement paste thus creates a non-equilibrium situation which lasts as long as the pressure of water vapour in the capillary pores has not decreased sufficiently, i.e. as long as it has not reached the value corresponding to that of ice. This can only happen if the pores become partially empty.

As shown in Figure 2.4, the surface of the water in a partially filled capillary pore is concave because the size of these pores is very small. Evaporation is therefore possible only if the relative humidity p/p_0 decreases sufficiently. Kelvin’s law establishes the relationship between the radius of curvature *r* of the surface of the water and the relative humidity p/p_o at which evaporation can start:

$$r = \frac{Z\,\gamma\sigma\,\cos\theta}{R\,T\,\ln\left(\frac{p}{p_o}\right)} \tag{2.3}$$

where *r* is the radius of curvature of the surface of water, p/p_o is the relative humidity, *R* is the gas constant, *T* is the thermodynamic temperature, γ is the molecular volume of water, σ is the surface tension and θ is the angle of contact, considered to be equal to 0°.

When the surface of water is concave, evaporation tends to increase the surface area and this requires an additional amount of energy, equal to the surface tension multiplied by the surface area increase. This explains why evaporation of water from such a surface is more difficult and can only occur if the relative humidity is sufficiently low.

It is well established that Kelvin's law applies to water contained in the capillary pores of hardened cement paste. This is why, for instance, when concrete dries, the larger pores are the first to become empty and why, on the other hand, the smaller pores are the first to become full again when moisture is available. This also explains why aggregates which are not saturated when concrete is mixed usually do not become saturated, unless special particularly unfavourable circumstances exist, because capillary pores are normally much smaller than aggregate pores. This last fact is extremely important as regards the influence of aggregate on the frost durability of concrete and is discussed at length in Chapter 5.

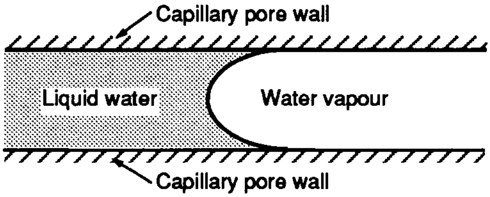

Figure 2.4 Curved liquid water–water vapour interface in a capilliary pore partially filled with water.

The distance between the curve corresponding to supercooled water and that corresponding to ice on the phase diagram for water (Figure 2.3) determines, as we have just seen, the relative humidity for supercooled water in the capillary pores. This distance increases as the temperature decreases, and the relative humidity for the water in these pores therefore decreases with the temperature. The radius of the pores that are affected by frost action therefore also decreases with the temperature. Using Kelvin's law (2.3) and (2.2), it is possible to calculate the exact relationship between the temperature and the pore radius. At −20 °C, for instance, the relative humidity for the supercooled water in the capillary pores is 82% and evaporation can occur in all pores with a radius larger than 0.006 μm.

According to Litvan, mechanical damage happens when the process of desorption, i.e. moisture transfer, cannot occur in an orderly manner, i.e. when the rate of freezing is too high, or the distance that water must travel to reach an external surface and freeze is too long. The very rapid drying process due to frost action, and thus the forced movement of water, can cause very high stresses and cracking. Moreover, at each freezing cycle, water that leaves the capillary pores tends to accumulate in all microcracks or in any space available. This water is not necessarily reabsorbed during thawing and the subsequent formation of ice can cause a microcrack to propagate, which explains the cumulative effect of the cycles. Finally, since the amount of water that becomes unstable increases as the temperature decreases, it is possible, if the freezing rate is high enough, that it cannot all reach an external surface. It thus freezes in an amorphous state which creates extremely high internal stresses.

Litvan's theory (for lack of a better name!) is, according to him, compatible with all known observations concerning the action of frost. The higher the freezing rate, the larger the amount of water that becomes unstable per unit time and the higher the risk of mechanical damage. Entrained air, which offers everywhere in the paste external surfaces where water can freeze, decreases the distance that water must travel and helps to protect the paste from frost action. The porosity of the paste, and thus the amount of water which must move when freezing occurs if the paste is saturated, increases with the water/cement ratio and this increases the risk of mechanical damage. Litvan has also studied the influence of de-icer salts, and he has come to the conclusion that their influence is simply due to the fact that their presence in the pore water solution decreases the saturation or vapour pressure (Figure 2.3). This decrease of the saturation pressure hinders the possible drying between natural freezing and thawing cycles. It also increases the difference between the vapour pressure over the supercooled water in the capillary pores and that over the ice formed on all external faces of the paste, and thus amplifies the phenomenon causing the flow of water through the paste.

The fundamental hypothesis of Litvan's theory is that water in the capillary pores cannot freeze *in situ* (this hypothesis is supported, at least in part, by work done by others). The theory explains clearly the fundamental phenomenon which forms the basis of frost action, i.e. the forced movement of water caused by the vapour pressure difference (it is interesting to note in this respect that Litvan has shown that frost action can cause damage to a porous body that is saturated with a liquid that does not expand on freezing!). In a way, it has certain similarities with Powers' hydraulic pressure theory because the forced movement of water necessarily creates significant internal stresses. It is, however, incomplete because it cannot establish a clear relationship between the spacing of air voids required to protect the paste, the freezing rate and the paste properties other than porosity.

There seem to be many contradictions between the theories of hydraulic pressure, osmotic pressure and Litvan's theory. As we shall try to explain, however, these contradictions are often more apparent than real, and in many respects the three theories complement each other. Even if they were all put forward to explain the problem of frost action in its entirety, each of them really explains only certain parts of the overall phenomenon.

The basic mechanism suggested by Powers in his hydraulic pressure theory to explain why water is forced out of the capillary pores during freezing is most probably incorrect. However, his theory describes extremely clearly how internal pressures are generated and explains very well the relationship between the freezing rate and the maximum distance that water must travel to reach an air void (where it can freeze without causing any damage).

In the osmotic pressure theory, the role of air voids is not clear. The effects of de-icer salts, however, are very clear and the theory helps to explain certain experimental results which indicate that long freezing periods can be very harmful in certain cases because they promote ice-crystal growth. This theory does not necessarily contradict the others. It probably simply explains a phenomenon which is less frequent when concrete is exposed to freezing and thawing cycles without long freezing periods in between. The fact that long freezing periods promote ice-crystal growth (as opposed to hydraulic pressures) even when there are no salts dissolved in the pore water was recognized by Powers as early as 1953.

Litvan has clearly shown why water must travel to the air voids during the freezing part of the freezing and thawing cycles. In his view, water cannot freeze *in situ* and desorption is necessary to reestablish the vapour pressure equilibrium. His theory explains qualitatively the observed relationship between the freezing rate and the necessary spacing of air voids but, unfortunately, does not satisfactorily describe the mechanism which creates the internal pressures and causes deterioration.

Litvan's theory does not really contradict the osmotic pressure theory, which probably simply analyses a different phenomenon. It contradicts, but only partly, the hydraulic pressure theory. It is quite possible to imagine that, if Litvan's theory allowed the calculation (for a given cement paste and a given freezing and thawing cycle) of the amount of water per unit time that becomes unstable and must travel to the air voids, the pressure required for this movement to occur could be calculated using equations derived from the hydraulic pressure theory. It must be accepted, however, that it will always be very difficult, particularly because of the extremely variable conditions to which real concrete is exposed, to suggest a theory which will completely explain the action of frost. It is clear, for instance, that even in well-controlled laboratory tests, concrete, because of self-desiccation, is almost never totally saturated. Moreover, hardened cement paste, and of course concrete, are very complex materials and it is certainly not enough only to take into account in the analysis of the problem the number and size of the pores. The characteristics of the microstructure, for instance, could very well influence the phenomenon.

Aggregates, which are often ignored because they increase the complexity of the problem, can also have a significant influence. Fortunately, as concerns the action of frost on the aggregates themselves, it is probable, as Powers has pointed out, that the hydraulic pressure theory is applicable because the pores are usually relatively large, the water contains no dissolved chemicals, and there are no gel pores.

2.2 DE-ICER SALT SCALING MECHANISMS

The theories described above were developed in order to explain globally the action of frost on hardened cement paste and concrete. It is now generally accepted, however, that there are two distinct manifestations of distress due to frost: internal microcracking and disruption, and surface scaling. This fact was mentioned by Powers in 1945, but the distinction between surface scaling and internal cracking was not systematically made by most investigators until relatively recently. Internal cracking leads to expansion and loss of mechanical properties and, ultimately, to complete destruction of the concrete. Surface scaling is characterized by a progressive loss of small cement paste or mortar particles (Figure 1.6). This process gradually exposes the coarse aggregate. In certain cases where scaling is very severe, the loss of coarse aggregate particles is possible and the concrete can be affected to a depth of more than 1–2 cm. Both types of deterioration can occur independently of each other.

Internal cracking and disruption are typical of the type of deterioration that can be observed when concrete is subjected in the laboratory to rapid freezing and thawing cycles. If, during such tests, concrete freezes in water, surface scaling can occur in addition to internal cracking, but if concrete freezes in air (and is not adequately protected by sufficiently closely spaced air voids), a very typical map cracking can be seen (Figure 2.5).

Are the basic mechanisms responsible for scaling very different from those causing internal cracking? There is no definite answer to this question. It is clear that the mechanisms causing internal pressures (hydraulic, osmotic or other) are at least partly responsible for scaling, since it has been shown many times that air entrainment helps to protect concrete from scaling. There are, however, many aspects of the problem that are particular to scaling, apart from the fact that de-icer salts can be involved in the problem of surface scaling.

Excessive bleeding, bad finishing procedures, plastic shrinkage cracking, overworking of the surface during the finishing operations, lack of curing and early exposure to relatively high temperatures can all weaken the concrete surface and be an indirect cause of rapid scaling when concrete is exposed to freezing in water with or without de-icer salts being present (Figure 4.13). The concrete surface, or 'skin', is different from the body of the concrete. It contains more paste and is more susceptible to damage such as water/cement ratio increase due to bleeding, or shrinkage-induced micro-cracking. It is also directly influenced by drying which can modify the capillary pore structure and increase the freezable

Figure 2.5 Typical map cracking on a concrete specimen caused by repeated cycles of freezing and thawing in air (after Pigeon and Lachance, 1981).

water content (Chapter 3). If concrete is placed on a sunny and windy day, bleed water will evaporate as soon as it reaches the surface. This will tend to compact the surface (because of the capillary forces between the cement grains) and thus to create a weak zone due to more bleed water being trapped under the dense surface. Such a porous and weak zone can also be due, for similar reasons, to overworking of the concrete surface. Overworking should in any event always be avoided, because it can significantly reduce the air content of the surface layer.

At the surface of concrete, the tensile stresses due to the action of frost can more easily cause cracking (and the loss of small paste particles), because of the discontinuity of the material which could facilitate the opening of cracks. When concrete freezes in water (very often, scaling seems to occur only under this condition), all voids close to the surface (even air voids) can become filled with water. Generally, for various reasons and certainly in part due to self-desiccation (resulting from the hydration process) which increases paste porosity, concrete is not totally saturated during freezing and this is an important factor that helps to protect concrete from frost action. However, if the surface is covered with water, the top layer of concrete (including the aggregates, the porous zones at the aggregate-paste interface, and all other micro- or macrovoids) can become fully saturated. This, in addition to the fact that ice can form in any small crack or defect of the surface, certainly helps to amplify the problem.

It has been known for many years that de-icer salts very significantly increase the surface scaling due to frost action. This became evident in the United States after the Second World War when most states adopted the ‘bare pavement’ policy, i.e. decided that, during the winter, snow would be removed from the roads, and the pavements would be kept completely bare by the use of de-icer salts. Laboratory tests by Verbeck and Klieger, reported in a famous 1957 paper, have shown very clearly the deleterious effects of various salts. and chemicals and the positive effect of air entrainment. They have also shown that the most damaging concentration is of the order of 3–4% (this value was found to vary slightly with the type of chemical: sodium chloride, calcium chloride, urea etc. (Figure 2.6)). According to Verbeck and Klieger, the surface scaling problem associated with the use of salts is mostly physical in nature, and not chemical, except in the case of very high salt concentrations. Of course, chemical attack can occur in certain cases, particularly under long term exposure. When the deicer salts that are used contain sulphates as impurities, for instance, the damage to the concrete surface can increase very significantly.

The presence of de-icer salts in the pore water of cement paste has two fundamental effects: it lowers the saturation or vapour pressure (this can be seen clearly in Figure 2.3) and it decreases the temperature at which ice formation is possible (Figure 2.7). De-icer salts can thus be considered to have beneficial as well as deleterious effects. The amount of ice formed is lower when the pore water contains dissolved salts, but water is more easily absorbed in the capillary pores if it contains a relatively small amount of dissolved salts. Litvan (1975) pointed out that one of the most important problems as regards de-icer salt scaling is perhaps simply that the degree of saturation of any field concrete exposed to frost is higher when it is subjected to salt applications because the pore water solution has a lower vapour pressure.

Powers and Helmuth have suggested that de-icer salts simply amplify the osmotic pressures generated when freezing occurs. Litvan has also explained that the presence of de-icer salts increases the difference between the vapour pressure over the supercooled water in the capillary pores and that over the ice formed on all external faces of the paste. Although these phenomena can certainly account for a good part of the problem, many other investigators have tried to analyse the possible particular mechanisms of this problem of scaling due to freezing and thawing cycles in the presence of de-icer salts.

Browne and Cady (1975), having observed that de-icer salt scaling involved the formation on the surface of the concrete of small flat flakes of paste or mortar, suggested

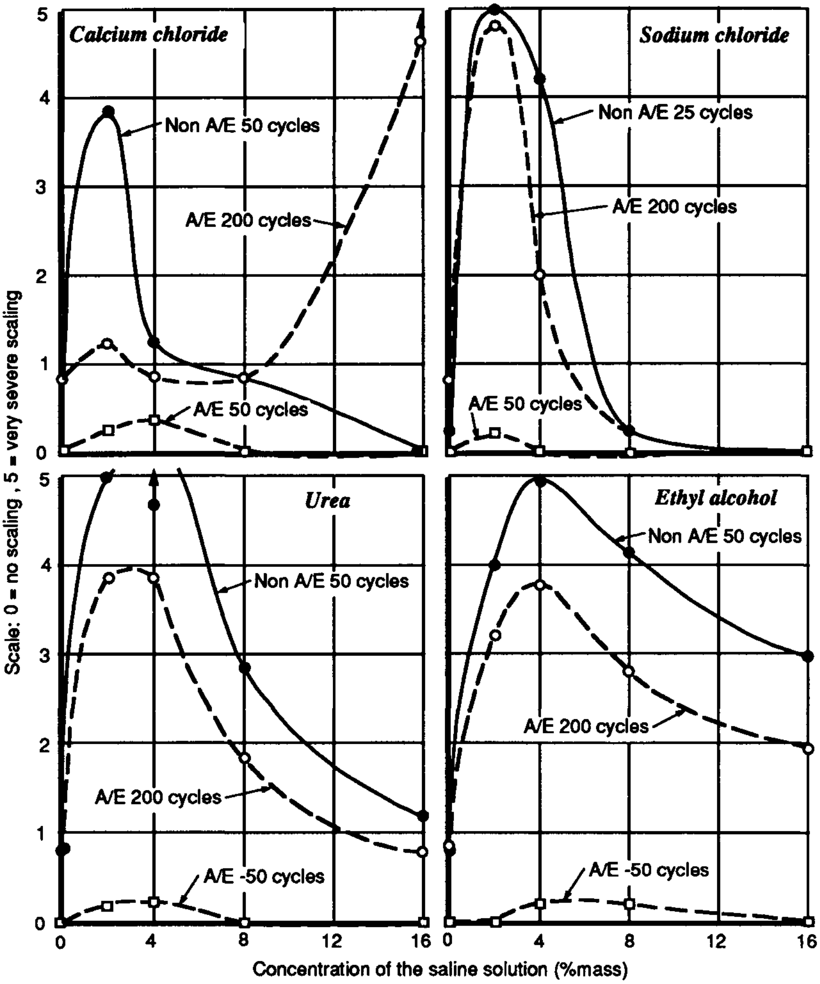

Figure 2.6 Influence of the concentration of the soultion and of the type of chemical on the degree of surface scaling due to freezing and thawing cycles in the presence of a due-icer solution (A/E: air entrained) (after Verbeck and Klieger, 1957).

that this process was related to the variation of salt concentration in the concrete and was due to hydraulic pressures. They consider that, over the fracture surface, the salt concentration is generally too great for ice to form. Under this surface, however, ice can form and generate large hydraulic pressures that are sufficient to detach the flakes from the surface. They unfortunately have not presented any data (besides that on salt concentration) to support this hypothesis.

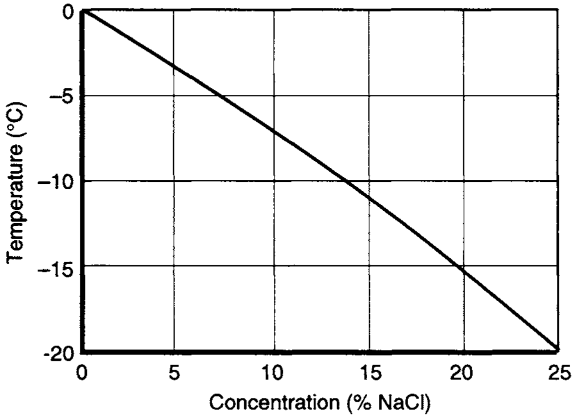

Figure 2.7 Relationship between the temperature at which ice formation is possible and the concentration of a sodium chloride solution.

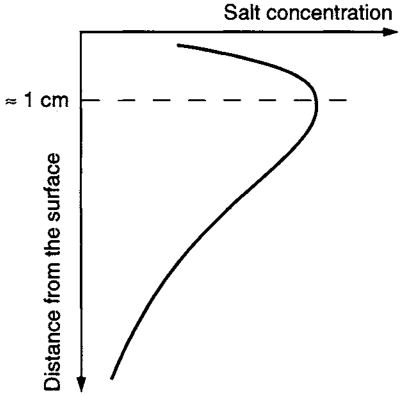

Figure 2.8 Typical salt concentration profile beneath the surface of field concretes subjected to periodical salt applications (after Rösli and Harnick, 1980).

It is evident that the salt concentration in any concrete subjected to salt applications will vary from the surface to the body of the concrete (Figure 2.8). This can generate certain thermodynamic phenomena, such as osmotic pressures, related to the various degrees of ice formation in the different concrete layers. In certain cases, ice formation will tend to block the flow of water due to osmosis and this can create high stresses in certain layers. It is further possible, since supercooling occurs, that the formation of ice at lower temperatures will occur more rapidly and thus increase the possibility of damage.

When de-icer salts are applied to a thin layer of ice that has formed on concrete (as can occur when the roads are slippery due to freezing rain and salts are used to clear them up), the temperature of the concrete surface decreases very rapidly and this causes a thermal shock that can induce cracking (Rösli and Harnick, 1980). Melting of the ice requires a large amount of energy. This energy is mainly taken from the concrete whose temperature thus drops fairly rapidly. Figure 2.9 shows the temperature profile, from the concrete surface inwards, immediately after the application of de-icer salts to a frozen layer of water on this concrete surface. The temperature drop at the surface of the concrete is quite clear.

On the basis of what they considered to be a typical salt concentration profile in concrete (Figure 2.8), Harnick *et al.* (1980) suggested a layer by layer freezing phenomenon leading to surface scaling. Because the outer layer of the concrete is subjected to rain, it contains relatively little de-icer salt and ice formation is possible at temperatures only a few degrees below 0 °C. In the layer underneath, however, the salt concentration is high and ice formation does not generally occur. This creates stresses due to the different expansions of the two layers, and scaling occurs. These authors have not explained if this variable expansion is due to ice formation (which would directly explain the damage) or to the contraction of the paste during freezing when it is well protected by entrained air voids.

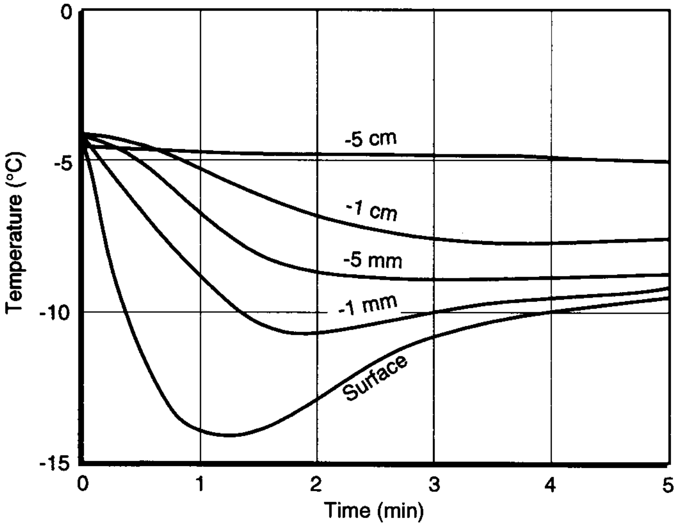

Figure 2.9 Typical temperature profiles in concrete, as a function of the distance from the surface, after a sodium chloride application to a 1 mm ice cover at −5 °C (after Rösli and Harnick, 1980).

Having noticed that 'New Jersey' concrete barriers (used as separators on motorways) often suffered severe scaling on the face exposed to the south these concrete barriers with thermocouples. They found that there could be only, Hudec *et al.* (1986) studied the temperature variations at the surface of many freezing and thawing cycles in a single day when alternate sunny and cloudy periods occurred during the winter season, and that the total number of cycles per year could be extremely large. They suggest that this could explain why scaling is so frequent.

The growth of salt crystals has been mentioned as another phenomenon which can contribute to surface scaling. This can occur if the pore water solution reaches supersaturation (Harnick *et al*., 1980). A major cause of scaling could also simply be the fact that when a dry concrete surface is wetted, there tends to be a water front, particularly since the salt concentration is much higher in the outer layers (Figure 2.10). When freezing occurs, only the saturated top layer can be damaged.

De-icer salt scaling is now recognized as the most important frost problem in many countries, and extensive testing as well as fundamental research programmes have been initiated recently and are still going on. In spite of all the research that has been done in the last 50 years, much remains to be learnt concerning the fundamental mechanisms which are the cause of de-icer salt scaling. Apart from the fact that, in most cases, air entrainment significantly increases the scaling resistance of concrete, the technical literature is full of contradictions that cannot readily be explained. Part of the problem certainly originates from the fact that field concretes are exposed to conditions which are substantially different from the usual laboratory test conditions. This topic is discussed in Chapter 7.

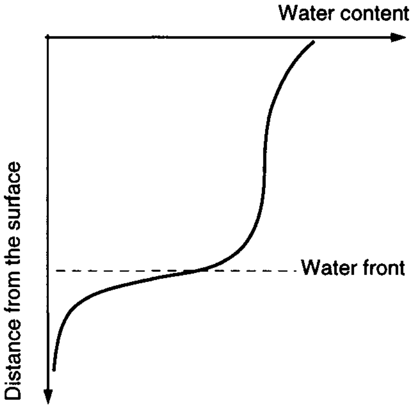

Figure 2.10 Penetration of water into a relatively dry concrete (after Rösli and Harnick, 1980).

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Chapter 3
Basic Concepts Related to Frost Resistance

When concrete freezes in a saturated state, tensile stresses are generated in the paste (and in the aggregates). As we have seen, these stresses can basically be due either to the flow of water, or to the formation of ice crystals in capillary pores already filled with water. If the concrete is not correctly protected by sufficiently closely spaced air voids, microcracking and, eventually, complete disruption of the concrete can occur. Before we examine (in Chapter 5) the various parameters that can influence the frost resistance of concrete (such as the water/cement ratio, cement and aggregate characteristics, curing etc.), there are many basic concepts related to frost resistance (other than the theories presented in Chapter 2) that must be clearly described because they are necessary to understand many aspects of this very complex problem. One of these is the various ways in which concrete can deteriorate, another is the process of ice formation in saturated cement pastes and yet another is the characteristics of the air-void system that are required for good frost resistance. Some investigators have come up with different hypotheses to explain the frost resistance of concrete, others have developed special tests that help to understand how concrete reacts when it is subjected to freezing and thawing cycles, and some have developed **frost resistance numbers** that combine into a single parameter the most significant factors determining the frost resistance of any given concrete. This chapter describes this important information.

3.1 DETERIORATION DUE TO FROST ACTION

As explained in Chapter 2, there are are two types of deterioration due to freezing and thawing cycles: surface scaling, and cracking in the body of the concrete. Cracking due to the internal pressures generated by the action of frost in the hardened cement paste (or in the aggregates) is not very common nowadays, probably because most concretes exposed to freezing and thawing cycles are sufficiently protected by the use of air entrainment.

Internal cracking can normally only be noticed in concrete elements that are saturated or nearly so at the time of freezing. This is more likely to be the case in structures such as pavements, bridge piers and dams, in the section close to the water line. Internal cracking is, of course, typical of the deterioration that occurs when fully saturated concrete specimens are subjected to cycles of freezing in air and thawing in air or water in the laboratory (Figure 2.5).

One form of cracking due to frost that has been observed relatively frequently in the United States is called D-line cracking. As can be seen in Figure 3.1, this type of damage occurs mostly along the joints or along structural cracks in concrete pavements and sidewalks (thus the name D-line meaning deterioration line). The exact cause of D-line cracking is disputed, but according to Cordon (1966), it is probably due to frost action (in the paste or in the aggregates). It occurs close to the joints simply because that zone has, through the joint or crack, easy access to moisture from the subsoil. Of course, D-line cracking should not occur in properly air-entrained concrete made with good quality aggregates. The fact that it is particularly evident at the intersection of joints could be due to stress concentrations of thermal origin in such areas (Cordon, 1966).

Surface scaling (Figure 1.6) is the most frequently observed form of frost damage. It should not be confused with spalling. Scaling can be defined as the progressive loss of small particles or flakes (Browne and Cady, 1975) of cement paste or mortar not more than a few millimetres thick, whereas spalling is due to the swelling of corroding steel reinforcement that lifts and detaches chunks of concrete as thick as the concrete cover on the reinforcement. Similarly to internal cracking, it often occurs in very localized areas. It is not uncommon, for instance, to find a badly scaled section of a sidewalk next to another section only very slightly damaged (Figure 3.2). This is generally due to the fact that the spacing factor (for various reasons which will be discussed in Chapter 6) sometimes varies significantly from one load of concrete to the next. It can also be related to different degrees of saturation during freezing due to variations in the drainage of the structure.

Since scaling gradually exposes the coarse aggregate (Figure 3.3), it is often believed that scaling is always related to the quality of the aggregate. This is not correct.

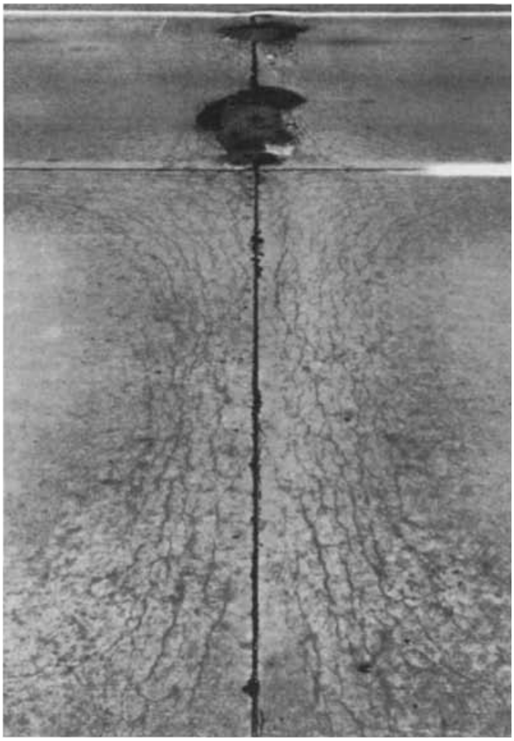


Figure 3.1 Section of a pavement affected by D-line cracking (courtesy of Construction Technology Laboratories).

Aggregate can influence the scaling process through various mechanisms such as expulsion of water during freezing that creates pressure at the aggregate–paste interface, but scaling is also possible even when good aggregates with a very low porosity are used. The aggregate-paste interface generally has a higher porosity than the bulk of the paste even in low water/cement ratio concretes made with such good aggregates (Maso, 1980), and this can influence the scaling process. However, scaling can also often be directly related to inadequate air entrainment irrespective of the quality of the aggregate.

When concrete contains aggregate particles that are frost susceptible (i.e. that will crack if frozen when saturated, Chapter 5), or that are simply weak or highly cleaved, a phenomenon known as **pop-outs** can be observed. This phenomenon, which can be considered as a form of scaling, is described in Figure 3.4 and the deterioration it causes is illustrated in Figure 3.5. If a crack forms in a piece of aggregate close to the surface, this crack will tend to be parallel to the surface. Since the mortar cover on the aggregate is weak in tension, a conical shaped particle will be detached from the surface as shown in Figure 3.4, creating a hole known as a pop-out with the broken particle clearly visible at the bottom of the hole. Pop-outs do not really cause serious problems to the concrete. They only damage its appearance. Of course, if the number of weak or frost-susceptible particles is excessive, significant internal damage and loss of mechanical properties can result.

Figure 3.2 Severely scaled section of a sidewalk (due to freezing in the presence of de-icer salts) next to slightly damaged sections.

Very often, scaling first occurs over coarse aggregate particles that are very close to the surface. As shown in Figure 3.4, due to the pressure created at the interface by the water

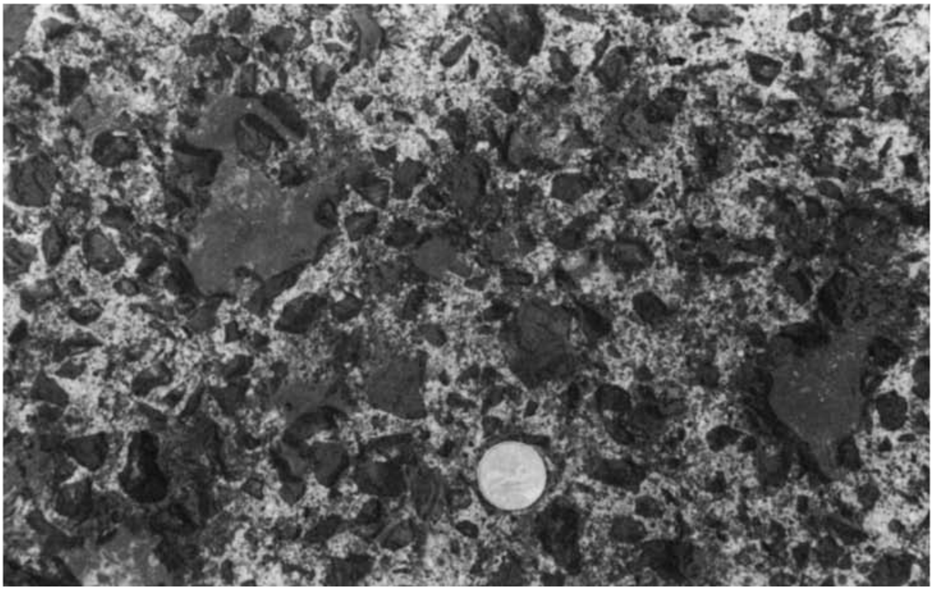
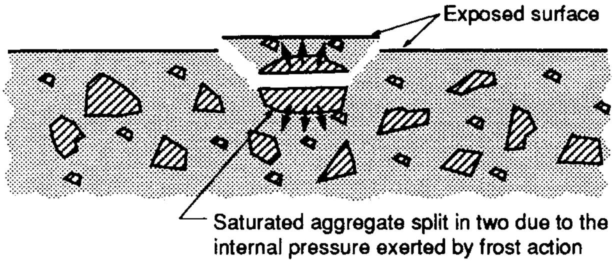
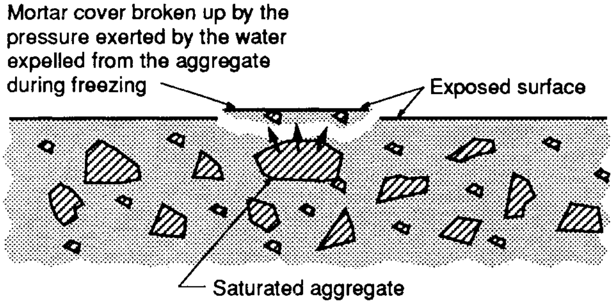


Figure 3.3 Exposed coarse aggregates on a concrete surface affected by scaling.



(a) Classical pop-out



(b) Type II pop-out

Figure 3.4 Schematic representation of the formation of pop-outs: (a) classical pop-out; (b) type II pop-out.

that is expelled from the aggregate during freezing, the thin mortar or paste cover over the particle can simply break away, thus exposing the aggregate surface. Unfortunately, some investigators also refer to this type of deterioration as pop-outs. As this phenomenon is very different from that due to frost-susceptible or weak particles, and to avoid confusion, it is referred to here as ‘type II pop-outs’.

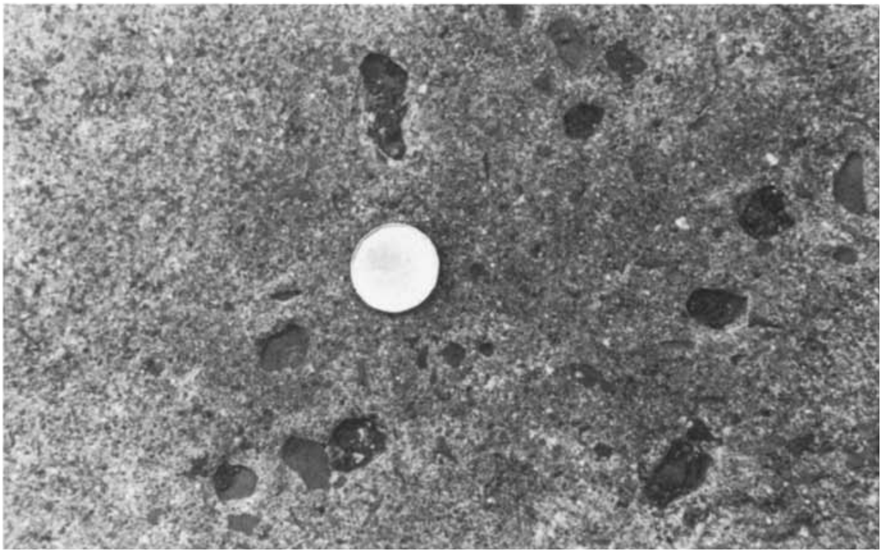


Figure 3.5 Typical pop-outs on a concrete surface.

3.2 ICE FORMATION IN HARDENED CEMENT PASTES AND CONCRETES

All three theories described in Chapter 2 are based on the assumption that the formation of ice in the capillary pores of hardened cement paste is restricted in one way or another. In the hydraulic pressure theory, the restriction is considered to be due to the chemicals present in the pore water solution. In the osmotic pressure theory (as well as in the diffusion theory which is a simplified version of it), the surface tension of water in the capillary pores is considered to be a major cause of restriction to ice formation. In Litvan’s theory, the basic assumption is simply that water cannot freeze *in situ*.

In view of the importance of the problem of ice formation as regards the frost resistance of concrete, it is not surprising that a relatively large number of investigators have studied it. Some of these investigators have analysed the process of ice formation using mainly theoretical thermodynamic considerations (Radjy, 1969; Setzer, 1976), others have measured the expansion of cement paste specimens during freezing (Helmuth, 1960; Litvan, 1972), and many have used differential thermal analysis or low temperature calorimetry (Litvan, 1972; Bager and Sellevold, 1980; Banthia *et al.,* 1989).

From thermodynamic considerations, it can be shown that the amount of freezable water in hardened cement paste increases gradually as the temperature decreases, because the temperature at which ice can form is a function of the size of the pores (Figure 1.3). As the temperature decreases, the size of pores in which ice formation is possible also decreases and this in turn increases the freezable water content. However, all freezable water does not necessarily freeze immediately when the required temperature is reached. Under atmospheric pressure, the melting point of ice is 0 °C, but 0 °C is not necessarily the freezing point of water.

As experiments have shown, even if some freezable water exists at temperatures just below 0 °C, supercooling of water in the pores almost always occurs because the formation of ice requires a nucleation process. Nucleation can be spontaneous but, in capillary pores, this implies a high degree of supercooling (Helmuth, 1960). It can start at a solid surface in contact with the supercooled water, but this does not seem to be possible in the pores of hardened cement paste, since the solid surfaces of the pores are necessarily covered with a thin layer of adsorbed water and this water cannot freeze at temperatures higher than −78 °C (Powers and Brownyard, 1948). Nucleation therefore is probably generally due to seeding with an ice crystal generally formed on the outer surface of the sample (Helmuth, 1960). Of course, the pore water solution always contains a certain amount of dissolved substances (mainly the alkalies Na_2O and K_2O) and this lowers the melting point of ice.

The fact that cement paste contains a large amount of adsorbed (gel pore) water that cannot freeze at temperatures higher than −78 °C is extremely important. It not only affects the nucleation process, but also provides the paste with a continuous system of very small channels filled with unfrozen water. This system of small channels connects all capillary pores (even if the capillary pore system itself is discontinuous as it should be in good quality concrete) and allows water from small capillary pores where ice has not formed to feed slowly the growth of ice crystals in larger pores (Adler-Vignes and Dijkema, 1975).

Low temperature calorimetry is a very interesting way to study ice formation in porous bodies. This technique, which requires sophisticated equipment, consists of slowly cooling (and subsequently of heating) a sample of any porous material partially or completely saturated with water (or some other appropriate fluid) and measuring the heat flow associated with the process. The results of this type of test are generally reported in the form of graphs showing the amount of heat evolved as a function of the temperature decrease or increase (Figure 3.6). In this figure, from le Sage de Fontenay and Sellevold (1980), the heat flow is presented as 'apparent heat capacity' in cal/°C/g, which means that the amount of heat transported from (during cooling) or to (during heating) the specimen being tested is simply equal to the area under the curve (Bager and Sellevold, 1980). The peaks on the graph correspond to ice formation (during cooling) and to the melting of ice (during heating) because the phase transition of water from the solid to the liquid state requires a certain amount of heat known as the heat of fusion and, inversely, the transition from the liquid to the solid phase releases this heat of fusion. Precise calculations to obtain the amount of ice formed can be made, taking into account the variation of the heat capacities of the liquid water and ice as a function of temperature.

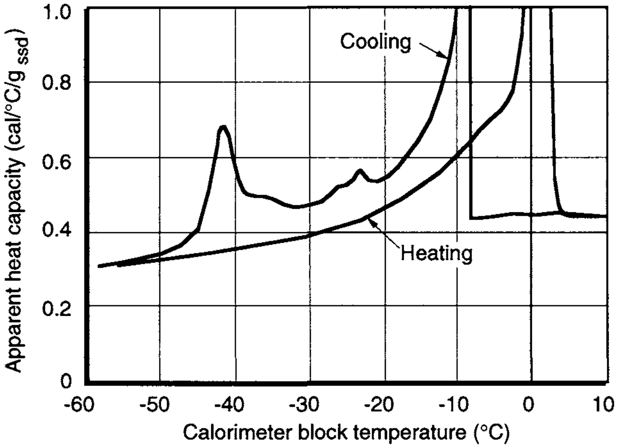


Figure 3.6 Low temperature calorimetry results for a mature Portland cement paste at a water/cement ratio of 0.6 (after le Sage de Fontenay and Sellevold, 1980)

The use of low temperature calorimetry allows determination not only of the amount of ice formed, but also of the temperature at which it forms. In the graph of Figure 3.6 there is a first large peak at approximately −10 °C that indicates that ice formation in this particular sample (mature hardened cement paste with a water/cement ratio of 0.6) only began at that temperature. This is clear evidence that supercooling can be a very important phenomenon. There are two other peaks on the graph: a very small one at approximately −20 °C and a second large one slightly below −40 °C. Ice, therefore, does not form very gradually, even when a sample is cooled very slowly (in this case 3.3 °C/h), but forms mostly at relatively well-defined temperatures. The first peak corresponds to the freezing of a significant amount of water in the larger capillary pores, and the other peaks to the freezing of water in smaller pores. The fact that ice forms at well-defined temperatures can be related to the phenomenon of nucleation by seeding from ice crystals. As soon as ice forms somewhere in the sample, the phenomenon spreads rapidly throughout the sample in all pores where there is a sufficient amount of freezable water at that temperature (and where the dimension of the ‘neck’ or entrance of the pores is sufficiently large).

Sellevold and his co-workers have used the low temperature calorimetry technique to analyse the influence of many parameters on the quantity of ice formed during freezing. They have shown, for instance, that the amount of ice formed in concretes cured at high temperatures is much larger than that in similar concretes cured normally, probably because curing at high temperatures produces a coarser capillary pore system. They have also demonstrated that the amount of ice that forms tends to be larger after the first cycle of cooling and heating, which indicates that some form of damage to the microstructure or that a change in the characteristics of the pore system occurs during the first cycle.

The most significant finding from the calorimetry tests by Sellevold and his associates is probably the extreme importance of what Sellevold calls the **moisture history** of concrete. As can be seen in Figure 3.7, the amount of ice formed in a given sample can be up to five or six times larger if the specimen is dried and resaturated before the test instead of being tested in the virgin state, i.e. directly after curing. This of course has extremely important implications concerning frost resistance. Tests have shown, for instance, that an increase in the drying temperature from the usual 23 °C to only 45 °C has substantially reduced the salt scaling resistance of certain types of concrete (Sorensen, 1983).

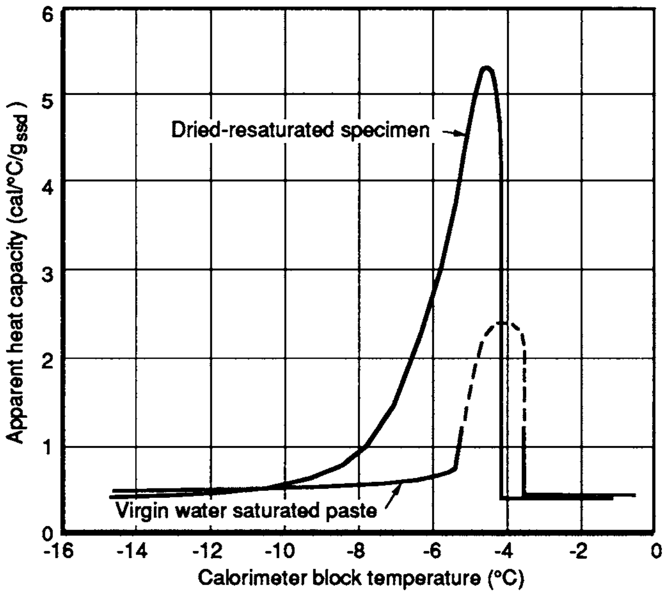


Figure 3.7 Low temperature calorimetry results showing the influence of drying on the amount of freezable water in a mature Portland cement paste at at a water/cement ratio of 0.6 (after Sellevold *et al.,* 1983).

The basic reason for the reduction of the scaling resistance due to drying is that, in addition to causing microcracking, drying can significantly alter the microstructure of cement paste. Microcracking seems to have relatively little influence on the scaling resistance, but if drying is sufficiently intense (i.e. if the drying temperature is sufficiently high or the drying period sufficiently long), some of the hydration products can be disrupted (in part due to the loss of some of the gel pore water). As shown in Figure 3.8, this tends to increase the average size and continuity of the capillary pores, and thus the freezable water content. Because of their very refined pore structure, certain types of concretes, such as high performance concrete or those containing silica fume, are much less influenced by this phenomenon. Considering its implications as regards the relevance of the standard tests now being used to determine the salt scaling resistance of concrete, the influence of drying certainly represents an area where further research is needed.

The aggregate–paste interface in concrete, probably in good part due to the so-called ‘wall effect’, is generally much more porous than the bulk of the paste (Maso, 1980). It is probably the presence of this interface that reduces the frost resistance of certain low water/cement ratio concretes because very little ice is formed in mature hardened cement pastes with a water/cement ratio below 0.4. In very low water/cement ratio concretes, however, particularly when silica fume is used, the interface between paste and aggregate has a porosity closer to that of the bulk of the paste.

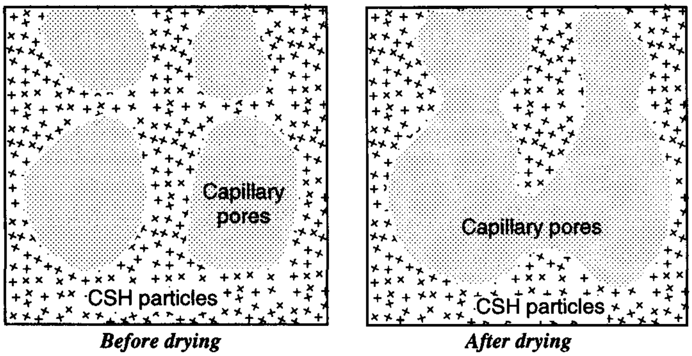


Figure 3.8 Schematic illustration of the influence of drying on the continuity of the capillary pores in hardened cement paste.

3.3 REQUIRED AIR-VOID CHARACTERISTICS

It is clear from the theories that were described in Chapter 2 that, as regards frost resistance, the most important parameter of the air-void system is the spacing of the air voids. (The method recommended by ASTM Standard C 457 (which is based on the work of Powers and others) to determine the various characteristics of the air-void system (mainly the total air content, the specific surface and the spacing of air voids) is explained in the next chapter.) The most obvious question that can be asked concerning frost resistance is ‘what value of the spacing factor is necessary to protect concrete against frost damage?’

Powers in his 1949 paper mentioned the value of 250 μm, and later, in 1954, published results from rapid freezing and thawing tests carried out in his laboratory that indicated that this value was applicable to a relatively wide range of concretes. Many engineers still consider this value to be correct and use it as a reference point.

The most often mentioned value, 200 μm (or 0.008 in!), comes from a paper by Backstrom *et al.* published in 1958. This paper states (again on the basis of rapid freezing and thawing tests) that the required value varies between 100 and 200 μm (0.004 to 0.008 in), depending on the type of concrete. It is, however, the value of 200 μm that was adopted afterwards by many regulating bodies and agencies and that is now the most widely recognized value.

In most countries where natural freezing and thawing cycles occur, the rate of cooling or freezing rarely exceeds 2 or 3 °C/h (Pigeon and Lachance, 1981; Cordon, 1966). Why then was the value of 200 μm obtained from rapid freezing and thawing cycle tests (at more than 8 °C/h) so rapidly accepted, since Powers’ work had clearly shown the importance of the freezing rate? The answer is most probably because that value is typical of correctly air-entrained concretes and it was then evident from all the data being published (field as well as laboratory) that air entrainment was a necessary protection against frost action.

The reasons behind this apparent contradiction between field experience (showing that a value of 200 µm is necessary to give concrete an adequate protection against 'slow' natural freezing and thawing cycles) and laboratory testing (showing that a value of 200 or 250 µm is necessary to protect concrete against rapid cycles) were studied recently by Pigeon and co-workers using what they termed the **critical spacing factor**. This concept is based on the assumption that for any given concrete subjected to any given freezing and thawing cycle test, there exists a critical value of the spacing factor beyond which concrete deteriorates rapidly when subjected to the test. Laboratory data has shown this assumption to be correct in a very large number of cases (Pigeon, 1989).

The critical spacing factor concept can be used to evaluate the relative frost durabilities of various concretes and also to compare various types of freezing and thawing cycle tests. For instance, if, for the same test, the critical spacing factor is lower for one type of concrete than for another, it means that this concrete has a lower frost durability since it requires more protection (closer air voids) for good durability. In the same way, if, for the same concrete, the critical spacing factor is lower for one type of test than for another, it means that this test is more severe since more protection is required for good durability.

The determination of a single value of the critical spacing factor represents a large amount of work because it requires the fabrication and testing of many concrete mixtures with the same basic characteristics but different air-void systems. Figure 3.9 shows an example of the results of the determination of a critical spacing factor (Pigeon *et al.,* 1986). In this particular case, 17 similar concrete mixtures were fabricated with the same ordinary Portland cement, the same fine aggregate, the same limestone coarse aggregate, the same

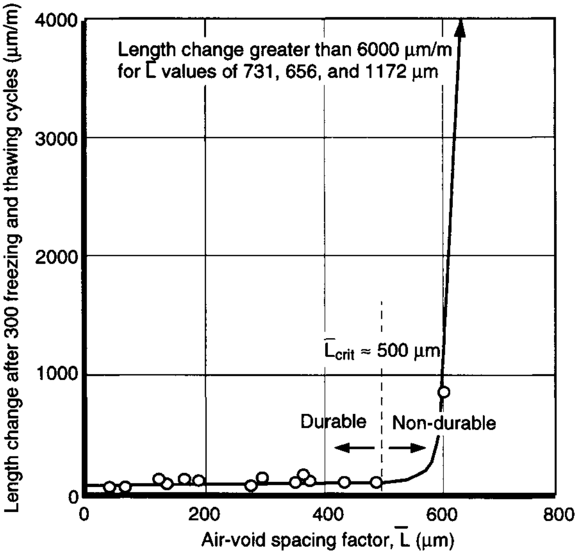


Figure 3.9 Freezing and thawing test results showing the existence of a critical value of the air-void spacing factor for an ordinary Portalnd cement concrete with a water/cement ratio of 0.5 (the tests were performed according to ASTM C 666, procedure A, on 17 similar concretes with various air-void spacing factors; after Pigeon *et al.,* 1986).

water/cement ratio and various dosages of an air-entraining agent. These concretes were all cured 14 days in water at 23 °C and then subjected to freezing and thawing cycles in water at an approximate freezing rate of 8 °C/h. The results of the freezing and thawing tests (i.e. the length change after 300 cycles) are given in the figure as a function of the air-void spacing factor (determined on samples of each of the hardened concretes). For all values of the spacing factor lower than about 500 µm, the length change after 300 cycles is extremely small and indicates that no significant cracking has occurred in the specimens. For higher values, length change is very significant and increases extremely rapidly with the spacing factor. The critical value of the spacing factor is thus approximately 500 µm (the precision of the determination of course increases with the number of concretes tested) for this particular concrete subjected to this freezing and thawing test.

Table 3.1 presents the results of the determination of the critical spacing factor for various types of concretes tested in similar conditions (the value of 500 µm from Figure 3.9 is given in this table). The influence of the various parameters involved (such as the type of cement and the value of the water/cement ratio) will only be discussed in Chapter 5, but the results in the table can serve to illustrate the use of the critical spacing factor concept. For instance, the critical spacing factors for the normal Portland cement concretes made with and without a superplasticizer (for the same water/cement ratio of 0.5) are approximately equal, which shows that superplasticizers *per se* have little effect on frost resistance. The results indicate, however, that at the same water/cement ratio of 0.5, the use of silica fume tends to decrease frost resistance since the critical spacing factor for the silica fume concretes is significantly lower than that for the normal Portland cement concretes.

Table 3.1 Critical spacing factors (µm) obtained for various types of concretes subjected to 300 freezing and thawing cycles in water and in air (after Pigeon, 1989).

Water/binder ratio	Freezing and thawing in water			Freezing and thawing in air
	Type 10	Type 10+SF	Type 30+SF	Type 10+SF
0.50	500	250	–	400
0.50 (SP)	500	200	–	400
0.30 (SP)	400	300	>800	450
0.25 (SP)	750	–	>800	–

Type 10: normal Portland cement.
Type 30: high early strength Portland cement.
SF: silica fume.
SP: superplasticizer.

Pleau (1986) has reviewed in depth the technical literature on this question of the relationship between frost durability and spacing factor. In most cases where the values of the spacing factor were available and the characteristics of the concretes as well as of the freezing and thawing cycles clearly described, the results were found to be consistent with those in Table 3.1.

Pigeon *et al.* (1985) have used the critical spacing factor concept to analyse the influence of the freezing rate (Figure 3.10). Their results have confirmed what Powers and Litvan had stated earlier on the basis of theoretical considerations. They also tend to show that concretes with values of the air-void spacing factor much higher than 200 or 250 μm can satisfactorily resist 300 cycles of freezing and thawing when the value of the freezing rate is close to the highest values observed under natural conditions (about 2 °C/h). This particular aspect of the problem of frost resistance will be specifically addressed in the chapter on exposure conditions. It should be stated right away, however, that 200 μm is nevertheless a good and safe design value for concretes exposed to severe weathering in northern climates, probably in good part because values of that order of magnitude are generally required for good resistance to scaling due to freezing in the presence of de-icer salts. It is also possible, though this has never been clearly demonstrated, that, as mentioned in Chapter 2, freezing cycles with long freezing periods are more harmful to concrete and that lower values of the spacing factor are thus required for satisfactory protection against such cycles. It is important to note that the values in Table 3.1 represent the spacing factors required to resist a particular test only and that other results would be obtained with other tests. These values should therefore never be considered or used as safe design values.

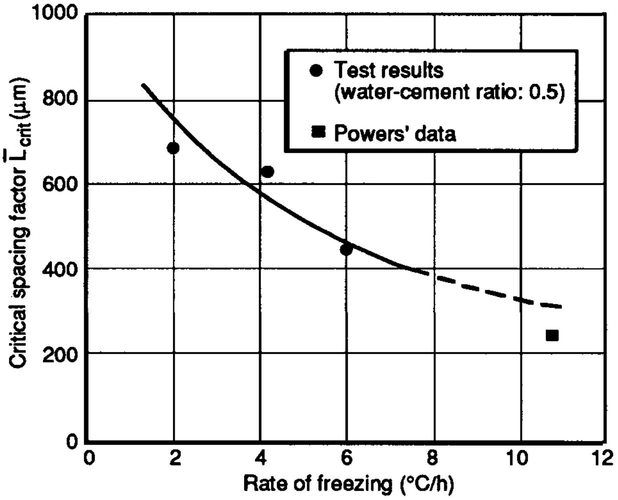


Figure 3.10 Variation of the critical air-void spacing factor value with the rate of freezing (during freezing and thawing cycle tests) (after Pigeon *et al.,* 1985).

Apart from the known fact that correct air entrainment is needed in most cases for good de-icer salt scaling resistance (Verbeck and Klieger, 1957; Sommer, 1979), little information is available concerning the exact relationship between the spacing factor and the de-icer salt scaling resistance. The data that exist tend to show that there is no critical spacing factor for scaling resistance, and that surface deterioration increases gradually with an increase in the spacing factor (Bordeleau *et al.,* 1992). The available information also indicates that, although 200 μm should normally be considered as a safe design value, the optimum value of the spacing factor for scaling resistance varies with the type of concrete. This value can be higher than 200 μm, for instance, for certain high performance concretes (Gagné *et al.,* 1991).

The field data in Figure 3.11 illustrate the influence of the spacing factor on the scaling resistance. In this figure the surface deterioration of a number of sidewalks only a few years old is plotted against the air-void spacing factor measured in cores taken from the sidewalks. For low values of the air-void spacing factor, the performance can be good or bad (because factors other than air-void characteristics can of course affect the scaling resistance), but at high values, the performance seems always to be bad and there is certainly no clearly defined critical value.

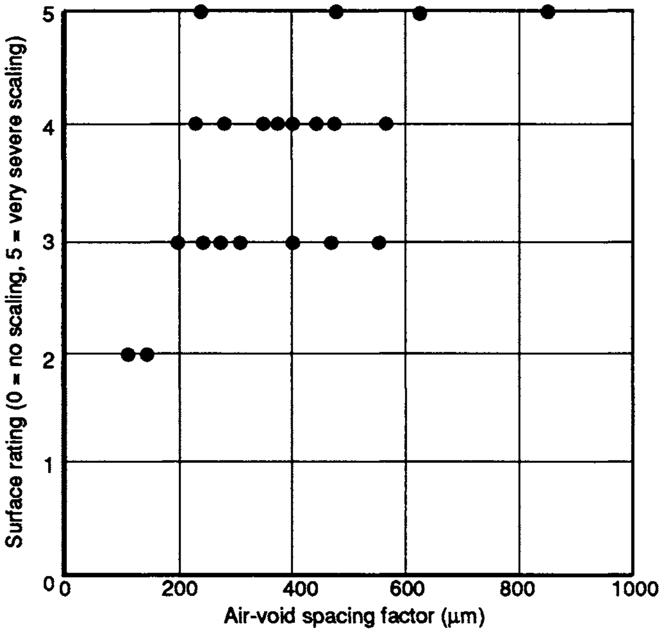


Figure 3.11 Relationship between the intensity of surface scaling and the value of the air-void spacing factor for a number of sidewalks from an urban area in the province of Québec.

3.4 OTHER HYPOTHESES CONCERNING FROST ACTION

A new hypothesis to explain the frost resistance of air-entrained concretes has been put forward recently by Litvan (1983). This hypothesis does not fundamentally contradict his model of frost action as described in Chapter 2. Using mercury intrusion porosimetry, Litvan found that the pore volume in the range 0.35–2 μm was much higher for air-entrained concretes than for non-air-entrained concretes. In fact, the pore volume in this range was found to be almost negligible for non-air-entrained concretes.

Litvan has estimated that the mean spacing of these 0.35–2 μm pores in air-entrained concretes is about 2 μm. This value is approximately 100 times smaller than the common value of the spacing factor of air voids in properly air-entrained concrete. According to this new hypothesis, the beneficial effect of air entrainment would be due to these

0.35–2 μm pores, and not to the incorporation of air bubbles (10–1000 μm in size), because these pores could act as 'micro air voids' to protect the cement paste against freezing and thawing cycles. Litvan believes that the ratio between the quantity of air bubbles and that of these pores in the paste is probably constant, which would explain why the role of these pores has not been detected by the various investigators studying the frost resistance of concrete.

The frost resistance of concretes incorporating superplasticizers has been the subject of much debate ever since these admixtures were introduced in the 1970s. It was found that, in certain cases, the resistance of superplasticized concretes (with spacing factors higher than 200 (μm) to rapid cycles of freezing and thawing could be very good (Malhotra, 1981). Litvan considers that the use of superplasticizers probably tends to reduce the number of air-entrained bubbles without affecting the number of 0.35–2 μm pores. The presence of these pores could therefore explain the good frost resistance of superplasticized concretes even when the spacing factor of the air voids is significantly higher than the usually recommended value of 200 μm.

Certain investigators (Mielenz, 1968; Gjorv *et al.,* 1978; Mather, 1978) have found, contrary to others (Powers, 1954; Backstrom *et al.,* 1958; Pigeon, 1989), that the correlation between frost damage and air-void spacing factor is not always very clear. The influence of the 0.35–2 μm pores could also explain this lack of clear correlation.

If this hypothesis is correct, the determination of the characteristics of the air-void system using the methods described in ASTM Standard C-457 would not be very useful to predict the frost resistance of concrete, and mercury intrusion porosimetry should be used instead.

It is evident that, in order to act as 'micro air voids', the 0.35–2 μm pores must not be filled with water when concrete freezes. On the other hand, it is known that the largest capillary pores in hardened cement paste (which are about the same size as the pores observed by Litvan in air-entrained concretes) rapidly become empty when the relative humidity decreases slightly below 100% in concrete. The validity of Litvan's new hypothesis is thus related to the degree of saturation of concrete at the time of freezing. It cannot apply to fully saturated concrete, but could help to explain why the frost resistance of concrete increases so rapidly when the relative humidity decreases below 100%. Since, in most laboratory freezing and thawing tests, concrete is fully saturated, this hypothesis cannot explain the good durability of superplasticized concretes (this topic is discussed in Chapter 5). It cannot apply either to the resistance to scaling, since scaling generally only occurs when the surface of the concrete is covered with water at the time of freezing. It must also be mentioned that the technique of mercury intrusion porosimetry is based on many assumptions that are not necessarily all valid in hardened cement paste.

3.5 SPECIAL TESTS

One of the tests that was developed to analyse the frost resistance of concrete is particularly interesting because it is the only one that really attempts to predict the length of the period during which concrete in the field will be totally immune from frost damage. This test, which is called the critical degree of saturation test (Fagerlund, 1971), has the advantage of drawing attention to the fundamental causes of the deterioration of concrete by frost. This is why it is briefly reviewed in this chapter, which presents some basic concepts related to frost resistance.

The first part of the critical degree of saturation test consists of exposing specimens of a given concrete which have been previously equilibrated at various degrees of relative humidity, or for which the various degrees of saturation of the capillary pores have been determined, to freezing and thawing cycles. Except on rare occasions, due to the nature of the phenomenon, concrete is either immune to freezing and thawing cycles or is very rapidly destroyed by such cycles (Fagerlund, 1971). The results of the freezing and thawing tests therefore allow the determination of the critical degree of saturation S_{CR}.

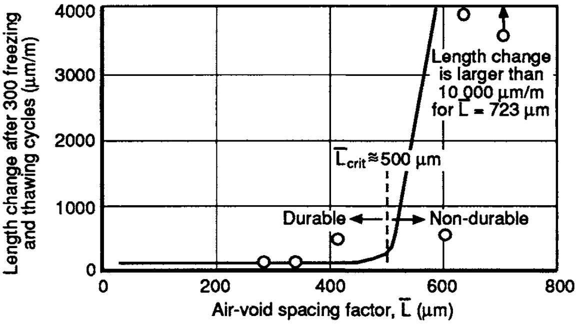
In the second part of the test, the length of time necessary for the degree of saturation in a sample of the same concrete to reach S_{CR} is determined. The results of water suction tests over a certain period of time, for instance, can be used to predict this length of time, which is considered to be the useful service life of the concrete under consideration. The service life will depend on many factors, such as easy access to moisture, and the result of the test, in terms of the number of years that concrete will be immune to frost, must be interpreted with care.

When the capillary pores in concrete are fully saturated in a specimen that is subjected to freezing and thawing cycles, as is normally the case when the procedures described in ASTM Standard C 666 (Chapter 4) are followed, two basic factors control the frost resistance: the rate at which the temperature decreases and the distance that water must travel to reach the nearest air void. However, concrete in the field is not always fully saturated, which is why the results of the ASTM tests can only be used to compare the frost resistance of different concretes, and cannot readily be used to predict the service life of concrete.

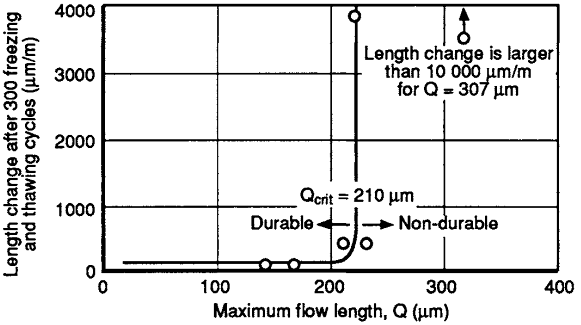
According to Fagerlund (1971), the observation that a critical degree of saturation can be determined for almost any type of concrete is due to the fact that there exist in concrete critical distances, these being related to the degree of saturation of the capillary pores. The frost resistance of a given concrete is therefore not just related to its intrinsic characteristics (water/cement ratio, air-void spacing factor etc.) but also to the conditions that it will be subjected to during freezing. Concerning the problem of salt scaling, which usually only occurs when the surface of the concrete is covered with water or with a salt solution, it is thus evident that this concept of the critical degree of saturation cannot be directly applicable.

The critical dilation test is another test that has been used by many investigators to understand the mechanisms of destruction of concrete by frost (Valore, 1950; Powers and Helmuth, 1953; Helmuth, 1960; MacInnis and Beaudoin, 1968). It is based on the measurement of the length change of concrete during freezing and can thus be used to obtain relatively rapid indications of the frost susceptibility of concrete subjected to freezing in various conditions. If concrete is well protected by sufficiently closely spaced air voids, the length of the specimen decreases as the temperature drops below 0 °C but, if enough ice forms in the capillary pores, expansion occurs (see Figure 4.2). This test, although not used very commonly, is now a standard ASTM procedure (C 671) and is described in more detail in the next chapter.

Since the spacing factor defined in ASTM C 457 is only an estimate of the real spacing of air voids in cement paste, many investigators have developed ways to characterize better the spacing of air voids (this is briefly discussed at the end of Chapter 4). Figure 3.12 shows the relationship between the air-void spacing factor and the deterioration due to freezing and thawing cycles for one common concrete mixture. It also shows the same data, but with the spacing factor being replaced by the 'flow length' (Chapter 4). The flow length clearly allows a more precise determination of the critical value of the spacing of air voids. These data also confirm the basic hypothesis that the deterioration due to frost is related to the pressure generated by the flow of water during freezing.



a) Existence of a critical value of the air-void spacing factor ($\bar{L}_{crit}$).



b) Existence of a critical value of the maximum flow length (Q_{crit}).

Figure 3.12 Freezing and thawing test results showing existence of a critical value of the air-void spacing factor for an ordinary portland cement concrete with a water/cement ratio of 0.5 and the existence of a critical value of the flow length for the same concrete. (a) Existence of a critical value of the air-void spacing factor ($\bar{L}_{\text{crit}}$). (b) Existence of a critical value of the maximum flow length (Q_{crit}) (after Pleau, 1992).

3.6 FROST RESISTANCE NUMBERS

Even if the air-void spacing factor is the most important parameter concerning frost resistance, other parameters also have an important influence. It would therefore be useful to be able to characterize the ability of a given concrete to resist freezing and thawing cycles with a single number that would take into account all the major factors that influence the resistance to frost. One such number was suggested by Gjorv *et al.* in 1978. It is calculated using the equation

$$N = \left(\frac{A_{300}}{p}\right) \times \left(\frac{1}{W/C}\right) \times f_c \tag{3.1}$$

where N is the frost resistance number, A_{300} is the volume of air in the voids smaller than 300 μm (as a percentage), p is the paste content of the concrete, W/C is the water/cement ratio and f_c is the compressive strength (in MPa).

The parameters in this equation were chosen to include the three main factors that Gjorv *et al.* consider to influence significantly the frost resistance of concrete. The water/cement ratio is a relatively good indication of the capillary porosity and thus of the amount of freezable water. The compressive strength is directly related to the tensile strength which controls the intensity of the internal stresses that the concrete can withstand without cracking, and $A_{300/p}$ is related to the spacing of the air voids (p is used because the air in concrete is contained in the paste and it is the total amount of air in concrete that is measured). As will be seen in Chapter 4 (and also in Chapter 6), the relationship between air content and spacing factor is not very precise, mostly because the larger air voids have a significant influence on the total air content, but less influence on the spacing factor. The assumption made by Gjorv *et al.* that voids larger than approximately 300 μm do not contribute significantly to the spacing (and thus to the protection of the paste against frost) therefore appears to be quite reasonable. Of course, the frost resistance number can only

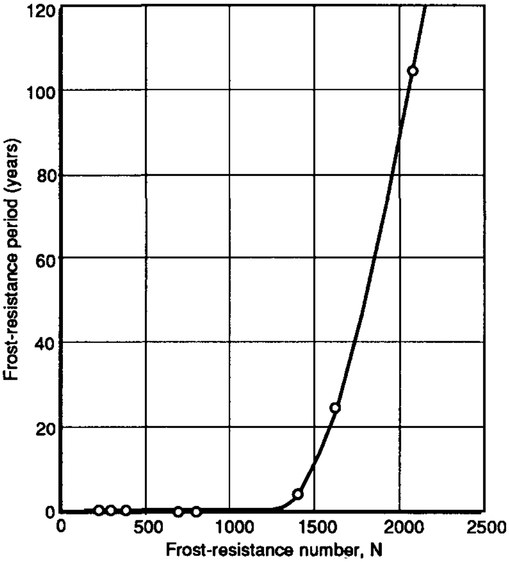


Figure 3.13 Relationship between the frost resistance period and the frost resistance number (after Gjorv *et al.,* 1978).

be calculated if the size distribution of the air voids is known (the techniques that can be used to determine this distribution will also be discussed in Chapter 4).

The validity of this frost resistance number was verified by subjecting a number of concretes to the freezing and thawing test put forth by Fagerlund in 1971 (the 'critical degree of saturation test'). The results of these tests are reproduced in Figure 3.13 which shows that the frost resistance increases extremely rapidly as the value of the frost resistance number increases beyond approximately 1500.

Another type of frost resistance number, the pore factor P_F, is presently used in Scandinavia and seems to give a reasonably good indication of the frost durability of concrete in the field. The pore factor takes into account only the total air content and the capillary porosity of concrete and is calculated as

$$P_F=A/(A+c) \tag{3.2}$$

where P_F is the pore factor, A is the fraction of the total volume of concrete occupied by air and c is the capillary porosity (calculated as a fraction of the total volume of concrete).

A and c are calculated by measuring the weight of a concrete sample in four different successive conditions: in air after drying to constant weight at 105 °C W_1, then in air after a sufficient length of time in water W_2, then in air after 2 h of pressure saturation at 10 MPa W_3, and finally in water W_4:

$$A=(W_3-W_2)/(W_3-W_4) \tag{3.3}$$

$$c=(W_2-W_1)/(W_3-W_4) \tag{3.4}$$

When a sample of concrete is soaked in water after drying, it is considered that only the capillary pores become filled with water. This explains why the capillary porosity is calculated using (W_2-W_1). However, if sufficient pressure is exerted, even the air voids become filled with water, thus the use of $(W_{3\_}W_2)$ to calculate the air content. Of course, the difference between the weight in water and the weight in air when the sample is fully saturated is equal to the weight of a volume of water equal to the volume of the sample.

Good frost durability is expected when the pore factor is larger than 20–25%. Such a value is typical, for instance, of normally cured 0.40–0.45 water/cement ratio concretes with an air content of approximately 6%.

The pore factor is less precise than the frost resistance number *N,* because it is based on the total air content, because it does not take into consideration the strength of concrete (although one could argue that strength is related to capillary porosity) and because the aggregate can influence the measurement of capillary porosity. It is nevertheless a relatively simple test to perform (the only special piece of equipment required being the 10 MPa pressure cell) and it can certainly be very useful because it indicates the frost resistance of a given concrete without the need for long freezing and thawing cycle tests.

In a recent paper, Goeb (1988) has suggested a method to predict the deicer salt scaling resistance of concrete. This method takes into account not only the characteristics of the concrete mixtures, but also the construction practices, including the finishing method, the type and length of curing, as well as the time after curing before the first de-icer application. It allows the calculation of the probability of scaling resistance, the maximum value being of course 100. In Goeb's paper, indications are given on how to calculate this probability by subtracting from the basic value of 100 certain numbers that are a function of the various parameters considered.

The frost resistance number, the pore factor and the 'probability of scale resistance' are all useful tools with which to predict the frost durability of concrete. Their main advantage is simply that they all indicate that good frost durability can only be achieved with good quality, properly air-entrained concrete that is placed using sound construction practices.

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Chapter 4
Laboratory Tests

A number of standardized laboratory tests are available to study the frost resistance of concrete and of concrete-making materials. These tests are often used to determine the cause of the deterioration observed in existing structures exposed to freezing and thawing cycles. They can also be used to assess the potential frost durability of concrete (or of concrete-making materials), and then be a very useful tool for those who must design mixtures for concrete structures which will be exposed to a freezing and thawing environment. Laboratory tests are, of course, extensively used in fundamental or applied research to analyse the basic mechanisms of frost action in concrete and the influence of various parameters on the frost resistance of concrete.

4.1 CONCRETE TESTS

Many laboratory tests have been developed to study the durability of concrete exposed to freezing and thawing. Some of them, such as the ASTM C 671 critical dilation test, are related to the fundamental aspects of frost behaviour. Many are designed to test the resistance of concrete to internal microcracking due to freezing and thawing cycles (such as the ASTM C 666 rapid freezing and thawing test), and others are intended to characterize the resistance to scaling due to freezing in the presence of de-icer salts (such as the ASTM C 672 salt scaling test). Although each of these laboratory tests gives valuable information about a given aspect of frost resistance, none of them provides a global understanding of the complex mechanisms responsible for frost damage. The choice of a laboratory test is then strongly dependent on the type of information which is needed and, in many cases, it is necessary to carry out more than one test.

4.1.1 Critical Dilation Test

Regardless of the mechanisms considered responsible for frost damage (ice formation, hydraulic or osmotic pressures, vapour pressure difference etc.), most investigators agree that the building up of internal disruptive stresses during freezing is accompanied by a corresponding expansion of the cement paste (Powers, 1954; Powers and Helmuth, 1953; Litvan, 1975). The dilation of cement paste during freezing is also supported by strong experimental evidence. The measure of this dilation can be used as an index of the potential durability of concrete: non-durable concretes are characterized by a large dilation which significantly increases during the repeated cycles of freezing and thawing, whereas durable concretes only exhibit a small dilation even after many freezing and thawing cycles.

The ASTM C 671 Standard test method describes a procedure to establish the period of frost immunity based on the critical dilation concept. Prior to the test, the specimens are conditioned and cured in order to simulate, as much as possible, the conditions (especially the degree of saturation) to which the concrete will be exposed in the field. The specimens are then placed in a water-saturated kerosene bath and cooled from 2 °C to −10 °C at a rate of 2.8 ± 0.5 °C/h. When the minimum temperature is reached, the specimens are immediately removed from the water-saturated kerosene and placed in a water bath at 2 °C until the next freezing cycle. During the cooling period the length change of the specimens and the temperature of the cooling bath are both recorded at regular time intervals. The length change of the concrete specimens is generally determined by casting stainless steel gauge plugs at the top and bottom of the specimens and then measuring their relative displacement using a linear variable displacement transducer (Figure 4.1).

The test procedure consists of carrying out a freezing cycle every 2 weeks and plotting, for each cycle, a graph showing the relationship between length change and time (a typical example of such a relationship is given in Figure 4.2). The dilation accompanying ice formation (in capillary pores) during freezing is obtained by measuring the maximum distance between the contraction curve and the straight-line extrapolation of the prefreezing curve as shown in Figure 4.2. For a frost-resistant concrete, this dilatation remains constant (or nearly so) during repeated cycles. On the contrary, for a non-durable concrete, this dilation increases very rapidly from one cycle to the next. According to the ASTM C 671 Standard, concrete is considered to be significantly damaged when the dilation increases by a factor of two or more between two successive cycles (the corresponding dilation is designated the critical dilation). The cycles are repeated until the critical dilation is exceeded or until the concrete specimens have been exposed to a sufficiently long period of test. For highly frost-resistant concretes, the critical dilation may never occur. Of course, the residual length change after the completion of all the freezing cycles also provides valuable information.

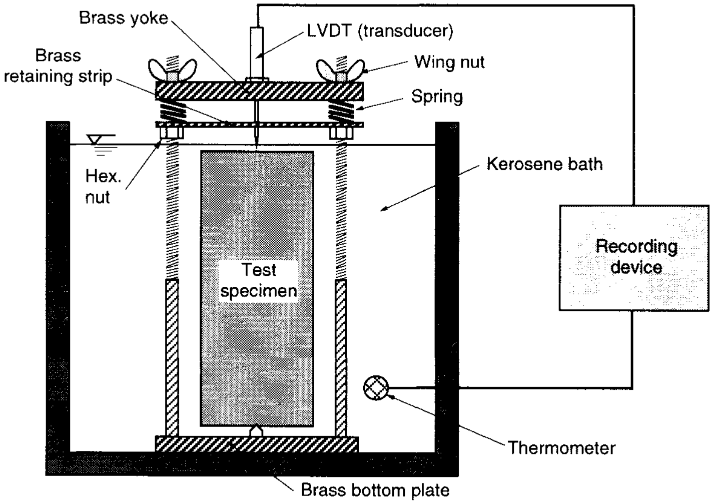


Figure 4.1 Experimental set-up for the ASTM C 671 critical dilation test.

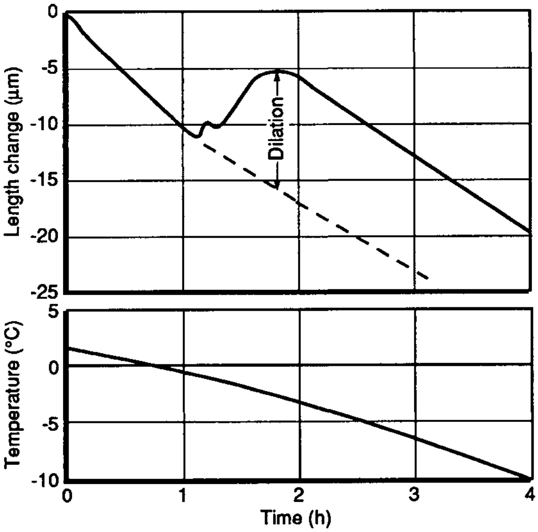


Figure 4.2 Typical length change variation of a concrete specimen during the cooling period of a freezing and thawing cycle (after ASTM standard C 671).

In the ASTM C 671 test procedure, the frost immunity period that is determined corresponds to the length of time during which critical dilation does not occur (it is generally expressed as the number of weeks since the start of soaking in the 2 °C water bath to the time of occurrence of critical dilation). This frost immunity period represents the length of time of water immersion required to produce significant frost damage in concrete specimens exposed to slow freezing and thawing cycles. Thus a concrete will be expected to be frost resistant if, under field conditions, the longest period of water immersion does not exceed the frost immunity period.

As previously mentioned, frost resistance is not an intrinsic property of concrete and the concept of the frost immunity period has the great merit of expressing the frost durability of concrete as a function of natural exposure conditions (the critical degree of saturation is the only other test which attempts to correlate the frost durability to field conditions). Furthermore, the rate of cooling chosen for the test (2.8 °C/h) is of the same order of magnitude as the maximum natural cooling rates (Chapter 7). By providing basic information about ice formation in hardened cement paste, this test procedure also contributes to a better understanding of the fundamental mechanisms responsible for frost damage.

The critical dilation test also has a number of limitations. The relatively small number of freezing cycles which can be produced in a reasonable time is perhaps one of the most important (it would take almost 6 years, for instance, to produce the 300 freezing and thawing cycles required by the ASTM C 666 test procedure). The test can separate concretes with a very good frost resistance from those with a very poor durability, but it cannot assess correctly the performance of marginal concretes for which the deterioration may proceed more slowly and become significant only after a large number of cycles. Another limitation is related to the fact that, since the freezing period is relatively small (about 4 h), the effect of long freezing periods is neglected; however, in practice this condition is quite common and can contribute to increased frost damage by promoting ice accretion (due to osmotic pressures or free energy differences).

4.1.2 Resistance to Rapid Freezing and Thawing

One of the best ways of assessing the frost resistance of concrete is to subject concrete samples to repeated cycles of freezing and thawing. The ASTM C 666 Standard describes a test method in which concrete specimens (typically 75×100×400 mm prisms) are subjected to 300 cycles of rapid freezing and thawing in water (procedure A) or freezing in air and thawing in water (procedure B). Figure 4.3 shows a schematic illustration of the apparatus most commonly used to produce freezing and thawing cycles in water (according to procedure A). In this machine, the concrete specimens are placed in metal boxes and surrounded by approximately 3 mm of water. Freezing is produced by a cooling plate located under the metal boxes while thawing is produced by electrical elements placed between the boxes. This apparatus has the advantage of avoiding, contrary to procedure B, the displacement of water during the cycles. It also ensures a high degree of saturation and reduces to a minimum the amount of water to be cooled or heated.

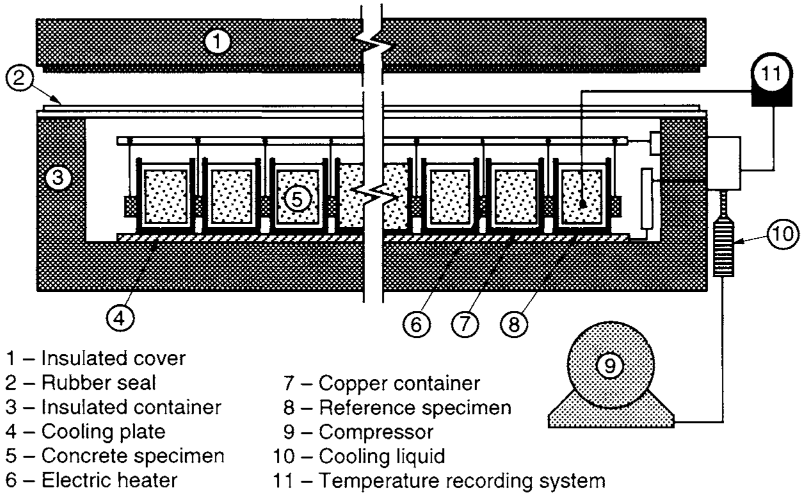


Figure 4.3 Typical equipment for the freezing and thawing cycle test in water.

The freezing and thawing cycle for both procedures must be adjusted in such a way that the temperature decreases from 5 to −18 °C and increases back to 5 °C in not less than 2 h and not more than 5 h. Since the thawing period must not be less than 25% (for procedure A) or 20% (for procedure B) of the total time required for a cycle, the corresponding cooling rates range from 6 to 15 °C/h. Figure 4.4 shows a typical freezing and thawing cycle (the heat released by the ice formation is responsible for the flattening of the curve a few degrees below 0 °C). At regular intervals (not exceeding 36 cycles), the concrete specimens must be removed from the apparatus and length change measurements (optional) and fundamental transverse frequency measurements (to determine the dynamic modulus of elasticity of the specimens) should be carried out. The apparatus used for measuring the fundamental transverse frequency is illustrated in Figure 4.5. The freezing and thawing cycles are repeated up to the completion of 300 freezing and thawing cycles or until the durability factor drops below 60% (whichever occurs first). The durability factor is defined as

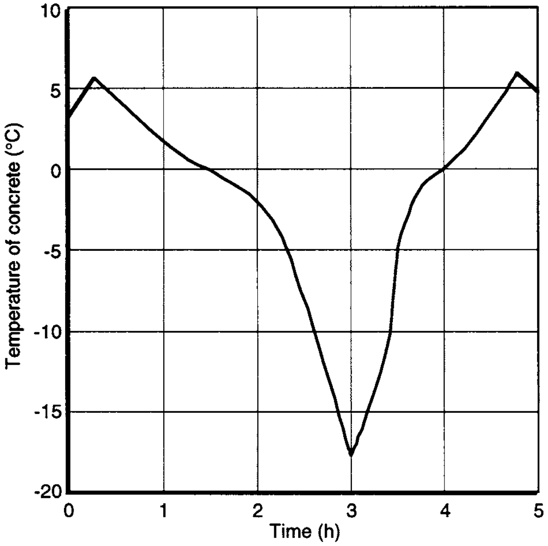


Figure 4.4 Typical freezing and thawing cycle in the ASTM C 666 rapid freezing and thawing in water test.

$$\text{Durability factor} = \frac{PN}{300} \tag{4.1}$$

where P is the relative dynamic modulus of elasticity at N cycles (as a percentage of the initial value, at 0 cycles) and N is the number of cycles at which P falls below 60% (N is taken to be 300 when P remains higher than 60% after the completion of 300 cycles of freezing and thawing).

The relative dynamic modulus of elasticity after c cycles, P_c, as a percentage of the initial value (at 0 cycles), can be computed as

$$P_c = \frac{n_c^2}{n_0^2} \times 100 \tag{4.2}$$

where n_c is the fundamental transverse frequency after c cycles of freezing and thawing and n_0 is the fundamental transverse frequency at 0 cycles of freezing and thawing.

Although it is not mentioned in the ASTM C 666 Standard, the relative dynamic modulus of elasticity can also be determined, though perhaps less precisely, using ultrasonic pulse velocity measurements instead of fundamental transverse frequency measurements (Figure 4.6). In this case, the value of P_c is given by

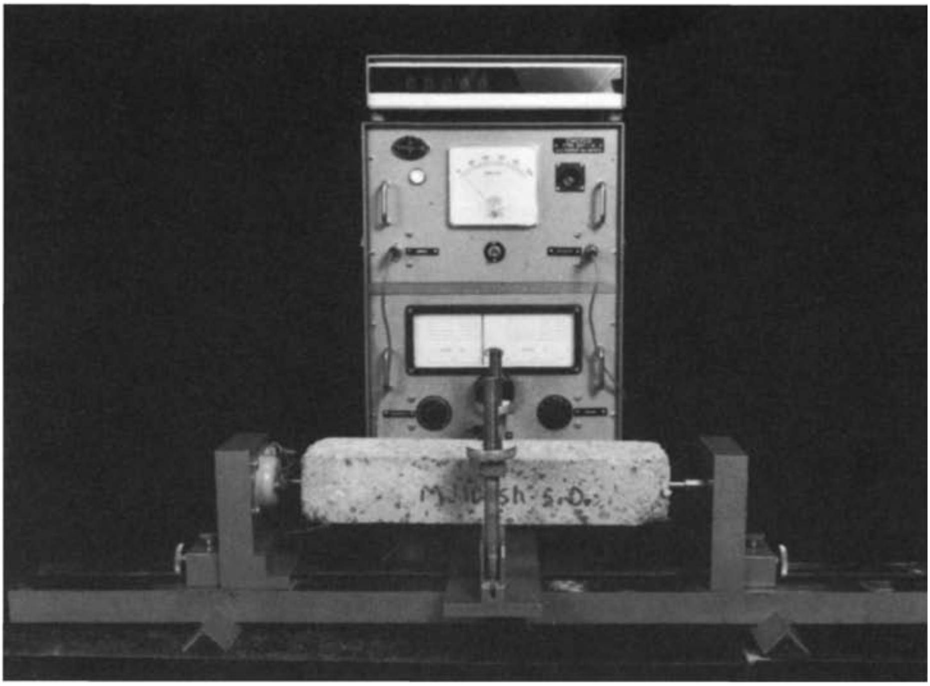


Figure 4.5 Equipment used for the measurement of the fundamental transverse frequency of a concrete specimen.

$$P_c = \frac{v_c^2}{v_0^2} \times 100 \tag{4.3}$$

where v_c is the ultrasonic pulse velocity after c cycles of freezing and thawing and v_0 is the ultrasonic pulse velocity at 0 cycles of freezing and thawing.

In this test method the reduction of the fundamental frequency (or of the pulse velocity) is used as an index of the extent of internal microcracking in concrete specimens. Experience has shown, however, that this measurement can be influenced by the scaling of the surfaces which can occur when the concrete specimens freeze in water (as is the case in procedure A). The transverse frequency is a function of the mass of the concrete specimen, i.e. heavier specimens have a higher frequency. Consequently, the loss of weight due to surface scaling leads to a lower frequency, and then, to a smaller durability factor. It has been demonstrated that concrete specimens suffering severe scaling can have durability factors as low as 60% without showing any significant microcracking, i.e. any significant change in length (Highway Research Board, 1959). In the case of ultrasonic pulse velocity measurements, a poor contact between the transducers and the concrete specimen (due to surface scaling occurring at both ends of this specimen) often results in a lower pulse velocity, and then in a lower durability factor even if no significant internal microcracking occurs. Figure 4.7 shows, for example, the relationship between the durability factor (as determined using pulse velocity) and the weight loss of specimens for concretes showing no significant internal cracking (i.e. with a length change smaller than 200 μm/m). In spite of the scatter of the results (due to the variable nature of surface scaling), this figure clearly indicates that the durability factor generally decreases with an increase in surface scaling. Durability factors smaller than 100% therefore do not necessarily indicate that concrete specimens are affected by internal microcracking.

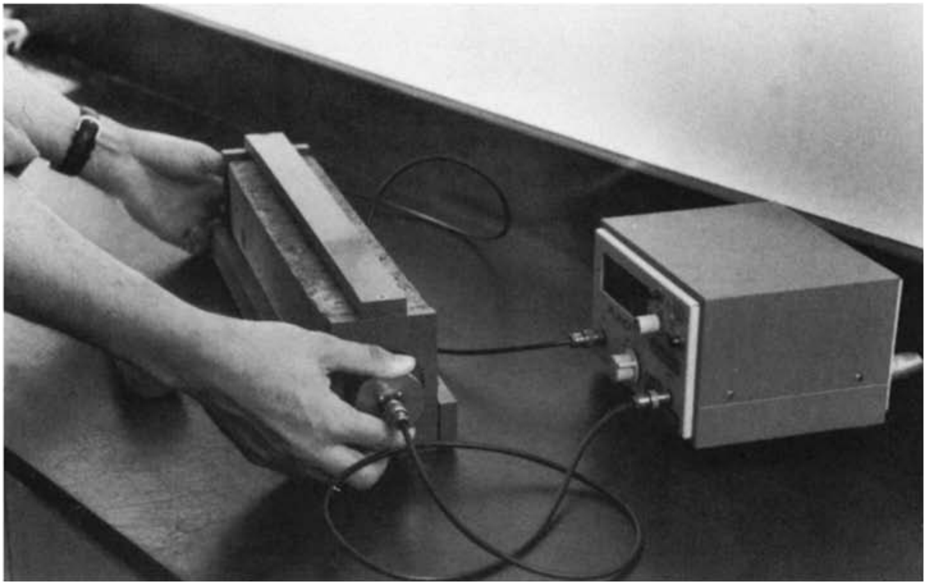


Figure 4.6 Apparatus used for ultrasonic pulse velocity measurements.

Although it is described as an optional procedure by the ASTM C 666 Standard, the length change of concrete specimens is generally considered as the most sensitive index of internal microcracking due to freezing and thawing cycles; Figure 4.8 shows two types of extensometers used to measure length change. Furthermore, this measurement is not affected by surface scaling. For most concretes, it is generally assumed that microcracking becomes

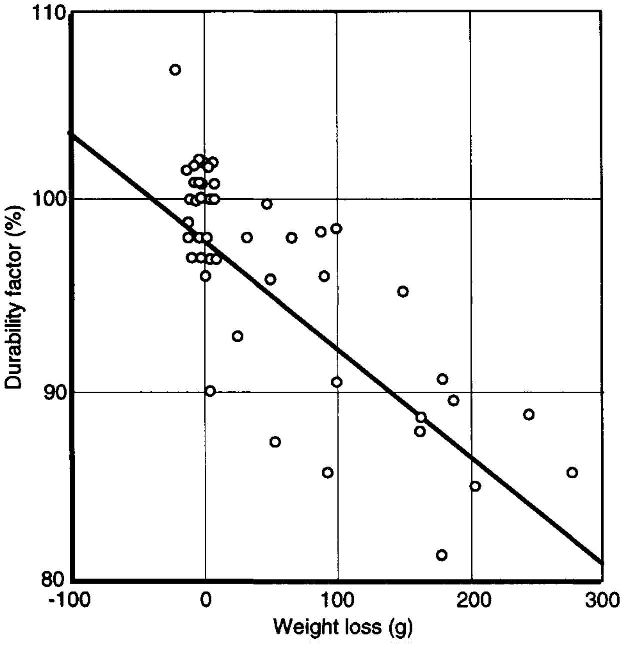


Figure 4.7 Relationship between the durability factor (determined from ultrasonic pulse velocity measurments) and the weight loss for a series of concrete specimens showing no significnt internal microcraking (i.e. with a length change smaller than 200 μm/m).

significant when the length change exceeds approximately 200 μm/m (the precision of this measurement is usually approximately equal to 10 μm/m). The length change is given by

$$\varepsilon_n = \frac{L_n - L_0}{L_0} \tag{4.4}$$

where ε_n is the length change after *n* cycles of freezing and thawing, L_n is the length between the two gauges on the concrete specimen after *n* cycles of freezing and thawing and L_0 is the initial length.

The ASTM C 666 test method offers the great advantage of subjecting concrete specimens to a large number of freezing and thawing cycles in a relatively short period (about 2 months). However, the major concern with this method is related to the possible variability of the laboratory testing conditions, as well as to how representative these conditions are as regards natural field exposure. For example, the cooling rate is one of the most important parameters governing frost durability, with higher cooling rates generally being detrimental to frost resistance (Chapter 3 and particularly Figure 3.10 showing the reduction of the critical spacing factor with the increase in the freezing rate). This cooling rate can vary from 6 to 15 °C/h in the ASTM C 666 test procedure while it rarely exceeds 2 °C/h in nature. This means that a concrete that shows significant deterioration during laboratory tests might be able to resist, without any damage, natural freezing and thawing cycles. It

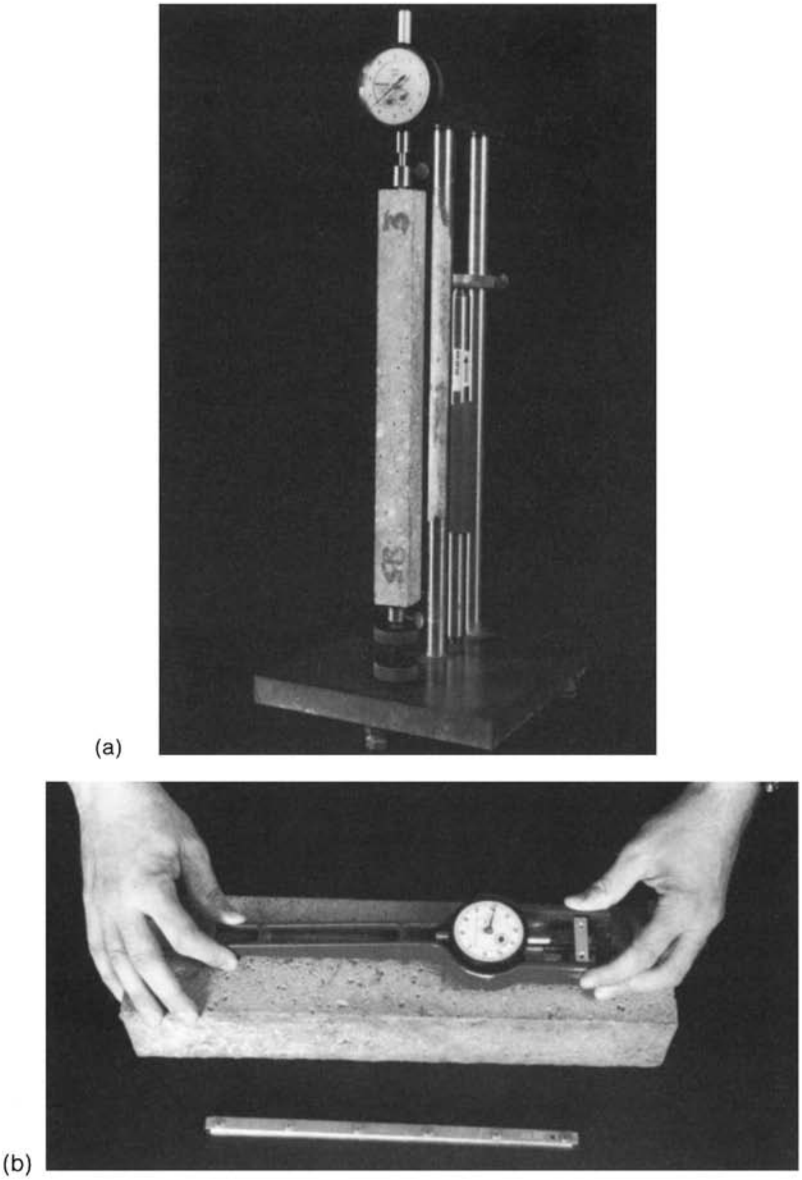


Figure 4.8 Two types of extensometers used for length change measurements. (a) Extensometer measuring the length at the centre line of the concrete specimen. (b) Extensometer measuring the length on both sides of the concrete specimen.

also means that a concrete can be considered frost resistant in one laboratory, while in another laboratory using the same testing procedure but a higher cooling rate, it would be considered non-resistant to frost action.

In the ASTM C 666 test method, as in the critical dilation test, the specimens are not subjected to long freezing periods. This is another major difference between the laboratory tests and natural exposure conditions. In addition, the concrete specimens are fully saturated during the entire cycling period and are not allowed to dry before the beginning of the tests, contrary to natural exposure conditions where concrete is generally exposed to frequent wetting and drying cycles. As mentioned in Chapter 3 the 'moisture history' of concrete as well as the degree of saturation are two important parameters which can significantly influence the frost resistance of concrete. This will be discussed in more detail in Chapter 7 which deals with exposure conditions and field performance.

4.1.3 Surface Scaling Resistance

ASTM C 672 Test Method

In Chapter 2, a clear distinction was established between internal microcracking and surface scaling, which are two very different forms of deterioration due to freezing and thawing. The ASTM C 672 Standard describes a test method designed to assess the scaling resistance of horizontal concrete surfaces exposed to frost in the presence of de-icing chemicals. In this test method, a minimum of two rectangular concrete specimens with a surface area of at least 72 in^2 (460 cm^2) and a minimum thickness of 3 in (7.5 cm) must be tested. Unless otherwise specified, the exposed surface of these specimens has to be finished with a flat wooden trowel. After a period of moist curing of 14 days at 73±3 °F (23±1.7 °C) and 100% relative humidity, the specimens are stored at the same temperature and a relative humidity of 45 to 55% for an additional period of 14 days. If the test is carried out to assess the influence of a protective coating on the scaling resistance of concrete, this coating must be applied at the age of 21 days in accordance with the manufacturer's recommendations concerning the amount to be applied and the method of application. If the influence of a curing compound has to be evaluated, this product must be applied at the proper time according to the ASTM C 156 Standard *Test Method for Water Retention by Concrete Curing Materials*. At 28 days, the flat top surfaces of the concrete specimens are covered with approximately 6 mm of a salt solution which is retained by an air-entrained mortar dike, a rubber membrane, or any other suitable material as illustrated in Figure 4.9. The salt solution is generally a 4% calcium chloride solution (i.e. each 100 mL of water contains 4 g of $CaCl_2$) although other chemical de-icers (such as sodium chloride or urea) and other concentrations may be used. The specimens are then subjected to a minimum series of 50 daily freezing and thawing cycles by alternately placing them in a freezing environment at 0±3 °F (−17.8±1.7 °C) for 16–18 h, and in the laboratory (at 73±3 °F (23±1.7 °C) and 45–55% relative humidity) for 6–8 h. At the end of each series of 5 cycles, the salt solution must be flushed off thoroughly and renewed. The extent of surface scaling is assessed by a visual rating after 5, 10, 15, 25 and 50 cycles. This rating (Table 4.1) ranges from 0 (for concrete surfaces showing no scaling) to 5 (for concrete surfaces suffering severe scaling with coarse aggregates visible over the entire test surface). Figure 4.10 shows typical concrete surfaces with different visual ratings after 50 cycles.

The ASTM C 672 test method is particularly meaningful, considering that surface scaling now represents the most common form of deterioration due to frost action. Furthermore, the conditioning of the concrete specimens (they are allowed to dry before testing) and the

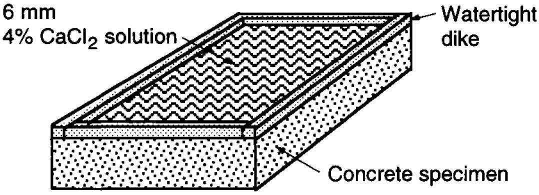


Figure 4.9 Typical concrete specimen for the ASTM C 672 de-icer salt scaling test.

Table 4.1 Visual rating of scaled surfaces according to ASTM Standard C 672.

Rating	Condition of surface
0	No scaling
1	Very light scaling (maximum depth of 3 mm, no coarse aggregate visible)
2	Slight to moderate scaling
3	Moderate scaling (some coarse aggregate visible)
4	Moderate to severe scaling
5	Severe scaling (coarse aggregate visible over entire surface)

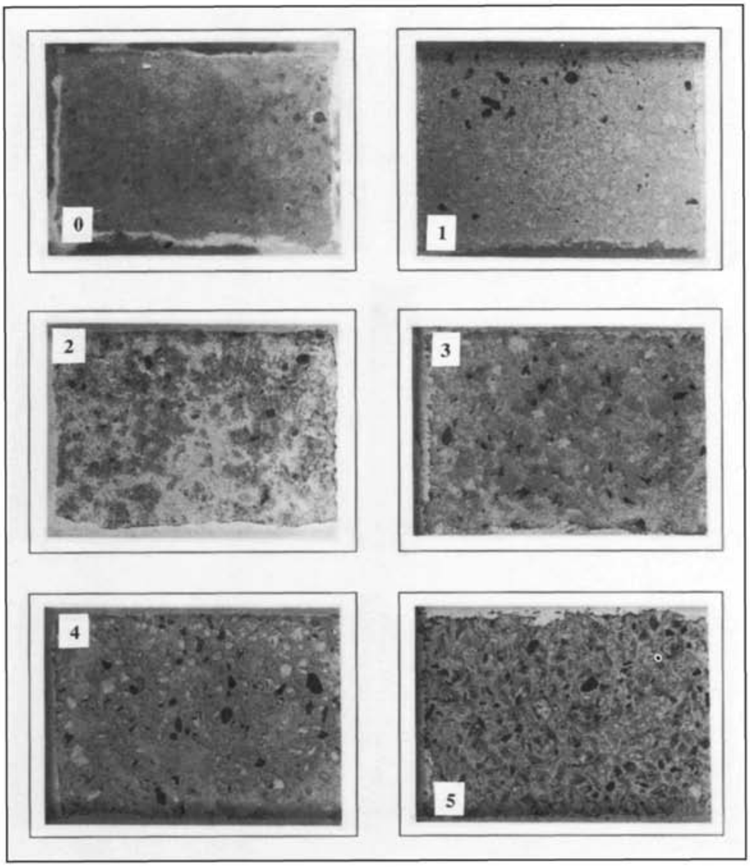


Figure 4.10 Concrete surfaces with different visual ratings after 50 freezing and thawing cycles in the presence of a de-icer salt solution.

characteristics of the freezing and thawing cycles (daily cycles with a relatively long freezing period) are more similar to natural exposure conditions. However the visual rating is influenced by the operator's subjectivity; the bar charts of Figure 4.11 indicate that even if, most of the time, two operators give the same rating (it happened for 48% of the total of 2580

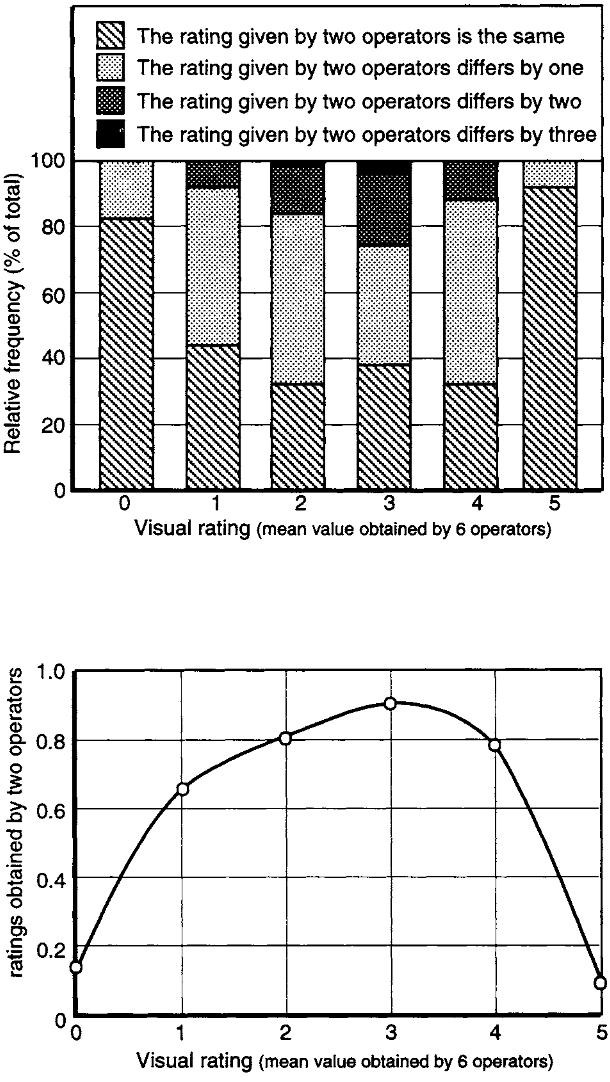


Figure 4.11 Influence of the operator's subjectivity on the ASTM C 672 visual rating of scaled concrete surfaces. The results are based on the 2580 paired values obtained by six operators examining 172 concrete surfaces to 50 freezing and thawing cycles in the presence of de-icer salts.

paired values studied), the difference of rating is often equal to 1 (41%), 2 (10%) and even 3 (1%). Based on the data reported in the bar charts, Figure 4.11 also gives a curve showing the mean difference of the visual rating obtained by two operators as a function of the mean rating (as determined by computing the average for six operators). This curve indicates that this difference is minimum for concretes showing very little (0 rating) or very severe (5 rating) deterioration and maximum for intermediate ratings (2–4). The same study of 172 concrete slabs examined by six operators has also indicated that the mean difference between the ratings selected by a single operator and the average value obtained for the six operators ranged from 0.03 to 0.94 which represents a significant difference (Beaupré, 1987).

In the last few years, many investigators have used the mass of scaled-off particles as a more rigorous index of surface scaling, although this practice has not been officially adopted by the C 672 Standard. Concrete is generally considered to have an adequate scaling resistance if the mass of scaled-off particles does not exceed 1 kg/m^2 after 50 cycles of freezing and thawing. Figure 4.12 shows the relationship between the mass of scaled-off particles and the visual rating for a series of tests carried out recently (in this figure, each point represents the mean value obtained on two concrete specimens, the visual rating being the mean value obtained by six operators). A statistical study of more than 150 concrete mixtures has shown that the precision of the measurement of the mass of scaled-off particles (assuming a 95% confidence level and not considering inter-laboratory variations) is approximately 25% (when the mass of scaled-off particles is lower than 1.5 kg/m^2) and 4% (when the mass of the scaled-off particles exceeds 1.5 kg/m^2) (Marchand *et al.,* 1995).

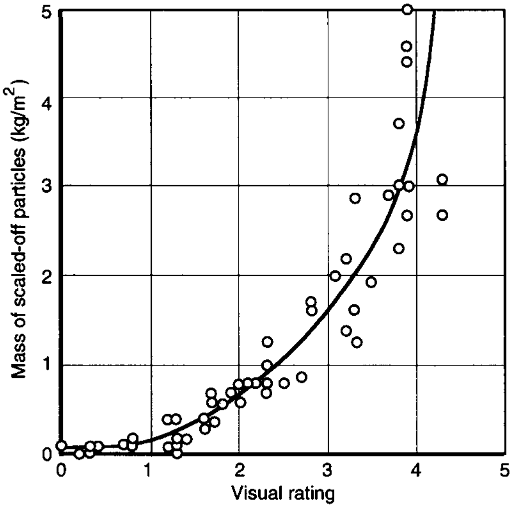


Figure 4.12 Relationship between the mass of scaled-off particles and the ASTM C 672 visual rating after 50 freezing and thawing cycles for 172 concrete mixtures.

Most of the time, the mass of the scaled-off particles or residues increases quite linearly with the number of freezing and thawing cycles (Figure 4.12). It is not uncommon, however, to observe a relatively large mass of residues (of the order of 0.5 kg/m^2 to sometimes more than 1 kg/m^2) during the first few cycles, the scaling process slowing down considerably afterwards (Figure 4.13). This large loss of mass observed during the first few cycles, which is obviously due to the presence of a weak surface layer, can be due to various phenomena, such as intensive drying, or perhaps excessive bleeding, bad finishing, or other surface problems. It should be noticed in this respect that a loss of 1 kg/m^2 represents the destruction of a layer of only 0.4 mm approximately over the surface of the specimen tested.

Böras Method

The Böras method defined in the Swedish Standard SS 13 72 44 is, in a way, an improved version of the ASTM C 672 surface scaling test. In this method, concrete specimens are still subjected to daily cycles of freezing and thawing, but the procedure was modified to be more representative of field exposure conditions, and also to allow a better control of the variables that can affect the results.

Depending on the type of information needed, the Böras method allows the use of concrete specimens made in the laboratory (150 mm cubes), or taken from structures (drilled cores with a diameter greater than 95 mm). The test surface can be either the top surface, or, normally, a sawn surface located 50 mm (for laboratory cubes), or 20 mm (for drilled cores) from the top surface. It can be in contact with a 3% NaCl solution (method A), or with tap water (method B). Generally, testing the top surface in contact with a salt solution is more interesting, because this condition is more closely related to the most severe field exposure conditions.

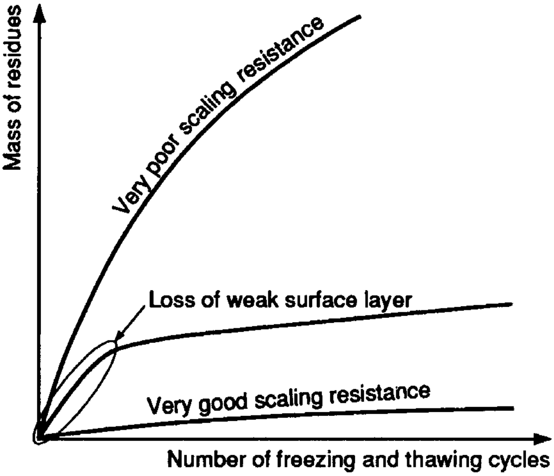


Figure 4.13 Typical de-icer salt scaling test results.

Prior to freezing and thawing, the concrete specimens are subjected to a well-controlled conditioning procedure. The cubes made in the laboratory are demolded after 24 h, placed in a tap water bath at 20±2 °C for 5–7 days, and then stored at 20±2 °C and 50+10% relative humidity. At 21±2 days, 50±5 mm thick slabs are sawn off the cubes parallel to the cast surface. After sawing, the specimens are stored at 20±2 °C and 50+10% relative humidity for another 7-day period. After being thermally insulated as illustrated in Figure 4.14, they are covered with about 3 mm of tap water for 3±1 days. In the case of laboratory concretes, a minimum of four 150×150 mm specimens should be tested (which represents a test surface of 900 cm^2). When the test is performed on drilled cores, the total surface tested should be at least equal to 400 cm^2 (this corresponds to six cores of 100 mm in diameter).

When method A is used (i.e. with a salt solution), the tap water on the test surface is replaced by an approximately 3 mm thick layer of a 3% NaCl solution not more than 15 min before the beginning of freezing. The concrete specimens are covered with a tight plastic film to prevent evaporation, and are subjected to 56 daily freezing and thawing cycles. During each cycle, the temperature in the salt solution must meet the requirements described in Figure 4.15, which means that the temperature ranges from about 20 °C to −20 °C, and must be higher than 0 °C for at least 7 h (but not more than 9 h). After 7, 14, 28, 42, and 56 cycles, the scaled-off particles are collected, dried and weighed. The result after n cycles m_n is calculated by dividing the mass of scaled-off particles (in kilograms) by the total area of exposed surface (in square metres). The de-icer salt scaling resistance can then be evaluated as shown in Table 4.2: the scaling resistance is considered adequate if, after 56 cycles, the mass of scaled-off particles (m_{56}) is less than 1.0 kg/m^2 and the m_{56}/m_{28} ratio is smaller than 2.0 (which means that the deterioration process did not accelerate during the second half of the test).

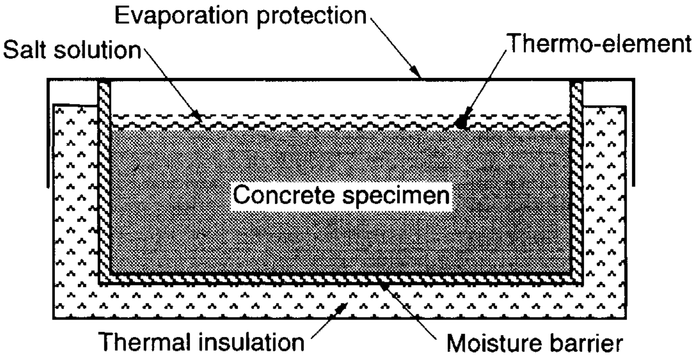


Figure 4.14 Concrete specimen prepared for the Böras test method.

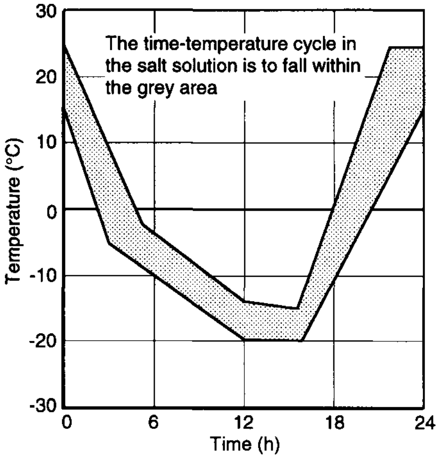


Figure 4.15 Freezing and thawing cycles as defined in the Böras test method.

Table 4.2 Assessment of the de-icer salt scaling resistance of concrete according to SS 13 72 44 (Böras method).

Frost resistance	Requirements
Very good	No specimen has more than 0.1 kg/m^2 material scaled after 56 cycles
Good	The mean value for the material scaled after 56 cycles (m_{56}) is less than 0.5 kg/m^2 at the same time as m_{56}/m_{28} is less than 2.0
Acceptable	The mean value for the material scaled after 56 cycles (m_{56}) is less than 1.0 kg/m^2 at the same time as m_{56}/m_{28} is less than 2.0
Unacceptable	If the requirements for acceptable frost resistance are not met

Note: m_{28} represents the mass of the scaled-off particles after 28 cycles of freezing and thawing.

The Böras method is quite similar to the ASTM C 672 test method, but it has many advantages. First, the freezing front progresses vertically from the top to the bottom of the specimen, which is more representative of what really occurs under field conditions. The method also provides a better assessment of the surface deterioration because this assessment is based on a quantitative measurement (the mass of scaled-off particles) rather than on the qualitative criteria described in the ASTM C 672 method (the visual rating) which are dependent on the subjectivity of the operator. Another non-negligible advantage is that sealing the concrete specimens prevents evaporation from the saline solution. This constant availability of a 3% NaCl solution on the test surface certainly reduces the variability associated with the test method. Although this has not yet been demonstrated, the variability associated with the Böras method is expected to be smaller than that associated with the ASTM C 672 method, simply because the test conditions are better controlled in the Böras method, while the surface areas tested are approximately equal.

Other

A different type of de-icer salt scaling test is now also used in certain countries in Europe. This test has not yet been standardized, and is not very widely used. The main difference between this test and the methods described above is that the concrete specimen is placed in a closed container which contains a small amount of a de-icer salt solution in the bottom. The surface that is subjected to cycles of freezing and thawing in the presence of a salt solution is thus the bottom surface of the specimen (Setzer and Schrage, 1991).

4.1.4 Other Test Methods

Paving Block Testing

In the last few years, paving blocks have been used increasingly for the construction of concrete pavements, both for residential and commercial applications. Paving blocks are made by compacting dry concrete mixtures, and their internal pore structure is thus very different from that of standard concretes. In addition to the usual spherical air voids (which are very difficult to entrain in dry concretes because of the small quantity of water available, Chapter 8), paving blocks also contain a lot of irregularly shaped air voids resulting from compaction operations. These voids cover a range of sizes similar to the range of sizes of spherical air voids (approximately 10 µm to 1 mm, see Chapter 8 on the durability of dry concretes) and they can have either a beneficial or a detrimental effect on the frost durability of concrete, depending on whether they reach a high degree of saturation or whether they remain empty under field conditions. Due to the particular nature of these concretes, and considering the fact that paving blocks in a pavement are expected to freeze while being completely surrounded by water, the Canadian Standard CSA A231.2-M85 (1985) describes a test method specifically designed to assess the frost resistance of paving blocks (this test method could also be extended to other types of dry concretes such as roller-compacted concrete).

Table 4.3 Visual rating of scaled surfaces according to Canadian Standard CAN3-A231.2-M85 (paving block test).

Rating	Condition of surface
0	No scaling
1	Very light scaling (maximum depth 3 mm, no coarse aggregate visible)
2	Slight to moderate scaling
3	Moderate scaling (some coarse aggregate visible over 50% of the surface)
4	Moderate to severe scaling (some coarse aggregate visible over 75% of the surface)
5	Severe scaling (coarse aggregate visible over 100% of the surface)

Prior to testing, the specimens are oven dried for a minimum of 24 h at 110±5 °C, allowed to stand in the laboratory until the temperature returns to the ambient temperature (23±3 °C), and placed in sealed containers filled with a 3% (by weight) sodium chloride solution, for

24 h. The specimens are then exposed to 50 daily freezing and thawing cycles (16±1 h of freezing at −15±2 °C and 8±1 h of thawing at 23±3 °C). After 10, 25 and 50 cycles respectively, the specimens are carefully washed with a 3% NaCl solution and the scaled-off particles are recovered, filtered, dried and weighed. The extent of scaling is also visually assessed according to the rating given in Table 4.3. According to this Standard, the paving blocks are rejected if the mass of scaled-off particles exceeds 1.0% of the initial dry mass of the specimens. This percentage corresponds approximately to a loss of mass of 0.4–0.5 kg/m^2, depending on the geometry of the block.

This test procedure exposes the concrete specimens to very severe conditions, the oven drying being expected to be particularly harmful, especially for concretes with a high porosity. It is quite possible that the severity of these conditions tends to reduce the differences observed between different concretes. This would of course make it more difficult to classify different paving blocks as a function of their relative durabilities, particularly for those having marginal durabilities. The presumably higher severity of this test method, however, is not yet supported by strong experimental evidence and research is still needed to assess more precisely the validity of this test procedure.

Critical Degree of Saturation

The determination of the critical degree of saturation is another method that was developed to assess the frost durability of concrete. This method (recommended by the RILEM 4-CDC Committee (1977)) is based on the experimental evidence that concrete can safely resist freezing and thawing cycles if, and only if, its degree of saturation is lower than a threshold value called the critical degree of saturation S_{CR}. The critical degree of saturation is an intrinsic property of concrete (Chapter 3), and different values of S_{CR} are associated with different concrete mixtures. A given concrete is considered as frost resistant if its degree of saturation under field exposure conditions S_{ACT} never exceeds S_{CR} (Fagerlund, 1971).

Experimentally, the critical degree of saturation can be determined in two different ways. First, the modulus of elasticity of concrete specimens kept at different levels of relative humidity and subjected to six freezing and thawing cycles can be measured. The relationship between the modulus of elasticity and the degree of saturation shows a clear break point which corresponds to the critical degree of saturation. A typical example of such a relationship is given in Figure 4.16. Another method consists of measuring the residual length change of concrete specimens after one or two cycles of freezing and thawing. The relationship between the residual length change and the degree of saturation also indicates a critical S_{CR} value, as illustrated in Figure 4.17. Both methods give similar values of S_{CR}.

The frost immunity period can be determined by studying the kinetics of capillary water absorption. A thin concrete specimen is immersed in water and weighed at different time intervals in order to obtain the relationship between the degree of saturation reached by water absorption S_{CAP} and the time of immersion. Figure 4.18 shows a typical example of such a relationship. This figure indicates that, in the first few hours, S_{CAP} increases very rapidly until it reaches a break point but, afterwards, the water content increases very slowly.

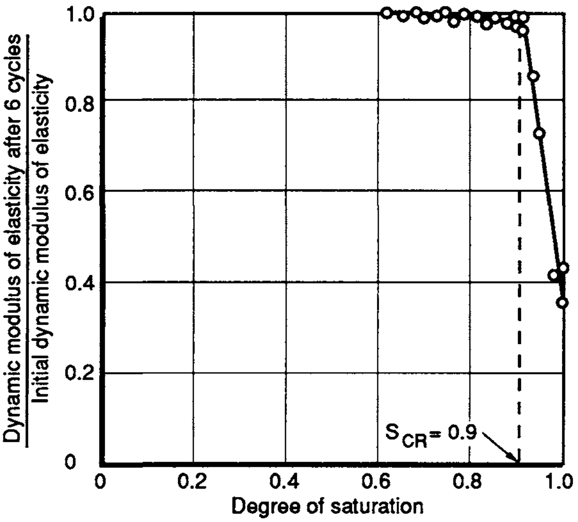


Figure 4.16 Relationship between the relative dynamic modulus of elasticity and the degree of saturation of concrete after six freezing and thawing cycles (after Fagerlund, 1977).

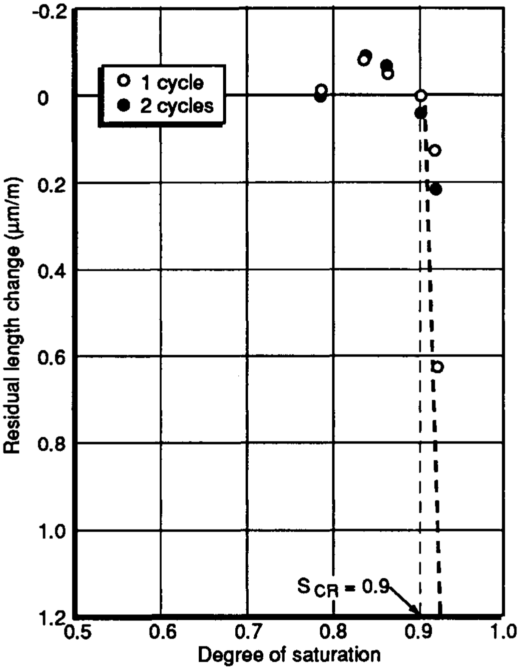


Figure 4.17 Relationship between the residual length change and the degree of saturation of concrete after one and two cycles of freezing and thawing (after Fagerlund, 1977).

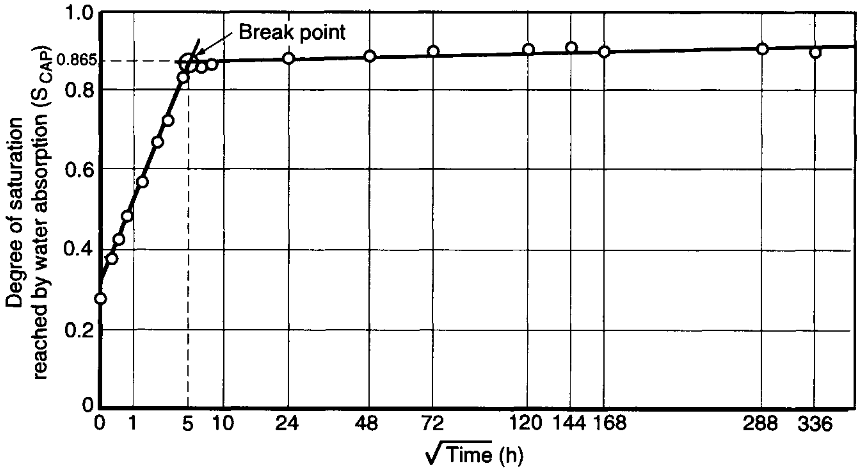


Figure 4.18 Relationship between the degree of saturation reached by water absorption (S_{CAP}) and the period of immersion (after RILEM 4-CDC Committee, 1977).

The degree of saturation corresponding to the break point (86.5% for the example given in Figure 4.18) roughly represents the highest humidity level that can be reached in concrete walls which are never kept in contact with water for very long periods of time (between rainfalls, the surface of the concrete is allowed to dry since the relative humidity of the surrounding air is lower than 100%). However, slabs and other building components can reach a higher degree of saturation if they are in contact with water for longer periods of time.

The frost durability of concrete is related to the difference between the critical degree of saturation S_{CR} and the degree of saturation under field exposure conditions S_{ACT}:

$$F=S_{CR}-S_{ACT} \tag{4.5}$$

Concrete will be frost resistant if it never becomes critically saturated, i.e. if $F>0$. The frost immunity period can thus be determined by studying the difference between S_{CR} and S_{CAP}, i.e.

$$F=S_{CR}-S_{CAP} \tag{4.6}$$

The value of F decreases with time (since S_{CR} is a constant and S_{CAP} increases with time), and the frost immunity period corresponds to the period of water absorption required for the value of F to reach zero, as shown, for example, in Figure 4.19. Concrete will thus be considered frost resistant if, under field exposure conditions, it is not in contact with water for a period of time longer than this frost immunity period.

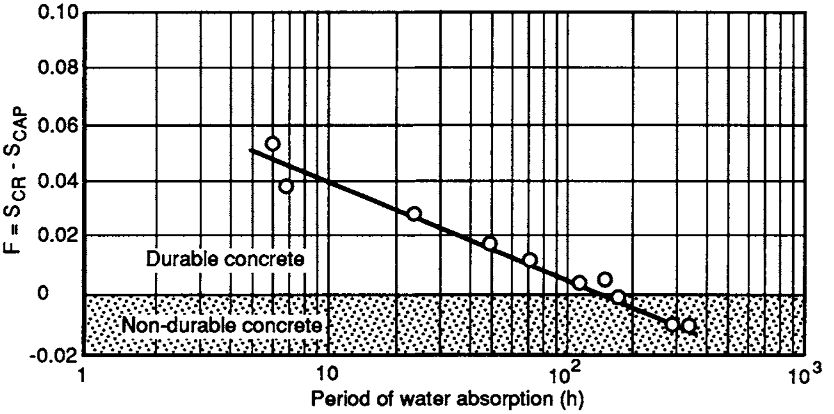


Figure 4.19 Relationship between the parameter *F* and the period of water absorption in the critical degree of saturation test (after RILEM 4-SDC Committee, 1977).

The most interesting aspect of the critical degree of saturation method is that the assessment of the frost durability of concrete is based on field exposure conditions. The concept of the frost immunity period emphasizes the fact that frost resistance is not only a function of the properties of concrete, but also a function of the field exposure conditions. However, the method requires a large number of long and tedious experiments which must be carried out with great care (the degree of saturation of the concrete specimens is especially important, and is not always easy to control during the testing procedure). This represents a serious drawback, and makes it difficult to use the technique as a routine test procedure.

It is important to point out that, in this test method, concrete is considered fully saturated (i.e. S=100%) when all voids (including both the capillary pores and the air voids) are full of water. Since the air voids cannot be filled by capillary suction, the role of air entrainment is thus simply to reduce below the critical S_{CR} value the maximum degree of saturation that concrete can reach (S_{ACT} or S_{CAP}). In properly air-entrained concretes, the degree of saturation obtained by capillary absorption should be lower than S_{CR}, which simply means that such concretes will almost never become critically saturated, and thus that their frost immunity period tends to infinity. The fact that the air voids cannot be easily filled by capillary suction also means that the very high degrees of saturation (near 100%) required to determine the critical degree of saturation (Figures 4.16 and 4.17) can only be obtained with vacuum saturation procedures.

The concept of the critical degree of saturation was initially developed to study the frost durability of porous materials such as stones or clay bricks for which the use of air entrainment is not possible. For such materials, the concept of the frost immunity period is particularly useful, since the real question is to determine if they can safely sustain the moisture levels reached under field exposure conditions. For concrete, however, the real question is to determine the volume of entrained air (or, preferably, the spacing factor of the air voids) required for good frost durability. From a practical point of view, it is simple and safe to assume that only the capillary pores will be full of water at the time of freezing. Consequently, it is less important to determine the maximum degree of saturation that concrete will reach under natural exposure conditions, and other laboratory procedures such as described in this chapter will generally yield satisfactory results.

4.1.5 Significance of Laboratory Tests as Regards to the Field Performance of Concrete

One of the main objects of laboratory tests is, of course, to predict the frost behaviour of concrete under field conditions. Natural exposure conditions, however, are so varied and complex that they are difficult to reproduce in the laboratory. Time is also a matter of great importance. In nature, frost damage usually occurs over a period of years while, in the laboratory, the tests must be accelerated to give results in a matter of weeks. However, it is difficult only to 'accelerate' natural phenomena and to reproduce in only a few weeks what will really happen in the field. Most of the time, the laboratory tests also increase the severity of the exposure conditions and amplify frost damage. This approach has the advantage of ensuring that only highly frost-resistant concretes will satisfactorily resist the laboratory freezing and thawing cycles. These concretes should therefore be completely frost resistant under field conditions. Moreover, concretes which would be non-durable under natural exposure conditions will suffer severe damage under laboratory test conditions. Although laboratory tests can separate the highly frost-resistant concretes from those with a very poor frost durability, they can fail to assess correctly the frost durability of concretes with intermediate durabilities, those for which durability is highly dependent on the exposure conditions (such as the degree of saturation, the cooling rate, the nature of the freezing and thawing cycle or the moisture history of concrete). Since laboratory conditions are usually more severe than those occurring in nature, many concretes considered as non-durable according to laboratory tests would be frost resistant under field conditions. This emphasizes the importance of choosing the test which is best suited to study a particular aspect of frost action. This also indicates that great care should be taken in the interpretation of the results obtained from laboratory tests, since interpretation would be sensitive to the extent to which these tests really reproduce actual field conditions. Unfortunately, as just mentioned, these conditions are so diverse and so unpredictable, they can never be exactly reproduced in the laboratory. Due to their higher severity, however, laboratory tests can provide safe design criteria for concrete mixtures which have to be frost resistant. The question of the significance of laboratory tests is discussed in more detail in Chapter 7.

4.2 TESTS ON AGGREGATES

As explained in Chapter 5, aggregates can themselves be frost susceptible and break under repeated cycles of freezing and thawing. However, sound aggregates (i.e. aggregates not damaged by freezing and thawing cycles) can also be deleterious if they expel a significant amount of water during freezing, which will induce disruptive hydraulic pressures in the surrounding cement paste. The role of aggregates can be particularly important in relation to surface scaling, and the phenomenon of pop-outs is one type of common frost damage due to poor quality aggregates (Chapter 3). The interface between aggregate and cement paste is generally more porous than the bulk of the paste and this can also account for the influence of aggregate on the frost resistance of concrete.

4.2.1 Petrographic Examination

Basically, the petrographic examination of aggregates (ASTM C 295) aims at visually identifying the types of rock or the mineral constituents of an aggregate and determining their relative amounts. This objective is mainly achieved by the examination of a polished section of the aggregate (or of a piece of concrete containing this aggregate) under a stereoscopic microscope at a magnification ranging from 6× to 150×. The examination of thin sections under a polarizing microscope is also commonly used and, in some instances, complementary information can be obtained by other procedures such as X-ray diffraction analysis, differential thermal analysis, infrared spec troscopy or scanning electron microscopy.

Petrographic examination provides valuable information about the chemical composition of the main constituents of the aggregate as well as about their physical properties such as particle shape and size, surface texture or pore structure. This examination can also indicate the presence of coatings, of clay or of other contaminating substances, and can be used to determine the portion of the coarse aggregate which is composed of weathered or altered particles as well as the extent of that weathering or alteration (severe, moderate or slight). The correct interpretation of this test is not easy and requires a great deal of experience from the petrographer. Some minerals, such as chert or shaly materials, are well known for their generally poor frost resistance. However, the frost behaviour of an aggregate is related to so many parameters (some of these parameters, such as the exposure conditions which are of paramount importance but on which very little data is generally available, not being related to the intrinsic properties of the aggregate) that it is often difficult to pass a reliable and definitive judgment on its frost resistance. When available, the service record of an aggregate still remains one of the most reliable ways to predict the field performance.

4.2.2 Sulphate Soundness Test

In this test (ASTM C 88) a representative sample of an aggregate is subjected to repetitive cycles of immersion in a saturated solution of sodium sulphate (Na_2SO_4) or magnesium sulphate ($MgSO_4$) and oven drying at 110 °C. During the re-immersion, the rehydration of Na_2SO_4 (or $MgSO_4$) produces salt crystals in the pores of the aggregate particles. The growth of these crystals results in internal expansive forces which are considered similar to the disruptive pressures due to frost. The sulphate soundness test can be performed on both fine and coarse aggregates. Prior to the immersiondrying cycles, the aggregate sample is divided into individual fractions corresponding to each of the different sieve sizes. After the completion of the final cycle, each fraction of the sample is dried at 110 °C and sieved over the same sieve (for the fine aggregate) or over the sieve below, i.e. the sieve with openings 5/6 of those of the initial one (for the coarse aggregate). The material retained on the sieve is then weighed and the weight loss, i.e. the difference between this weight and the initial weight of the fraction of the sample tested, is computed and expressed as a percentage of the initial weight. Of course this weight loss provides only an indication of the potential frost resistance of the aggregate. According to the ASTM C 33 Standard *(Standard Specifications for Concrete Aggregates)* the aggregate is considered as unsound if, after 5 cycles, the weight loss for any fraction is higher than 10% (for fine aggregate) or 12% (for coarse aggregate) when sodium sulphate (Na_2SO_4) is used. Since the test is usually much more severe when magnesium sulphate ($MgSO_4$) is used instead of Na_2SO_4, the acceptance limits are significantly higher and correspond to a weight loss of 15% (for fine aggregate) and 18% (for coarse aggregate) after five cycles. The visual examination of particles larger than 19 mm can also provide valuable qualitative information about the nature of the deterioration (disintegration, splitting, crumbling, cracking, flaking etc.).

The main advantage of the sulphate soundness test is that it is simple and, contrary to the ASTM C 666 freezing and thawing test (which can also be used to study the durability of concrete made with a given aggregate), the results can be obtained in a relatively short period (only a few days compared to a few months for the ASTM C 666 test).

Unfortunately this test, even if it is widely used and relatively simple, has some major drawbacks. The first one is related to the fact that the deterioration of aggregates by frost is most probably due to hydraulic pressures and not to pressures due to crystal growth (Chapter 5). The fact that no account is taken of the severity of the exposure conditions is, of course, another important limitation of this test method. The frost resistance of aggregate, as well as that of concrete as a whole, is not an intrinsic property of the material, but it is strongly dependent on the exposure conditions (such as moisture content, minimum temperature, cooling rate or length of the freezing period).

The sulphate soundness can be considered as an indication of the overall quality of the aggregate. The weight loss of good quality aggregate is usually very low and that of highly porous and poor quality aggregate is very high. It is possible, however, that aggregates considered as unsound according to the requirements of ASTM C 88 could be frost resistant when used in concrete under natural exposure conditions, and that aggregates considered sound turn out to be deleterious.

4.2.3 Critical Dilation Procedures

As explained in Chapter 5, coarse aggregates can have a detrimental effect on the frost resistance of concrete even if they are intrinsically frost resistant (i.e. if a bulk sample of these aggregates would not be damaged when exposed to freezing and thawing cycles). Concrete can be damaged if the cement paste cannot accommodate the volume of water that is expelled from the aggregate during freezing, or if excessive internal stresses are generated inside the aggregates due to the low permeability of the surrounding cement paste which restricts water expulsion from the aggregates (this does not occur when the aggregates are not confined during freezing). According to the ASTM C 682 Standard, the frost resistance of coarse aggregates can be evaluated by measuring the critical dilation of air-entrained concrete specimens made with these aggregates. The concrete mixture has to be prepared in accordance with the ACI Recommended Practice 211.1 (*ACI Manual of Concrete Practice—Part 1,* 1991), with 307±3 kg/m^3 of type I Portland cement and a total air content of 6±1%. Whenever possible, the aggregates should be kept at a moisture level similar to that corresponding to the field conditions before preparing the concrete specimens (this is difficult to achieve and, when in doubt, aggregates should be used in a saturated state which represents the most harmful condition). The concrete specimens are stored in saturated lime water for 14 days and, whenever possible, should be brought to a moisture level similar to that expected to occur under field conditions at the time of initial freezing (if it is not possible, the Standard again describes a conditioning procedure to achieve a high moisture content). After the conditioning period, the concrete specimens are subjected to a critical dilation test in accordance with the requirements of the ASTM C 671 Standard. A frost immunity period is then determined, this period being defined as the longest period of water immersion for which critical dilation does not occur (section 4.1.1). The aggregates are considered frost resistant if this frost immunity period is longer than the maximum period for which the concrete is expected to be water saturated under field conditions.

Field experience has indicated that this test method is valid to classify aggregates with various frost susceptibilities (Larson *et al.,* 1965; Larson and Cady, 1969). Nevertheless the significance of the test results is highly dependent on the degree to which the conditions reproduced in the laboratory are representative of the conditions occurring in nature. For aggregates of intermediate quality, minor changes in the exposure conditions in the laboratory can have a significant influence on the test results. The reproduci-bility of the test conditions can also be affected by the difficulty of achieving and maintaining a given moisture level (experimentally, it is much easier to provide a fully saturated moisture condition).

The aggregates are often made up of many different fractions, some of them being more susceptible to frost action than others; care must then be taken to ensure that the sample used for the test is representative of the aggregate under study. The characteristics of an aggregate may vary significantly with the location from which it is extracted from the quarry and its frost durability can change accordingly. The frost susceptibility of an aggregate can also be related to the presence of a small amount of a highly unsound component. In this case ‘beneficiation’, i.e. the action of removing unsound particles from a given source of aggregate, could be an acceptable solution but it requires a very careful investigation.

4.2.4 Other Tests

Although it is not directly recommended in an ASTM Standard as such, one of the best ways of determining the durability of concrete made with a given aggregate is simply to prepare a good quality air-entrained concrete with this aggregate (in a saturated state) and to subject specimens of this concrete to the usual ASTM C 666 rapid freezing and thawing test.

Mercury intrusion porosimetry is not a standardized test but can be used to determine the pore structure of an aggregate. Data exist in the technical literature which allow the evaluation of the potential frost durability of concrete made with a given aggregate on the basis of the characteristics of the pore structure of the aggregate as measured with mercury intrusion porosimetry (Kaneuji *et al.,* 1980) or with other methods (Shakoor and Scholer, 1985).

Direct freezing and thawing tests on samples of an aggreagte cannot evaluate the performance of this aggregate in concrete, but can be useful in determining whether the aggregate is itself frost susceptible.

4.3 TESTS ON ADMIXTURES

4.3.1 Air-Entraining Admixtures

In order to be used as an air-entraining agent in concrete, an admixture must comply with the requirements of ASTM Standard C 260 *(Specification for Air-Entraining Admixtures for*

Concrete) and ASTM C 233 *(Method of Testing Air-Entraining Admixtures for Concrete)*. These standards describe a series of laboratory tests to verify that the admixture does not have any detrimental effect on the fundamental properties of concrete such as time of setting, slump, bleeding, compressive and flexural strength, length change on drying and, of course, to verify air content and resistance to freezing and thawing. Two series of concrete mixtures must be prepared: one with the admixture under study and another with a reference admixture, usually neutralized Vinsol resin. All mixtures must be prepared using a type I or type II Portland cement and proportioned according to ACI 211.1–91 *(Recommended Practice for Selecting Proportions for Normal Weight and Heavy Weight Concrete)*. The cement content is fixed at 307±3 kg/m^3 and the quantity of water and sand is adjusted to obtain a slump of 60±10 mm. The dosage of both air-entraining admixtures has to be adjusted to produce a total air content of 5.5±0.5%. At least 10 concrete prisms (five for each of the two air-entraining admixtures) must be prepared and subjected to 300 rapid freezing and thawing cycles in water at the age of 14 days in accordance with procedure A of ASTM Standard C 666. For the admixture under study to be considered acceptable, the concrete made with it must have a relative durability factor greater than 80% (with respect to that of the reference concrete) and its basic properties must not be significantly different from those of the reference concrete.

The quality of an air-entraining agent is related not only to its ability to produce an adequate total air content but also, and mainly, to its ability to produce a satisfactory air-void system containing a large number of closely spaced air bubbles. As will be demonstrated in Chapter 6, a satisfactory total air content does not necessarily guarantee an adequate spacing factor (Figure 6.6 showing the relationship between the spacing factor and the total air content). Past experience, based on both laboratory and field tests, has shown that concretes with a marginal spacing factor (250–350 μm) may be damaged by surface scaling (Sommer, 1979) even though they are generally adequately protected against internal microcracking caused by freezing and thawing cycles such as those produced using the ASTM C 666 test method. Unfortunately the requirements of ASTM C 233 and C 260 do not define any acceptance criteria concerning either the characteristics of the air-void system or the de-icing salt scaling resistance of concrete. In this respect the Canadian Standard CSA-A266.2-M78 is more severe since it specifically requires that the spacing factor obtained with an air-entraining admixture be not more than 200 μm for a total air content ranging from 5 to 7%.

The ability of an air-entraining admixture to produce an adequate air-void system with a sufficiently low spacing factor is a necessary but not sufficient condition to ensure the durability of concrete; it is also important that the characteristics of the air-void system remain constant from the time of mixing to the final setting of concrete on the job site. As discussed in Chapter 6, the stability of the air-void system is a matter of great importance which is too often neglected when the frost resistance of concrete is considered. It is important to note that, although all commercialized air-entraining agents meet the requirements of the Standards and all can produce a satisfactory air-void system, the stability of the air-void system is not guaranteed and can be influenced by many parameters. As will be discussed in Chapter 9, it is highly recommended that the concrete producers verify the stability of the air-void system for all air-entrained concrete mixtures they produce on a regular basis.

4.3.2 Water-Reducing, Retarding and Accelerating Admixtures

Other chemical admixtures, such as water-reducing, retarding and accelerating agents, may be used together with an air-entraining admixture in concrete mixtures. To verify that these admixtures have no detrimental effects on the frost durability of concrete, ASTM Standard C 494 recommends the preparation of two air-entrained concretes (with and without the admixture under study) and the testing of specimens of these concretes in accordance with the ASTM C 666 test method. The admixture is rejected if the durability factor of the concrete containing it is lower than 60% or is significantly different from the durability factor obtained for the reference concrete.

Even if certain chemical admixtures have no direct influence on the frost resistance of concrete, they can have a detrimental effect on the production and stability of the air-void system (Chapter 6). Superplasticizers, for instance, are known to produce larger air voids (the spacing factor is then higher, for a given air content, than that of a reference concrete) and, under certain circumstances, can be the cause of instability in the air-void system and thus create a significant increase of the spacing factor (Saucier *et al.,* 1990). The influence of admixtures on the characteristics of the air-void system is a major concern but is not covered by ASTM C 494 or by any other Standard.

4.3.3 Fly Ash or Natural Pozzolans

The use of pozzolanic mineral additives (such as fly ash or natural pozzolans) in the production of air-entrained concrete may increase the amount of air-entraining agent required to obtain a proper air content (this increase is often caused by the presence of carbon which partially absorbs the air-entraining agent). To assess the influence of a pozzolanic mineral additive on air entrainment, ASTM Standard C 311 recommends the preparation of a control concrete mixture with the amount of air-entraining admixture (generally neutralized Vinsol resin) required to produce a total air content of 5.5±0.5% in the fresh concrete. A second test mixture is batched, having the same proportions and the same air content, but 25% of the mass of the cement is replaced by the pozzolan under test. Both mixtures must comply with the requirements of ASTM Standard C 233 on the testing of air-entraining admixtures for concrete. If the amount of air-entraining admixture used for the test mixture is more than two times larger than the amount required for the control mixture, tests must be carried out in accordance to C 666 to assess the durability of concrete to freezing and thawing.

The chemical and physical characteristics of a pozzolan from a given source may vary significantly with time, and ASTM Standard C 618 provides uniformity requirements, one of them being that the dosage of air-entraining agent required to produce a given air content should not differ by more than 20% from the dosage needed with previous samplings of the same pozzolan. According to the ASTM C 311 test method, this requirement can be verified by preparing, at regular intervals, two mortar mixtures containing 300 g of Portland cement (type I or II), 75 g of the pozzolan, 1125 g of graded Ottawa sand and sufficient water to give a flow of 80–95% (as determined according to the ASTM C 305 Standard). An air-entraining agent (generally neutralized Vinsol resin) is added in sufficient quantity to produce an air content of 15–18% in the first mixture and 18–21% in the second mixture.

The quantity of air-entraining agent required to produce an air content of 18% is then determined by linear interpolation. The uniformity of the pozzolan is considered acceptable if this dosage does not vary by more than 20% from the average value established for the 10 preceding tests. The pozzolan may be rejected if it fails to meet this requirement.

The results of the ASTM C 311 test method must be interpreted with care. Lane (1991) considers the ASTM C 311 test method inadequate because the required 18% air content is too high, and suggests that 13% would be a more appropriate value. Since a very large amount of Vinsol resin (1.5–2.5 mL of admixture per kilogram of cement compared to 0.3–0.6 mL/kg used in typical concretes) can sometimes be necessary to produce an 18% air content, a pozzolan which meets the requirements of the Standard at such a high admixture dosage (needed to obtain an air content of 18%) can still have a detrimental effect on air entrainment if it is used at a smaller admixture dosage (needed to obtain an air content of 13%, as suggested by Lane).

4.4 DETERMINATION OF AIR CONTENT IN FRESH CONCRETE

The total air content of fresh concrete can be determined using three different methods, known as the pressure, volumetric and gravimetric methods. Air content (generally expressed as a percentage of the total volume of concrete) usually ranges from about 1 or 2% (for non-air-entrained concretes) to sometimes more than 10% (for air-entrained concretes) and can be measured on both fresh concrete or hardened concrete (by means of microscopic examination as explained in section 4.5). The value of the air content of fresh concrete is, however, much easier and faster to measure than that of hardened concrete and, most of all, it offers the great advantage of being available at the time of mixing and can then be used as an acceptance criterion at the job site (Chapter 9). This explains why air content is by far the most widely used parameter of the air-void system, although other parameters, such as the spacing factor, are known to be much more closely related to the frost durability of concrete.

4.4.1 Pressure Method (ASTM C 231)

The ASTM C 231 pressure test method is the most widely used and reliable method for measuring the air content of freshly mixed concrete. This method is based on the principle that, when pressure is exerted on a concrete sample, its volume is correspondingly reduced due to the contraction of the air voids (all solid constituents and water being considered as incompressible). The total air content can be estimated by measuring the difference in volume (using a type A air meter) or the difference in pressure (using a type B air meter) occurring during the test. The type A air meter is schematically described in Figure 4.20. It is formed by a cover assembly placed over a measuring bowl of known volume (typically 0.007^3 ($0.25\ ft^3$)) containing the concrete sample. This cover assembly is fixed to the bowl using a watertight clamping device and filled with water to a predetermined level (the water level being visible through a transparent opening). The test consists of applying a pressure over the system by using an air pump installed in the upper part of the cover assembly. This pressure causes a drop of the water level which is directly proportional to the decrease in the volume of the air voids. According to Boyle's law, the product of the pressure and the volume of an ideal gas (kept inside a closed vessel) is equal to a constant at a given temperature. Applying this principle to the air voids,

$$P_{atm} V_{a1} = P V_{a2} \tag{4.7}$$

where P_{atm} is the atmospheric pressure (i.e. the initial pressure inside the air voids), P is the operating pressure of the air meter, V_{a1} is the total volume of the air voids at atmospheric pressure, and V_{a2} is the total volume of the air voids at the operating pressure.

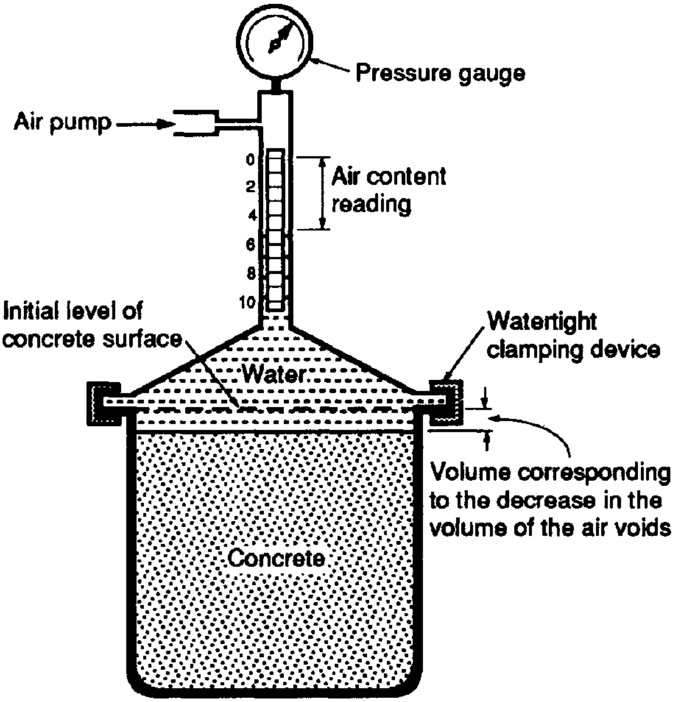


Figure 4.20 Type A air meter used for the ASTM C 231 pressure test method.

Since water is incompressible, the volume corresponding to the drop in water level inside the cover assembly is equal to the difference between the initial and the final volume of the air voids:

$$V_{a1} - V_{a2} = \frac{\pi d^2}{4} (h_1 - h_2) \tag{4.8}$$

where d is the inner diameter of the cylindrical water column in the cover assembly, h_1 is the height of the water column at atmospheric pressure, and h_2 is the height of the water column at the operating pressure.

Isolating V_{a2} in (4.8) and substituting in (4.7) gives

$$V_{a1} = \frac{P}{P - P_{atm}} \frac{\pi d^2}{4} (h_1 - h_2) \qquad (4.9)$$

Equation (4.9) gives the absolute volume of the air voids contained in the bowl V_{a1}, but it is usually more convenient to express the total air content as a percentage of the total volume *A*. Thus:

$$A = \frac{25 P}{P - P_{atm}} \frac{\pi d^2}{V_b} (h_1 - h_2) \qquad (4.10)$$

where V_b is the volume of the measuring bowl. Equation (4.10) indicates that the total air content *A* is directly proportional to the water level drop $(h_1 - h_2)$, the rest of the equation consisting of constants related to the geometric characteristics of the apparatus (*d* and V_b), the atmospheric pressure P_{atm} and the operating pressure *P*. The apparatus is calibrated in order to give the total air content as a percentage just by reading the water level on a graduated scale placed beside the transparent opening (no computation is then needed).

The operating principle of the type B air meter is slightly different because a pressure difference is measured instead of a volume change as in the type A air meter. The apparatus is formed by two chambers joined together by a watertight clamping device (Figure 4.21). The operating principle consists of filling the lower chamber (or bowl) with a sample of consolidated concrete. Afterwards, the cover is firmly put into place above the concrete bowl and a small quantity of water is introduced into the petcock valves to fill all the free space left between the concrete surface and the steel cover and to prevent this space from being counted as air voids during the test. Using a manual pump, the air pressure inside the upper chamber is progressively increased until a predetermined value is reached. After closing the petcock valves, the upper and lower chambers are connected by opening an air valve. The concrete sample is then compressed by the released air pressure while the volume of air above the concrete sample is correspondingly increased. This increase in volume of the air in the upper chamber is accompanied by a reduction of the air pressure which is recorded by a pressure gauge placed over the upper chamber. Still according to Boyle's law,

$$P_1 V_{c1} + P_{atm} V_{a1} = P_2 (V_{c2} + V_{a2}) \qquad (4.11)$$

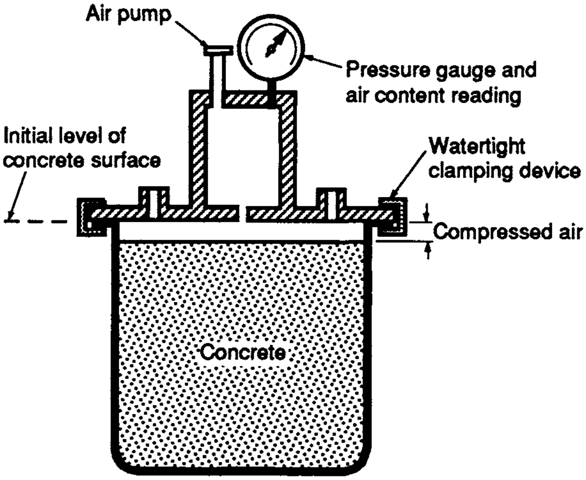


Figure 4.21 Type B air meter used for the ASTM C 231 pressure method.

where P_1 is the initial pressure in the upper chamber, P_2 is the final pressure in the upper chamber, P_{atm} is the atmospheric pressure (the initial pressure inside the air voids), V_{a1} is the initial volume of air in the concrete sample, V_{a2} is the final volume of air in the concrete sample, V_{c1} is the initial volume of air in the upper chamber, and V_{c2} is the final volume of the air in the upper chamber.

Considering that the apparatus is a closed vessel with a fixed volume, and assuming that all solid constituents and water are incompressible, the total volume of air in this system must remain constant. Therefore,

$$V_{a1}+V_{c1}=V_{a2}+V_{c2} \tag{4.12}$$

Substituting (4.12) in (4.11) yields

$$V_{a1} = \frac{(P_1 - P_2)}{(P_2 - P_{atm})} V_{c1} \tag{4.13}$$

The air content can also be expressed as a percentage of the total volume of concrete:

$$A = \frac{(P_1 - P_2)}{(P_2 - P_{atm})} \times \frac{V_{c1}}{V_b} \times 100 \tag{4.14}$$

where V_b is the volume of the measuring bowl. Equation (4.14) shows that, although the relationship is not linear, the total air content *A* is proportional to the difference of pressure measured during the test ($P_1 - P_2$). To provide an easier use, the apparatus is calibrated in such a way that the air content is directly displayed on the pressure gauge (no computation is then needed).

The relationship between the air content measured on the fresh concrete (using a type B air meter) and on corresponding samples of hardened concrete (using a microscopic analysis) for a large number of samples from laboratory as well as field concretes can be seen in Figure 6.5. This figure indicates that, for air contents smaller than about 8%, the results are well distributed on both sides of the line of equality which means that both methods give similar results, although the results are quite scattered (for reasons explained in Chapter 6, the difference between the air content in the fresh and the hardened concrete is often significant, sometimes more than 2%). For higher air contents, however, the values measured on the fresh concrete are generally lower than those obtained on the hardened concrete. This observation has been confirmed by other experimental studies (Hover, 1989; Gay, 1982; Burg, 1983), and the reason behind this phenomenon is still disputed. It was suggested that this discrepancy could be related to the air-void size distribution since the pressure inside an air void is inversely proportional to its diameter, and the smaller air voids are then less compressible than larger ones (Gay, 1982). In concretes with high air contents, the presence of a large number of very small air voids which are less compressible than larger ones could be sufficient to underestimate the total air volume. Although this concept is valid, a theoretical analysis has demonstrated that the error is negligible for air voids larger than about 50 μm and that, even if smaller voids are quite numerous and contribute significantly to protect the cement paste against frost action, their volume represents only a small fraction of the total air volume and this cannot account significantly for the differences measured (Hover, 1988). Another mechanism was proposed by Mielenz *et al.* (1958): the increase of the internal pressure for the small air voids could rapidly lead to the dissolution of the air in the surrounding liquid, which in turn would lead to an underestimate of the total air content since this dissolved air would subsequently reform into larger bubbles which are visible during the microscopical examination of hardened concrete.

4.4.2 Volumetric Method (ASTM C 173)

The air meter used for the determination of the air content of freshly mixed concrete by the volumetric method (ASTM C 173) is schematically described in Figure 4.22. This apparatus is formed by a top section placed above a bowl of known volume, not smaller than 0.002 m^3 (0.075 ft^3). The top section, which has a volume at least 20% larger than that of the bowl, is equipped with a transparent graduated neck and a watertight screw cap placed at the upper end of this neck. The test method consists of filling the bowl with a well consolidated sample of concrete and then attaching and tightening the top section onto this bowl. Using a metal funnel inserted into the neck (to minimize disturbance), water is progressively added until a calibrated level (visible through the transparent graduated neck) is reached. After placing the screw cap on the top of the neck, the apparatus is inverted and agitated until the concrete settles free from the bottom (which is now at the top). With the neck elevated, the apparatus is then rocked and rolled in order to remove all the air voids contained in the concrete sample (this air escapes to the upper end of the top section). When all the air voids appear to have been removed, the apparatus is set upright, jarred lightly, and allowed to stand until the air rises to the top. This operation is repeated until the level of water in the graduated neck reaches a constant value. If needed, a small quantity of isopropyl alcohol can be poured into the neck to remove the foamy mass on the surface of

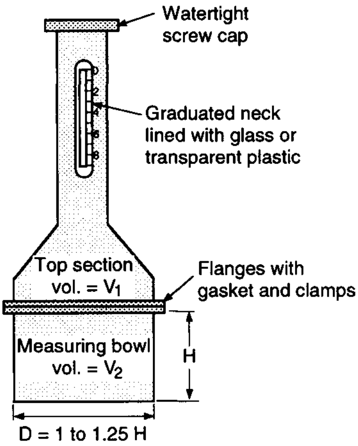


Figure 4.22 Air meter used for the ASTM C 173 volumetric test method.

the water. Since the space initially occupied by the air voids has been replaced by water, the water level drop ($h_1 - h_2$) in the graduated neck is directly proportional to the total air content. This air content is given by the relationship

$$A = \frac{(h_1 - h_2)A_{\text{neck}}}{V_b} \times 100 \tag{4.15}$$

where A is the air content (expressed as a percentage of the total volume of concrete), h_1 is the initial height of the water column in the graduated neck, h_2 is the final height of the water column in the graduated neck, A_{neck} is the area of the cross-section of the neck, and V_b is the volume of the bowl.

As in the pressure method, the air meter is calibrated in such a way that the air content is directly displayed on a graduated scale. The volumetric method is not influenced by the type of aggregate (dense, cellular or lightweight) nor by its moisture content. This represents an advantage in comparison to the pressure and gravimetric methods. However this method is more tedious than the pressure method and also more operator sensitive (which can account for a lower precision). Few data are available concerning the precision of this test method, but indications are that it generally underestimates the total air content (Ozyildirim, 1991) because the time required to extract all the air voids from the cement paste is often too long (sometimes more than one hour may be needed). Although this method is not very widely used for concrete (most people preferring the pressure air meter), it is often used to measure the air content in mortars.

4.4.3 Gravimetric Method (ASTM C 138)

In the gravimetric method (ASTM C 138), the air content is given by the difference between the theoretical unit weight of concrete (based on the known composition of the concrete mixture and the known characteristics of the concrete-making materials) and the measured unit weight of concrete. This measured unit weight W is obtained by weighing a calibrated bowl of known weight and volume (usually about 7000 cm^3) filled with a well consolidated sample of concrete. Thus

$$W = \frac{W_c - W_b}{V_b} \tag{4.16}$$

where W_c is the weight of the bowl filled with concrete, W_b is the weight of the empty bowl and V_b is the volume of the bowl. The theoretical unit weight of concrete T can be obtained by the equation

$$T = \frac{W_w + W_c + W_{fa} + W_{ca}}{\dfrac{W_w}{G_w} + \dfrac{W_c}{G_c} + \dfrac{W_{fa}}{G_{fa}} + \dfrac{W_{ca}}{G_{ca}}} \tag{4.17}$$

where W_w, W_c, W_{fa} and W_{ca} are the weights of water, cement, fine and coarse aggregates (in a batch of the mixture) respectively, and G_w, G_c, G_{fa} and G_{ca} are the specific gravities of water (1000 kg/m^3 at 4 °C), cement, fine and coarse aggregates. The value of T, as calculated using (4.17), must be corrected to take into account the fraction of the mix water absorbed by the dry (or partially dry) aggregates or the excess water surrounding the moist (or wet) aggregates.

The air content (expressed as a percentage of the total volume) is given by

$$A = \frac{T - W}{T} \times 100 \tag{4.18}$$

Past experience has demonstrated that the air content obtained using the gravimetric method is not very accurate. With this method, the exact amounts of each component added to the concrete mixture, as well as their physical characteristics, must be known. In practice, however, it is not always possible to obtain this information easily with the required accuracy. In addition, the corrections related to the moisture content of the aggregates are often difficult to establish precisely. It is also difficult to measure the unit weight of concrete W with a very high precision. Unfortunately, small errors in the determination of the mix proportions, of the material characteristics or of the measured unit weight are sufficient to cause a significant error in the determination of the air content. For example, Figure 4.23 shows the relationship between the air content measured with both the pressure and the gravimetric methods on a large number of laboratory concretes. Clearly, the data reported in this figure are quite scattered, even if they are fairly well distributed over both sides of the line of equality.

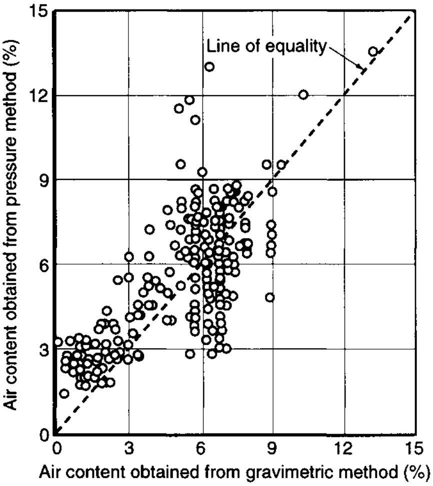


Figure 4.23 Relationship between the air content of fresh concrete obtained from the ASTM C 231 pressure test method and the ASTM C 138 gravimetric test method for 263 different concrete mixtures.

4.5 MICROSCOPIC DETERMINATION OF AIR CONTENT AND OTHER CHARACTERISTICS OF THE AIR-VOID SYSTEM

4.5.1 Fundamentals

In the two previous chapters, the paramount importance of an adequate air-void system for the protection of concrete against freezing and thawing cycles has been underlined many times. The basic characteristics of this system, such as the air content, the specific surface of the air voids and, particularly, their mean spacing (the so-called spacing factor), cannot be directly measured in a three-dimensional (3D) volume. Fortunately these characteristics can be obtained from the microscopic examination of the air-void circles intercepted by a planar surface (in a concrete sample).

The problem can be analysed in different ways, as schematically illustrated in Figure 4.24. First, the diameters of all the circular prints of air voids intercepted by the planar surface can be recorded along with the total surface occupied by these voids, the cement paste and the aggregates. Knowing the distribution of the air-void circles in this two-dimensional (2D) field, it is possible to reconstruct mathematically the 3D distribution using some simplifying assumptions. The mathematical equations are based on the laws of stereology, the science which studies the mathematical relationship between the characteristics of a system of particles dispersed in a 3D volume and the projection of this system on a surface, a line or a group of discretized points. Recording circle diameters is time consuming and not very convenient when performed by ‘hand’. It is appropriate, however, when a computer-assisted image analysis system is available (this subject is covered in section 4.5.6).

The second method consists of scanning the planar concrete surface with a given number of regularly spaced lines of traverse (Figure 4.24). The chords intercepted by the air voids, the cement paste and the aggregates are then recorded separately. Knowing the distribution of the chords intercepted in this one-dimensional field, it is possible to reconstruct mathematically the 3D distribution assuming some simplifying hypotheses. This method corresponds to the '(Rosiwal) linear traverse method', described in the ASTM C 457 Standard.

In the third method, observations are made over some discretized points regularly distributed along lines of traverse across the entire surface (Figure 4.24). For each observation the operator only has to decide if the point is located over an air void, an aggregate or cement paste (the number of air voids intercepted along the lines of traverse is also recorded). It is still possible to reconstruct mathematically the 3D distribution from the observations made in this discretized field (0D), again with some simplifying assumptions. The 'modified point count method', recommended by the ASTM C 457 Standard, is based on this principle.

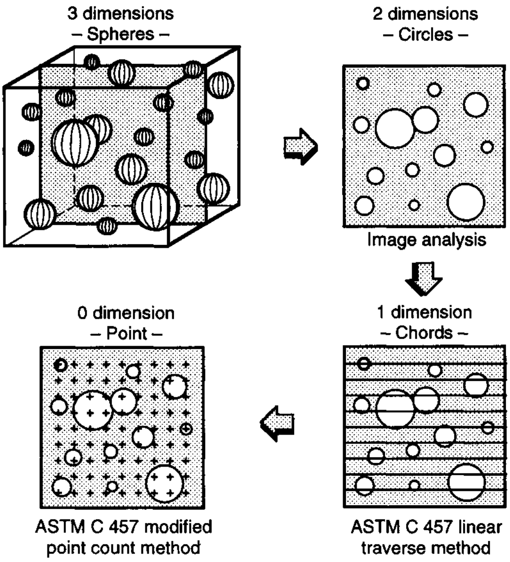


Figure 4.24 Schematic illustration of the different methods available to determine the characteristics of the air-void system of hardened concrete.

4.5.2 Sampling and Preparation of the Concrete Specimens

The concrete specimens subjected to microscopic examination usually come from cylinders cast at the job site, from cores drilled from an existing structure, or sometimes from prisms cast in the laboratory. Since concrete is a heterogeneous material, the sampling must ensure that the specimens chosen are representative of the whole volume of concrete under consideration. This can be achieved by taking several specimens at different locations in the concrete. According to the ASTM C 457 Standard, a minimum of three concrete samples must be examined when an existing structure is under study. The orientation of the concrete specimens is determined by the kind of information which is expected by the user. A specimen oriented perpendicular to the finished surface will give valuable information about the characteristics of the air-void system in the body of the concrete delivered at the job site. However a specimen parallel to the exposed surface and located just a few millimetres below this surface may be useful to detect a possible detrimental effect of surface finishing on the air-void system.

Prior to the microscopical examination, the concrete specimens must be polished in order to provide a perfectly planar and smooth surface where the air voids and the aggregates can be clearly distinguished from the cement paste. This can be achieved by lapping (over a rotating steel plate) the surface with successively finer silicon carbide abrasive pastes. It is important to provide the concrete with a good curing prior to the lapping process because, when the paste is strong, the risk of pulling out small particles of paste or aggregate from the surface is reduced and the overall quality of the image seen under the microscope is improved (it is a good practice to saw the concrete slabs and soak them in water for a few days before lapping).

4.5.3 Test Procedure and Computation of the Air-Void Characteristics

The polished concrete specimen is placed on a movable carriage device under an optical microscope with a magnifying power in the range from 50× to 125× (Figure 4.25). The carriage device is arranged in such a way that it can be displaced in two perpendicular directions. Essentially the method consists of following with the cross-hairs of the microscope

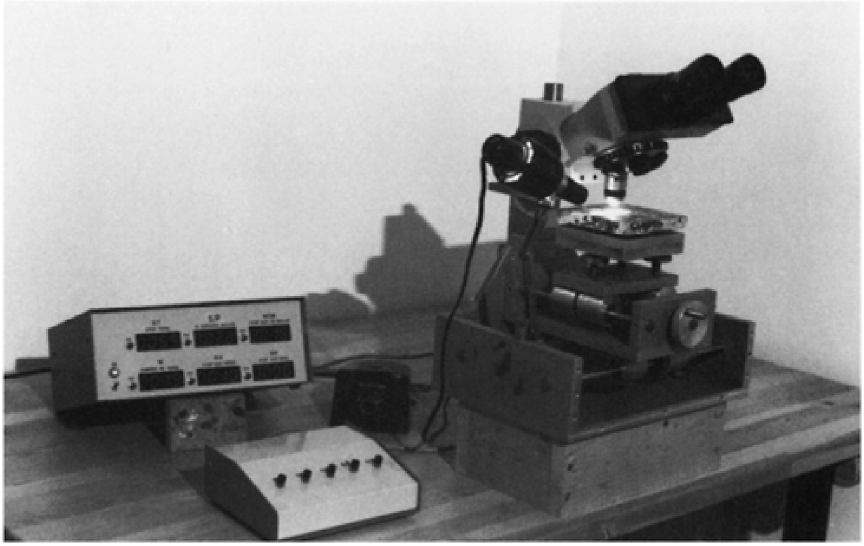


Figure 4.25 Typical set-up used for the ASTM C 457 microscopical determination of the characteristics of the air-void system of hardened concrete.

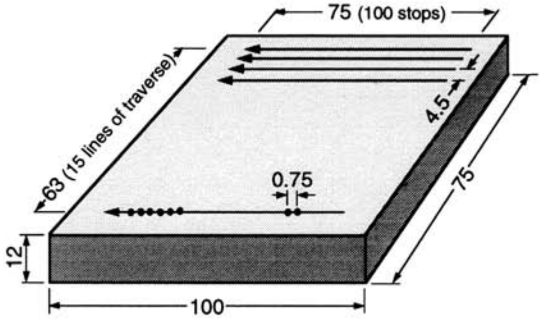


Figure 4.26 Schematic description of a typical test procedure for the ASTM C 457 microscopial determination of the characteristics of the air-void system of hardened concrete (dimensions in millimeters).

a given number of regularly spaced lines of traverse distributed over the entire surface of the specimen (Figure 4.26) and in recording the number N of voids intercepted and, depending on the method used, the total length of traverse L_t, the cumulative length of the chords intercepted in air voids L_v and in cement paste L_p (for the linear traverse method), or the total number of point counts S_t, the number of point counts over an air void S_v and over cement paste S_p (for the modified point count method). In order to provide sufficient precision, the ASTM C 457 Standard defines minimum requirements concerning the surface covered by the examination, the total length of the lines of traverse and, for the modified point count method, the number of point counts. These requirements are a function of the maximum size of the aggregates (for samples containing larger aggregates, the quantity of cement paste per unit area is reduced and the area examined must be correspondingly increased), and are summarized in Table 4.4.

Table 4.4 Minimum requirements of the ASTM C 457 Standard for the microscopical determination of the characteristics of the air-void system of hardened concrete.

Nominal maximum size of aggregates (mm)	Minimum surface area observed (cm^2)	Minimum length of traverse (mm)	Minimum number of points
150	1613	4064	2400
75	419	3048	1800
38	155	2540	1500
25	77	2413	1425
19	71	2286	1350
13	65	2032	1200
10	58	1905	1125
5	45	1397	1000

The ASTM C 457 Standard gives the mathematical equations necessary to compute the characteristics of the air-void system from the measured chord intercepts (or point counts). These equations were developed from stereo-logical considerations (Powers, 1949). For the linear traverse method the air content A, generally expressed as a percentage of the total volume of concrete, is equal to the ratio of the cumulative chord intercepts in air voids L_v to the total length of traverse L_t:

$$A = \frac{L_v}{L_t} \times 100 \tag{4.19a}$$

When the modified point count method is used, $L_v = S_v \times I$ and $L_p = S_p \times I$ where I is the distance between the regularly spaced points. Thus,

$$A = \frac{S_v}{S_t} \times 100 \tag{4.19b}$$

The specific surface of the air voids α, which represents their surface area divided by their volume, is calculated as

$$\alpha = \frac{4N}{L_v} \tag{4.20a}$$

for the linear traverse method, and

$$\alpha = \frac{4N}{S_v I} \tag{4.20b}$$

for the modified point count method. (Without going into the details of the various assumptions behind the equations, it should be sufficient to point out that the size of the voids is necessarily related to the total length of traverse through the air voids divided by the number of air voids observed along the lines of traverse.)

The specific surface is a function of the mean size of the air voids: larger values of α correspond to smaller air voids. It typically ranges from about 10 mm^{-1} (for non-air-entrained concretes) to more than 40 mm^{-1} (for air-entrained concretes).

The spacing factor $\bar{L}$ is defined as half the mean distance between the periphery of air voids. Physically it represents the average maximum distance that water, located at any point in the cement paste, must travel to reach the nearest air void. According to Powers (1949), the spacing factor can be computed in two different ways. First, the volume occupied by cement paste may simply be divided by the total surface area of the air voids to obtain the mean thickness of cement paste around the voids:

$$\bar{L} = \frac{L_p}{4N} \tag{4.21a}$$

for the linear traverse method, and

$$\bar{L} = \frac{S_p I}{4N} \tag{4.21b}$$

for the modified point count method.

The second method considers that all air voids have the same diameter and are distributed in a well-arranged cubic array throughout the cement paste (Figure 4.27). Based on these assumptions, the spacing factor (i.e. the distance from the farthest point in the cement paste to the nearest air-void wall) is then equal to the half-distance between the periphery of two air voids located in the opposite corners of the cube:

$$\bar{L} = \frac{3}{\alpha}\left[1.4\left(\frac{p}{A} + 1\right)^{1/3} - 1\right] \tag{4.22}$$

where *p/A* is the paste/air ratio (i.e. L_p/L_v or S_p/S_v).

Equations (4.21) and (4.22) are equal only for a paste/air ratio *(p/A)* of 4.342 and, since they are both known to overestimate the real spacing of air voids (because of the simplifying assumptions which are never satisfied), the ASTM C 457 Standard recommends the use of the formula which gives the smallest value:

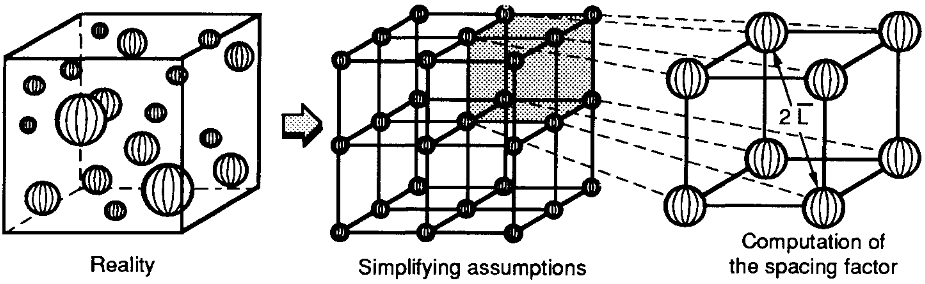


Figure 4.27 Cubic arrangement of the air voids in cement paste which is hypothesized for the computation of the spacing factor using equation (4.20).

$$\bar{L} = \frac{L_p}{4N} \text{ or } \frac{S_p I}{4N} \tag{4.23}$$

when *p/A* is less than 4.342, and

$$\bar{L} = \frac{3}{\alpha}\left[1.4\left(\frac{p}{A} + 1\right)^{1/3} - 1\right] \tag{4.24}$$

when *p/A* is greater than 4.342.

4.5.4 Precision of Measurement

The precision of the microscopical determination of air-void characteristics is a function of many parameters, such as the quality of polishing, the microscope magnification and, of course, the sampling size. The very small air voids (i.e. those with a diameter ranging from approximately 10 to 25 μm) only occupy a small volume, but can have a large influence on the value of the spacing factor. These voids can only be seen under the microscope if the quality of the polishing is very good and if the magnification level is sufficient. It is thus always better to use a magnification level of 100× or more and not the lower magnification levels allowed by the Standard. The operator's subjectivity is also frequently pointed out as one of the major sources of error.

It is difficult to assess theoretically the precision of this measurement and, until recently, most investigators were mainly concerned with the statistical variability of air content (Sommer, 1979; Langan and Ward, 1986). However a recent analysis of more than 600 air-entrained concretes (Pleau *et al.,* 1990), examined according to the modified point count method, has allowed the defini tion of a precision statement for the three most important parameters of the air-void system. The results obtained are presented in Figure 4.28 which shows the maximum error (expected to occur once in 20 times) as a function of the number of concrete slabs examined (for each slab, the examination consisted of 1500 point counts distributed along a 1125 mm line of traverse covering a 71 cm^2 surface). This figure indicates that the maximum error decreases exponentially with the number of slabs examined. For example the maximum error decreases from 27.8% to 16.0% (for A), from 25.0% to 14.4% (for α) and from 19.4% to 11.2% (for $\overline{L}$ when three slabs are examined instead of only one. This represents a significant improvement. The figure also indicates that A is less accurate than α which is also less accurate than $\overline{L}$. This can be explained by the fact that A is only a function of S_v, α is a function of S_v and N, and $\overline{L}$ is a function of S_V, N and S_p (equations (4.19), (4.20) and (4.22)); the accuracy increases with the number of parameters involved in the computation because one is unlikely to obtain, simultaneously, a large error in all parameters. Furthermore, the precision of A, in addition to being related to the surface covered by the examination (which takes into account the heterogeneity of the material), is only a function of the number of point counts, while the precision of α and $\overline{L}$ is a function

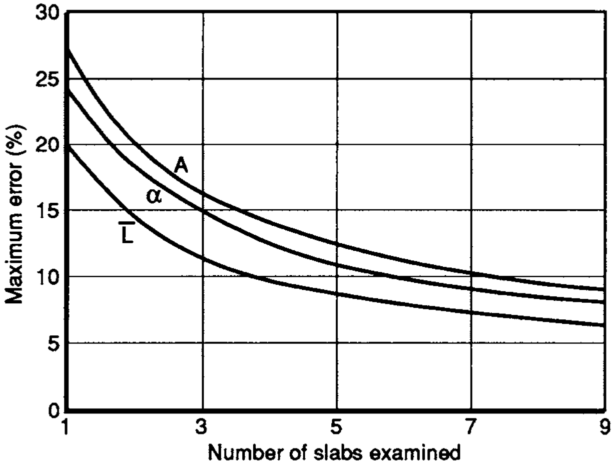


Figure 4.28 Influence of the sampling size on the precision of the ASTM C 457 microscopial determination of air content, specific surface of air voids, and air-voids spacing factor (after pleau *et al.,* 1990).

of the number of point counts and of the total length of traverse. When the minimum requirements of the ASTM C 457 Standard are strictly satisfied for a nominal maximum size aggregate of 19 mm (i.e. 1250 point counts distributed on a 2286 mm length of traverse covering a surface of 71 cm^2), the precision of the microscopical examination is evaluated at approximately 28%, 20% and 16% for A, α and $\overline{L}$, respectively.

The precision statement described above indicates the variability of the measurement associated with a single operator (i.e. the maximum error expected to occur when it is always the same operator who performs the examination). However, the microscopical examination is subjective, and two different operators examining the same concrete specimen will not necessarily obtain the same result. A recent study has concluded that, for experienced operators, the difference between them was significant for, roughly, half of the paired operators investigated (Pleau and Pigeon, 1992). When this difference is significant, the maximum deviation can reach 12% in some extreme cases, but the mean value of the deviation was found to be equal to 3% (for A and α) and 5% (for $\overline{L}$). It seems reasonable to add these mean values to the maximum errors associated with a single operator to estimate the precision of the overall testing procedure. The results obtained are summarized in Table 4.5. Experience indicates, however, that the differences can be much more important for operators with a limited experience (and can even reach 50% in such cases), which demonstrates the importance of properly training new operators.

Many investigations are presently being carried out (mainly in the form of round-robin tests) to assess the precision of the microscopical examinations performed in different laboratories using different equipment, different operators and different procedures.

Table 4.5 Maximum error (95% probability level) associated with the modified point count method of ASTM C 457 (%) (after Pleau and Pigeon, 1992).

	Air content	Specific surface	Spacing factor
ASTM minimum* requirements	31	23	21
Laval procedure** (2 slabs)	23	21	19
Laval procedure*** (3 slabs)	19	17	16

* 1350 point counts distributed along a 2286 mm length of traverse and a 71 cm^2 surface area.

** 3000 point counts distributed along a 2250 mm length of traverse and a 135 cm^2 surface area.

*** 4500 point counts distributed along a 3375 mm length of traverse and a 202.5 cm^2 surface area.

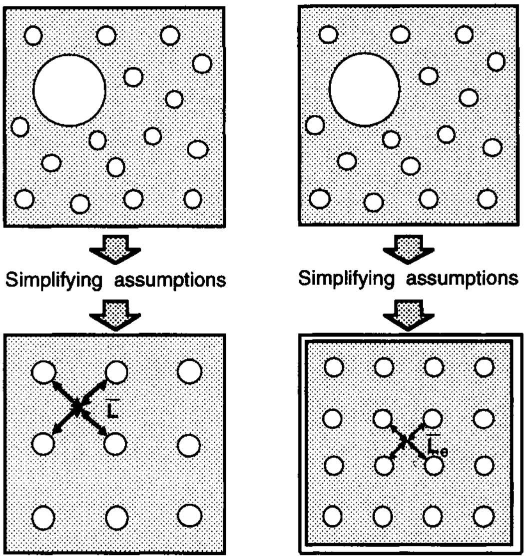
4.5.5 Influence of Large Air Voids on the Spacing Factor

ASTM C 125 establishes a distinction between entrapped air voids (characteristically 1 mm or more in dimension and irregular in shape) and entrained air voids (typically between 10 and 1000 μm in diameter and spherical or nearly so). Even if entrapped air voids can account for a significant percentage of the air content, they are undoubtedly much less numerous than entrained air voids and the real average spacing of the voids in concrete is little affected by these entrapped voids. However, a smaller value of the spacing factor is generally obtained when entrapped air voids are neglected in the computation of the spacing factor (Sommer, 1979; Walker, 1980; Langan and Ward, 1986). This apparently paradoxical phenomenon is due to the fact that, in the mathematical calculations, all voids are assumed to have the same size. This assumption is evidently not satisfied and this is so significant that the presence of only a few large air voids is sufficient to cause an important increase in the mean diameter of the air voids, which leads to a smaller value of the specific surface, and then, to a greater spacing factor. Figure 4.29 illustrates this phenomenon.

Figure 4.30 (from Pleau *et al.,* 1990) shows the relationship between the spacing factor computed neglecting the entrapped air voids, denoted $\overline{L}_e$, and the usual spacing factor. In the tests carried out by Pleau *et al.* using the modified point count method, each void in which more than one point count was made was considered as an entrapped air void (voids larger than approximately 1 mm were thus considered as entrapped since the distance between two adjacent point counts was 750 μm). Figure 4.30 indicates that $\overline{L}_e$ can be considerably lower than $\overline{L}$. For example, the spacing factor can decrease from 300 to 200 μm when these large air voids are neglected. In many cases, $\overline{L}_e$ is more representative than $\overline{L}$ for assessing the potential resistance of concrete to freezing and thawing (as is clear in Figure 4.29, the average maximum distance that water must travel in the paste to reach an air void is closer to $\overline{L}_e$ than $\overline{L}$) and the user of ASTM C 457 could take advantage of computing it. The computation of $\overline{L}_e$ can also be useful to detect deficiencies in the mechanisms of air entrainment or placing techniques.

4.5.6 Determination of Air-Void Characteristics by Computer-Assisted Image Analysis

In the past few years the techniques of computer-assisted image analysis have progressed very rapidly and have found applications in many fields of interest. The development of these techniques has been encouraged by the continuing increase of the power and affordability of computers, especially microcomputers. A number of such automatic systems have been developed to determine the characteristics of the air-void system in hardened concrete (MacInnis and Racic, 1986; Chan, 1987; Houde and Meilleur, 1983; Laurençot *et al.,* 1992). In these systems a camera is placed over the microscope and connected to the computer. A program digitizes the image, identifies the air voids, measures their planar surface and records the results in a database. This procedure is repeated until the total number of images analysed is large enough to achieve a satisfactory precision. It is difficult for a computer to distinguish the air voids from the cement paste or concrete aggregates and, most of the time, a special treatment of the concrete surface is required, in addition to the usual lapping process, prior to the image analysis. This treatment usually consists of applying a black ink on the surface of the concrete specimen and of filling the voids with a white paste (composed of aluminium oxide, corn starch or any other suitable material). A clear binary image is then obtained where all the voids are easily discernible since they are white and the remainder of the surface is black.



Air-void distribution according to the ASTM C457 Standard

Air-void distribution assuming that the large air void does not exist

Figure 4.29 The influence of entrapped air voids on the computation of the spacing factor (after Pleau *et al.,* 1990).

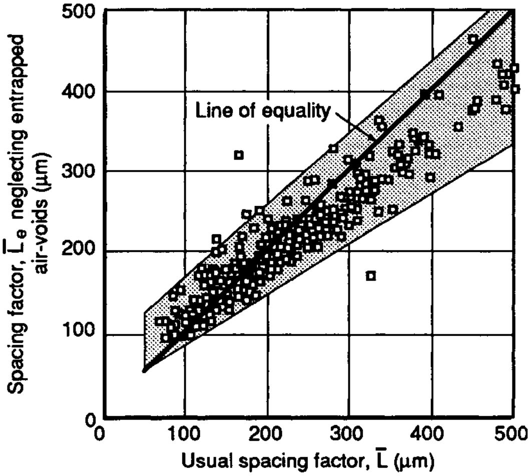


Figure 4.30 Relationship between spacing factor neglecting entrapped (> 1 mm) air voids $\overline{L}_e$ and usual spacing factor $\overline{L}$ (after Pleau *et al.,* 1990).

Image analysis avoids the long and tedious procedure of microscopical examination, and the characteristics of the air-void system can be automatically computed, which represents a considerable benefit. It also avoids the operator's subjectivity which constitutes another significant advantage. However, some surface defects (such as aggregate pull-outs, broken paste, cracks or debonding at the interface between cement paste and aggregates) can be counted as air voids which adversely influence the accuracy of the test results and emphasize the great importance of the surface treatment. When a binary image is used, the paste content (as well as the aggregate content) cannot be directly measured. The paste content is not involved in the computation of the total air content or the specific surface of air voids, but is needed to determine the spacing factor. This paste content may be assumed arbitrarily, measured on the fresh concrete (section 4.4.3), obtained from a manual ASTM C 457 microscopical examination (which partially cancels the benefit of the image analysis) or can be deduced from the known volumes of the components added to the mixer (although it often happens that this information is not available or cannot be determined with a sufficient accuracy). Some work is in progress to develop automatic systems which do not require a binary image and can detect the aggregates as well as the air voids.

The precision of the air-void characteristics as determined using image analysis can vary significantly from one system to another, and it is not possible to determine a general precision statement. It is highly recommended that the results obtained from the image analysis be regularly compared to those obtained from the manual microscopical examination, to be sure that the correlation between them is good enough.

Image analysis offers another significant advantage in that it provides the size distribution of the diameters of the circular voids intercepted by the surface of the concrete examined. This distribution is closer to the distribution of the sphere diameters in the cement paste than is the distribution of the chords obtained from the linear traverse method described in the ASTM C 457 Standard. It can be used to assess better the real spacing of air voids by using the protected paste concept described below.

4.5.7 Protected Paste Concept

As previously mentioned, the frost durability of concrete is closely related to the spacing of air voids which determines the maximum distance that freezable water must travel through the cement paste to reach an escape boundary where ice crystals can grow freely without generating disruptive pressures. The spacing factor $\overline{L}$ is defined as the mean half-distance between the outer boundaries of two adjacent air voids and, in the computation, it is assumed that all voids have the same size and are equally distant from each other. Of course, these two assumptions are not sastisfied, and the spacing factor is thus only a gross estimate of the real spacing of air voids in concrete.

As early as 1951, mathematical relationships were developed to estimate better the real spacing of air voids from the results of the Linear Traverse Method described in the ASTM C 457 Standard (Lord and Willis, 1951). Since the computations were too long and tedious, Lord and Willis developed a graphical method to avoid them. This method shows that the number of air voids contained per unit volume of concrete is much larger than assumed in the computation of the $\overline{L}$ value, and that the spacing factor consequently always overestimates the real spacing of air voids. (According to the results obtained by Lord and Willis, the number of air voids contained by unit volume of concrete can be as high as eight times the number of voids taken into account in the computation of the spacing factor.)

A few years later Philleo (1955) developed a different method for analysing the void distribution in air-entrained concrete, and introduced the protected paste concept. Philleo's method consists of determining the fraction of the cement paste which is located within a given distance of the nearest air void (Philleo, 1983). This distance is called the Philleo factor, and is defined by the ACI *Manual of Concrete Practice* as

> *a distance, used as an index of the extent to which hardened cement paste is protected from the effects of freezing, so selected that only a small portion of the cement paste (usually 10%) lies farther than that distance from the perimeter of the nearest air void.*

Assuming that the air voids are randomly distributed in the cement paste, and considering that 90% of the paste is located within a distance S of the nearest air void, the Philleo factor S can be computed as

$$S = \frac{0.62}{N^{1/3}}\left[\left(\ln\frac{1}{1-A} + 2.303\right)^{1/3} - \left(\ln\frac{1}{1-A}\right)^{1/3}\right] \qquad (4.25)$$

where N is the number of air voids per unit volume of cement paste, and A is the air content of the cement paste (expressed as a fraction of the air-entrained paste volume).

Using the linear traverse method, the chords intercepted in air voids can be measured and classified in discrete size groups to obtain a void-size distribution. The number of air voids per unit volume of cement paste cannot be easily obtained from this distribution, but it can be approximated by counting only the chords in the smallest group, provided that the chord lengths in this group are at least as short as the diameter of the smallest air void in the system.

The Philleo factor theoretically provides a more realistic estimate of the real spacing of air voids than the ASTM spacing factor and it should be better suited to assess the frost durability of concrete. Experience indicates that for most normally air-entrained concretes, S is approximately equal to 100 µm while N ranges from about 40 to 60 voids per cubic millimetre, but very few data are available concerning the relationship between the Philleo factor and the frost durability of concrete.

In the development of his method, Philleo used only an estimated value of N and, for simplicity, he neglected the size distribution of the air voids in the computation of S (i.e. all the air voids are assumed to be equal in size). Other researchers working on the protected paste concept have tried to provide a better estimate of the spacing of air voids by taking into account the measured size distribution of the air voids (Larson *et al.,* 1967; Natesaiyer *et al.,* 1992, 1993; Pleau, 1992). Pleau (1992) has developed a computerassisted mathematical method to determine the three-dimensional distribution of the air voids from the recorded size distribution of the length of the chords intercepted by a line of traverse or, preferably, from the recorded size distribution of the diameters of the circles intercepted by a plane. The flow length Q_{98} developed by Pleau is defined in such a way that 98% of the cement paste is located within that distance from the nearest air void. It is thus quite similar to the Philleo factor, except that it is determined much more precisely, since it takes into account the recorded void-size distribution. As mentioned in Chapter 3, the flow length was found to be a better indicator of the freezing and thawing resistance of concrete than the

ASTM spacing factor. Pleau's method, however, like many others, requires sophisticated equipment, and will have to be simplified before it becomes a routine procedure in most laboratories.

4.6 DETERMINATION OF THE SPACING FACTOR IN FRESH CONCRETE

Recently, two methods have been developed to measure the spacing factor directly on fresh concrete. In the first (Hansson and Henrichsen, 1993), a sample of mortar about 20 mm in diameter by 75 mm long is taken from the fresh concrete with a vibrating electric hammer drill. Afterwards, the mortar is mixed with a special fluid (in which air cannot be dissolved) to free the air voids from the mortar and entrap them in the fluid. The fluid is then placed in a vertical column and the voids move upward to the surface. The velocity of this upward movement is a function of the diameter of the air voids, the larger voids rising more quickly, followed by progressively smaller bubbles. The volume of air released at the top of the column is recorded by a laptop computer at regular time intervals (approximately 15 s) and the corresponding diameter of air voids is automatically computed. At the end of the test, which takes approximately 20 min, the size distribution of air voids is plotted and their specific surface can be easily determined. The spacing factor can also be computed using the specific surface of air voids and the total volume of air released from the mortar. However, since the test only involves the mortar fraction of the concrete, the total air content cannot be determined.

In the second method, the principle of refraction and reflection of light in optical fibres is applied to the detection of air voids (Ansari, 1991). The test consists of dragging a fibre-optic needle through the fresh concrete a distance of 30–50 cm for about 10 s. This needle is connected to a laptop computer and the air content is determined by analysing the reflected light intensity (the result is obtained from the average of ten readings at different locations). At present this method provides only the overall air content, but it is expected that it will be possible, in the near future, additionally to determine the size distribution of these voids and then assess the specific surface of air voids as well as their spacing factor. This test method is still under development.

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Chapter 5
Influence of Materials and Mix Characteristics

5.1 INTRODUCTION

Concrete is a heterogeneous material made of aggregates (variable in size and in mineral composition) embedded in a solid matrix of hardened cement paste, which results from the chemical reaction between water and hydraulic cement. (The most common type of hydraulic cement is Portland cement. Blended cements are made by adding mineral additives such as fly ash or ground blastfurnace slag to Portland cement. The frost resistance of concrete made with high-alumina cements is not covered by this book.) The frost resistance of concrete is thus a function of both the characteristics of the aggregates and the properties of the cement paste. There is also an interaction between the aggregates and the cement paste when concrete freezes (mostly movements of water through the aggregate—paste interface), and this too can have an influence on the frost resistance of the material.

Since aggregates represent about 75% of the total volume of concrete, their influence on the freezing and thawing durability of concrete should never be underestimated. Past experience has shown that aggregates are often associated with the problems most commonly encountered in practice, i.e. pop-outs and surface scaling (Chapter 3). The characteristics of the cement paste, of course, and particularly the water/cement ratio, are also of paramount importance and, contrary to the aggregate characteristics, can be modified according to the known durability criteria.

The last few years have been characterized by a significant growth, especially in North America, in the use of certain mineral additives (such as fly ash and ground granulated blastfurnace slag) as partial replacement for Portland cement. The influence of these additives on the frost resistance of concrete can be significant and has been the subject of many investigations. At about the same time, the use of silica fume and superplasticizers also raised a number of questions concerning the durability of concrete in cold climates, and especially the durability of high-strength concrete made with these products.

The materials that are used to make concrete and the characteristics of the mixtures can have an influence on the performance of concrete exposed to freezing and thawing cycles in three different ways. First, they can have an influence on the mechanisms of air entrainment and on the stability of the air-void system during transportation and during the placement operations. This particular aspect is thoroughly discussed in Chapter 6. Secondly, they can directly influence the resistance against internal microcracking due to frost action and, thirdly, they can affect the resistance to surface scaling due to de-icer salts. The difference between internal microcracking and surface scaling (Chapter 2) is a very fundamental distinction that should never be forgotten when the influence of the various parameters is being considered.

5.2 INFLUENCE OF MATERIALS

5.2.1 Main Constituents

Portland Cement

The chemical composition and the physical characteristics of Portland cement (the influence of mineral additives and of the use of blended cements will be discussed in another section of this chapter) have an influence on the hydration process and, therefore, on the durability of concrete exposed to freezing and thawing cycles. The influence of the cement is mainly related to the porosity of the cement paste, and involves two different mechanisms. The chemical composition and the physical characteristics of the cement influence the rate of hydration (and thus the total porosity for a given hydration period), and also the distribution of the hydration products in the capillary pores (and thus the size distribution of these pores). As explained in Chapters 2 and 3, the amount of freezable water in a cement paste depends directly on the total capillary porosity as well as on the size distribution of the capillary pores.

Although, in terms of ultimate (long term) strength, a slow rate of hydration is better, a rapid rate of hydration is often considered to be a very positive characteristic, because a good quality cement paste is then obtained in a relatively short period of time. This is particularly helpful when concrete is subjected to freezing and thawing cycles only a few days after casting, or after poor curing. The rate of hydration is mainly influenced by the chemical composition of the cement, and especially the relative proportions of tricalcium silicate (C_3S) and dicalcium silicate (C_2S), since C_3S reacts more rapidly than C_2S. The fineness of cement also has an influence because, in pastes made with high fineness cements, the surface of the cement grains directly in contact with the mixing water is increased, which in turn increases the rate of formation of hydration products.

The influence of cement on the size distribution of capillary pores is related to the fineness of the cement. Cements with a higher fineness have a larger number of particles per unit mass, which results in the formation of a larger number of smaller capillary pores. Furthermore, the finer cement particles tend to subdivide the space between the larger particles into smaller pores. This purely physical phenomenon leads to a finer pore-size distribution, although the total pore volume is not significantly affected. A finer distribution yields a lower amount of freezable water, since the amount of ice that can form at a given temperature decreases with the size of the pores (Chapter 2). The permeability of the paste is also reduced, and this reduction has both a positive effect (since the ingress of moisture into the concrete from outside is more difficult), and a negative one (since the higher resistance to the internal flow of water increases the internal disruptive pressures caused by the forced movement of water from the capillaries to the air voids during the freezing process).

For properly air-entrained concretes of the type commonly used in practice (with water/cement ratios ranging from approximately 0.40 to 0.50), it has not been possible, from the point of view of frost resistance, to establish any significant distinction between Portland cements of different types (according to ASTM Standard C-150) or cements of the same type produced by different companies (Tyler *et al.,* 1951). This is not necessarily true in the case of de-icer salt scaling resistance, but the laboratory data that are available indicate that the influence of the fineness and composition of Portland cements is generally not very significant (Rose *et al.,* 1989; Fagerlund, 1986). For high-strength concretes made with very low water/cement ratios, however, the type of cement was found in certain investigations to have an influence on frost resistance. This topic will be discussed in a later section of this chapter.

In the last decade, the use of limestone fillers as partial replacement for clinker in the manufacture of Portand cement has increased significantly. These fillers, generally used in small quantities (less than 5% of the total cement mass), are mainly composed of particles with a mean diameter similar to or slightly smaller than that of the cement grains. These particles can be considered chemically inert, and their action is mainly physical: they act as nucleation sites for the hydration products and a more uniform microstructure with a slightly refined pore structure is obtained. It is generally considered that limestone fillers, when they are used in small amounts, do not significantly influence the frost resistance of concrete, even if this particular aspect has never been rigorously investigated. When they are used in higher amounts, although the frost resistance of properly air-entrained concrete of sufficient strength does not seem to be affected seriously, the de-icer salt scaling resistance could be significantly reduced.

The production and the stability of the air-void system in fresh concrete can also be influenced by the composition and the characteristics of the cement. Soluble alkalies in the cement, for instance, can help to stabilize the air voids produced during the mixing process. On the other hand, compatibility problems between the cement and the admixtures can occur. These phenomena and others related to the influence of cement on air-void production and stability are discussed in Chapter 6.

Water

Apart from the influence that it can have on air entrainment in certain cases (Chapter 6), it is generally assumed that drinking water has no significant influence on the frost durability of concrete. The use of salt water is not allowed by most national standards but if, for special reasons, this type of water is to be used to make concrete exposed to a severe freezing and thawing environment, tests should be carried out to ensure that the dissolved salts will not have any deleterious effect on frost resistance.

Coarse and Fine Aggregates

Coarse aggregates, as previously mentioned, can have a very large influence on the frost resistance of concrete. Fine aggregates, however, are not normally frost susceptible, except for a few rare cases where they contain substances with an exceptionally poor frost behaviour. The good durability of fine aggregates is simply due to their small size which is almost always lower than the critical size beyond which the internal pressures caused by freezing water exceed the tensile strength of the aggregate (this phenomenon is described in detail in section 5.3.1).

The mechanisms of air entrainment are not normally affected by the coarse aggregate. Although in most cases the mineral composition of the fine aggregate has no great importance, its size grading can sometimes influence the mechanisms of air entrainment (this feature is discussed in Chapter 6). In certain rare cases of improperly designed concrete mixtures, a poor choice of gradings (for both the fine and the coarse aggregates), or an inadequate ratio between the fine and the coarse aggregates, can indirectly have a detrimental effect on the frost resistance of concrete by causing segregation or excessive bleeding.

5.2.2 Admixtures

Air-Entraining Agents

It has been widely accepted since the late 1940s that the presence of a large number of closely spaced air voids throughout the cement paste represents the most effective way of protecting concrete against frost damage. The incorporation of microscopic air bubbles into the cement paste is generally obtained by adding an air-entraining admixture to the mixing water. The most common products used as air-entraining agents are neutralized Vinsol resins, salts of fatty acids, salts of sulphonated hydrocarbon, and alkyl-benzyl sulphonates (Chapter 6).

The effectiveness of an air-entraining agent in not only characterized by its capacity to entrap or entrain a large volume of air, but also, and mainly, to entrain a large number of small air bubbles. Entrained air voids usually have a mean diameter of about 30–50 µm, while the air voids naturally entrapped during the mixing process (even in non-air-entrained concretes) are typically a few hundred micrometres in diameter. The ASTM C 260 Standard pertaining to the acceptance of an admixture as a valid air-entraining agent states that such an admixture should be able to produce an air-void system with a specific surface higher than 25 mm^{-1} and a spacing factor smaller than 200 µm for a total air content of 5–8%. Unfortunately, this standard only considers the production of the air-void system, and not the important property of the stability of this system with time. Nevertheless, all air-entraining admixtures meeting the requirements of this standard can produce a satisfactory air-void system in normal conditions, although some products may be more effective than others depending on the conditions in which they are used.

Water-Reducing Admixtures

Water-reducing admixtures can be classified into three main categories on the basis of their chemical composition: lignosulphonic acids and their salts, hydroxylated carboxylic acids and their salts, and other materials including melamine and naphthalene derivatives and sulphonated hydrocarbons. The use of these admixtures, all other parameters being constant, has no real influence on the intrinsic frost resistance of cement paste and concrete. However, like air-entraining agents, they can entrain air voids during the mixing process. The air content of concrete made with a water reducer but without an air-entraining agent is usually of the order of 2–4%, but the air voids in these concretes are much larger than those in correctly air-entrained concretes, and are then significantly less effective in protecting the paste against freezing and thawing cycles. Although the protection offered by these voids (the spacing factor usually ranges from 400 to 800 µm) can in certain cases be sufficient to protect concrete exposed to a relatively mild environment (less than full saturation, low rate of freezing, absence of de-icer salts etc.), this protection can no longer be considered adequate for severe exposure conditions. The air-entraining capacity of water reducers should therefore never be counted on.

When water-reducing admixtures are used in conjunction with air-entraining agents, the air-entraining ability of the water reducers may result in a reduction in the required dosage of the air-entraining agent to obtain a given air content. Recent studies indicate that this reduction can have a detrimental effect on the stability of the air-void system. This matter and others related to the influence of water reducers on air entrainment are discussed in Chapter 6.

It is known that, at relatively high dosages, certain water-reducing admixtures (particularly of the hydroxylated carboxylic acid type) tend to increase bleeding, probably in good part due to their retarding effect. In the summer, the dosage of these admixtures is sometimes deliberately increased to compensate for the loss of water due to evaporation from the concrete surface. This practice should be used with extreme caution, because excessive bleeding can weaken the concrete surface and can thus contribute to increased scaling due to freezing in the presence of de-icer salts.

Superplasticizers

The development of superplasticizers (also known as high-range water reducers) in the early 1970s is considered as one of the most significant advances in the recent history of concrete technology. These admixtures, which are generally sulphonated melamine formaldehyde condensates or sulphonated naphthalene formaldehyde condensates, can basically be used for two different purposes. Their first application is the production of flowing concrete (with typical slump values of about 200 mm) which is generally used in difficult placement conditions, for instance when the reinforcing steel in the formwork is very closely spaced. Superplasticizers are also widely used to increase the compressive strength of concrete by allowing a substantial reduction in the water/cement ratio for a given workability. At high dosages, these admixtures allow the making of concretes with compressive strengths that can easily exceed 100 MPa.

In the last 10 years, the freezing and thawing durability of superplasticized concretes has been widely investigated, but it still remains a controversial topic. At first, many studies indicated that air-entrained, superplasticized concretes with normal water/cement ratios (0.40–0.50) could exhibit a very good frost behaviour even if their spacing factor was significantly higher than the commonly accepted 200 μm limit, i.e. 300 μm or even 400 μm (Malhotra, 1981, 1982). It was then tentatively concluded that super-plasticizers had a beneficial effect on the frost resistance of concrete. However, a recent study clearly indicates that superplasticizers have no real influence on the intrinsic resistance of concrete to internal microcracking due to rapid freezing and thawing cycles (Pigeon and Langlois, 1991). This is illustrated in Figure 5.1 which shows the length change of concrete specimens after 300 rapid freezing and thawing cycles versus the spacing factor measured on these specimens for two series of perfectly similar concrete mixtures made with and without a superplasticizer. It can be seen that there is no significant difference between the two series of test results, which means that the critical spacing factor is the same for the superplasticized and the non-superplasticized concretes.

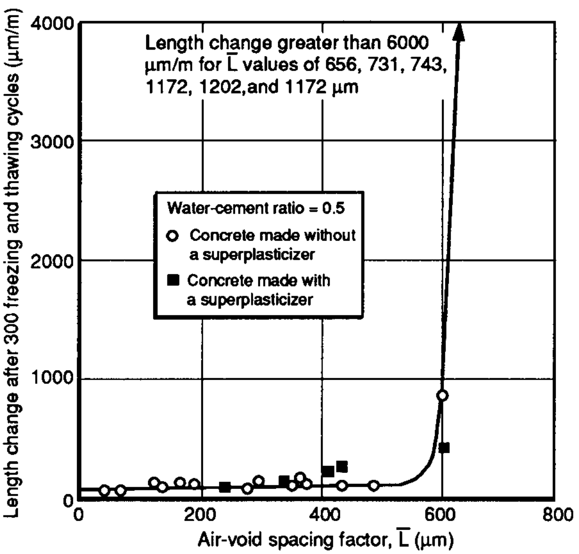


Figure 5.1 Relationship between the length change after 300 freezing and thawing cycles and the spacing factor for an ordinary Portland cement concrete and for the same concrete made with a superplasticizer (after Pigeon and Langlois, 1991).

In fact, the real influence of superplasticizers on the frost durability of concretes with normal water/cement ratios is related to their influence on air entrainment. Superplasticizers can influence both the production and the stability of the air-void system. Superplasticizers can entrain a certain number of air voids, but these voids are generally much larger than those obtained with air-entraining agents (Litvan, 1983; Tognon and Cangiano, 1982). The presence of the larger air voids in superplasticized concretes usually results in a smaller specific surface and, therefore, in a larger spacing factor for a given air content. Since the use of superplasticizers generally tends to produce a higher air content, the dosage of the air-entraining admixture is normally reduced in superplasticized, air-entrained concretes (with a 5–8% air content), which thus generally have spacing factors in the 300–400 μm range, i.e. higher than the usual 200 μm value for non-superplasticized, air-entrained concretes.

The fact that air-entrained, superplasticized concretes often have a spacing factor higher than the generally accepted 200–250 μm limit for the usual range of air contents (5–8%), as many studies have shown, is not necessarily detrimental to the resistance to freezing and thawing cycles. The value of the critical spacing factor (i.e. the maximum value of the spacing factor for which concrete shows no signs of internal microcracking) is often considerably higher than the 200 μm limit, even at freezing rates much higher than those occurring under field conditions. In Figure 3.9 it can be seen that, for the particular concrete and test conditions, the critical spacing factor is approximately 500 μm.

The influence that superplasticizers can have on the value of the spacing factor is much more important when the problem of surface scaling is considered. For concretes having similar spacing factors (and water/cement ratios), there is no reason to believe that the presence of a superplasticizer would have any significant effect on the scaling resistance, although this particular aspect has never really been investigated. However, field performance clearly indicates that, contrary to what is required for protection against internal microcracking due to freezing and thawing cycles, a spacing factor of the order of 200 μm is generally required to protect concrete against de-icer salt scaling (Chapter 7). It is thus important to ensure that superplasticized concretes with normal water/cement ratios (0.40–0.50) exposed to de-icing chemicals will have an adequate spacing factor. Useful information concerning the procedures to follow to ensure that a concrete mixture will have an adequate air-void system with a reasonable air content can be found in Chapter 6.

Other Admixtures

Many different types of admixtures are used in the concrete industry, such as set retarders, accelerators, pumping aids etc. Most of these are generally considered to have little influence on the freezing and thawing resistance of concrete, although very few data have been published on this subject. It should be remembered that the calcium chloride contained in many accelerators is not an anti-freeze product and that it cannot therefore protect the concrete mixture against early freezing.

5.2.3 Mineral Additives

Fly Ash and Blastfurnace Slag

Fly ash and granulated blastfurnace slag are two industrial byproducts that are commonly used as partial replacement for Portland cement. Fly ash has pozzolanic properties (i.e. it chemically reacts with the calcium hydroxide liberated by the hydration of cement to produce calcium silicate hydrates), and slag has hydraulic properties (i.e. when properly activated it reacts with water to form calcium silicate hydrates and other products). Concretes containing fly ash or blastfurnace slag generally have a more refined capillary pore system than ordinary Portland cement concretes. These additives also generally have a slower reaction rate, and can thus have a detrimental effect on the short term mechanical resistance. The long term strength, however, is normally little affected (it is even sometimes improved), as long as proper curing is provided.

The influence of fly ash or blastfurnance slag on the frost durability of concrete, and particularly on the de-icer salt scaling resistance, is still in dispute. As concerns the resistance to freezing and thawing cycles, the contradiction between some of the published test results can probably simply be explained by the slower reaction rate of these products, which means that concretes of different mechanical strengths are often compared. However, for two concretes having the same mechanical resistance, the frost resistance is not expected to be significantly different, because the capillary porosity of concretes containing fly ash or slag, although somewhat higher, is more refined. It seems that the use of fly ash or slag can sometimes modify the rate of deterioration of concretes having an inadequate air-void system, but the resistance of properly air-entrained concretes to freezing and thawing cycles is not detrimentally affected by the use of these materials.

Although it is possible to produce concrete containing significant amounts of fly ash that has an adequate scaling resistance (Bilodeau *et al.,* 1991), many test results indicate that the use of fly ash is detrimental to scaling resistance (Whiting, 1989). Part of the contradiction is again surely related to the slower reaction rate of fly ash, and to the variability of the properties of fly ash from one source to another. Increased bleeding and longer setting times could also increase the porosity of the surface layers and reduce the scaling resistance, but more research is clearly needed to understand the influence of fly ash on the scaling resistance of concrete. Few data have been published on the scaling resistance of concrete containing blastfurnace slag (Klieger and Isberner, 1967), and this subject also warrants further investigation.

Concretes containing very high quantities of fly ash (known as high volume fly ash concretes) are now used for certain applications. The mass of fly ash in these concretes represents close to 60% of the mass of cementitious materials and, with the use of superplasticizers, they can be made at water/binder ratios ranging between 0.27 and 0.38. When they are properly air entrained, these concretes are frost resistant, but they have a poor de-icer salt scaling resistance (Bilodeau and Malhotra, 1992).

Silica Fume

In recent years, silica fume, a byproduct of the silicon and ferro-silicon industry, has become a very common mineral additive. It is generally used as a 5–10% partial replacement for Portland cement and is often utilized in the production of high-strength concrete. The use of silica fume together with high superplasticizer dosages to produce very high-strength concretes (more than 100 MPa) is one of the most significant improvements in the concrete industry since the development of air-entraining agents.

Silica fume is composed of extremely small spherical particles of highly reactive amorphous silica, and thus has very particular and unique characteristics as a mineral additive. It usually contains more than 90% of amorphous silica, the remainder being composed of small quatities of alumina (Al_2O_3), ferrous oxide (Fe_2O_3), carbon (C) and some impurities. Silica fume has both a chemical and a physical action. First, it is an exceptionally high quality pozzolan which reacts chemically with the calcium hydroxide ($Ca(OH)_2$) resulting from the hydration of cement to produce calcium silicate hydrates. However, the most significant effect of silica fume is probably simply related to the very small size of its particles, which have a mean diameter of approximately 0.1 μm (approximately 100 times less than cement grains). These particles are dispersed in the water that surrounds the cement grains and serve as nucleation sites for the calcium silicate hydrates. A more uniform spatial distribution of the hydration products is thus obtained, which leads to a finer pore-size distribution without significantly modifying the total capillary pore volume (when silica fume is used as a partial cement replacement and not as an addition). In very high-strength concretes, the perfectly spherical shape of the silica fume particles allows an easier relative displacement of the solid particles, and it is therefore possible to fabricate concrete mixtures (using also superplasticizers) with extremely low water/cement ratios and sufficient workabilities.

The freezing and thawing behaviour of normal water/cement ratio concretes containing silica fume (the frost resistance of high-strength concrete is discussed in section 5.5) is obviously related to their pore structure. The finer pore-size distribution resulting from the use of silica fume has both a positive and a negative influence. As explained in Chapters 2 and 3, the smaller average size of the capillary pores decreases the total amount of freezable water. On the other hand, the finer pore structure also significantly reduces the permeability of the cement paste. According to Darcy's law, a less permeable paste offers a greater resistance to the liquid flow which correspondingly increases the disruptive internal pressures caused by movement of water through the paste to the air voids during freezing.

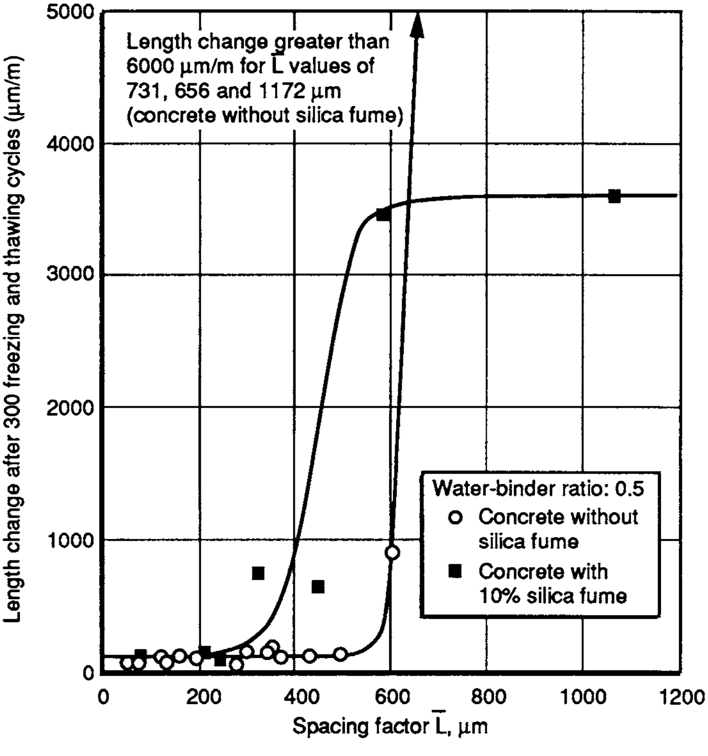


Figure 5.2 Relationship between the length change after 300 freezing and thawing cycles and the spacing factor for an ordinary Portland cement concrete and for the same concrete made with silica fume as partial replacement for Portland cement (after Pigeon *et al.*, 1986).

The overall effect of silica fume, as regards the resistance to internal microcracking, is then a function of the relative importance of the positive influence of the reduced amount of freezable water, and the negative influence of the lower permeability. Figure 5.2 shows the relationship between the length change of concrete specimens after 300 rapid freezing and thawing cycles versus their spacing factor for two series of otherwise similar concrete mixtures (with a 0.5 water/binder ratio) made with and without silica fume (Pigeon *et al.*, 1986). Clearly, in this particular case, the use of silica fume caused a decrease of the value of the critical spacing factor from 500 to 250 μm (when the critical spacing factor is lower, this means that the air voids must be more closely spaced to protect the concrete adequately against internal microcracking). For lower water/cement ratios, the positive effect of the smaller amount of freezable water may become dominant compared to the negative effect of the reduced permeability, which would result in an increase of the critical spacing factor. The influence of the water/cement ratio is discussed in section 5.4.

This negative effect of silica fume on the value of the critical spacing factor is, in part, counterbalanced by the fact that concretes containing silica fume have smaller air voids. This is simply due to the higher viscosity of pastes containing silica fume. Since air entrainment is more difficult (as in low water/cement ratio concretes), a higher dosage of the admixture is used and, for a given air content, these concretes thus generally have a smaller spacing factor than those which do not contain silica fume. It is clear, however, that special care should be taken to ensure that concretes containing silica fume will have a satisfactory spacing factor.

It is sometimes stated in technical publications that silica fume increases the resistance of concrete to freezing and thawing cycles. This belief is usually based on the fact that the deterioration of non-air-entrained concretes containing silica fume subjected to freezing and thawing cycles is generally lower than that of standard non-air-entrained concretes (Gjorv, 1983). This is clearly illustrated in Figure 5.2 which indicates that the length change after 300 rapid freezing and thawing cycles does not exceed 4000 µm/m for concrete mixtures containing silica fume, even with spacing factors larger than 1000 µm. However, the standard mixtures with spacing factors exceeding 700 µm were completely destroyed (length changes larger than 10 000 µm/m). The use of silica fume decreases the permeability of concrete and this can help to explain why it limits the deterioration of non-air-entrained concretes with a poor frost resistance. Nevertheless, it must be emphasized that concretes with normal water/cement ratios that contain silica fume must be air entrained to avoid unacceptable frost damage.

The resistance to de-icer salt scaling of concrete containing silica fume (again at normal water/cement ratios) has been investigated by many researchers. Although some apparently contradictory results are reported in the literature (Sorensen, 1983; Langlois *et al.,* 1989), it seems that, most of the time, the scaling resistance of adequately air-entrained concretes is not very significantly influenced by the presence of silica fume. On one hand, the lower permeability of the cement paste in silica fume concrete can have a positive effect by reducing the penetration of water and of chloride ions. On the other hand, scaling could be amplified because cement pastes containing silica fume generally have a more brittle microstructure (Langlois *et al.,* 1989).

Field tests have confirmed that air-entrained concretes containing silica fume can have a good de-icer salt scaling resistance under natural exposure conditions (Pigeon, 1987). However, special care should be taken when silica fume is used in hot weather concreting because the use of silica fume generally tends to reduce bleeding. Therefore, if the water coming to the surface through bleeding is not sufficient to compensate for the loss of water due to evaporation, plastic shrinkage cracks can appear which will weaken the surface and reduce its salt scaling resistance.

As is the case for the resistance to internal microcracking due to freezing and thawing cycles, it seems that silica fume often has a beneficial effect on the scaling resistance of non-air-entrained concretes. It is clear, however, that air entrainment is still required in normal water/cement ratio concretes containing silica fume to provide a satisfactory resistance against scaling in the presence of de-icing chemicals.

It was mentioned in Chapter 3 that drying can be harmful to the scaling resistance of concrete. However, experimental evidence exists which clearly indicates that the use of silica fume can significantly reduce the detrimental effect of drying on the scaling resistance of concrete (Sorensen, 1983). This observation is of particular interest, considering that most laboratory tests are conducted after a significant drying period. Experimental evidence also suggests that the use of silica fume can reduce the detrimental effect of high curing temperatures (Beaupré, 1987).

There is also some experimental evidence that, for certain concretes, the use of silica fume could have a negative effect on the scaling resistance of molded surfaces of air-entrained concretes (Pigeon, 1989). Although this phenomenon is disquieting, it seems that it cannot be considered as a general rule applicable to all concrete mixtures. Research is still needed to understand better this particular behaviour. It must be remembered that, most of the time, the concrete surfaces exposed to more severe exposure conditions are trowelled surfaces, not molded surfaces.

5.2.4 Other Products

Latex

Since they are very expensive (their price is often more than five times that of standard concretes), latex-modified concretes are usually only used for thin repairs. This type of concrete should be cured for only one day, and then be left to dry, in order to allow the formation of the latex membrane in the capillary pores.

The field performance of latex-modified concrete is generally considered to be very good (Bishara, 1979). This is attributed to its very low permeability, due to the presence of the latex film, and also to the fact that the latex emulsion acts as an air-entraining agent, which thus generally guarantees an adequate air-void system.

The critical spacing factor for one of these concretes was determined by Bordeleau (1990). It was found to be relatively low (at approximately 300 μm), probably because the movement of water to the air voids is difficult in such an impermeable material. The de-icer salt scaling resistance of latex-modified concrete, as determined in the laboratory, is extremely good (Bordeleau *et al.,* 1992). This is also clearly related to its very low permeability, which prevents the saturation of the surface layers.

Micro- and Macrofibres

The use of micro- and macrofibres to enhance various mechanical properties of concrete, particularly the ductility and the toughness, is becoming more and more common. Macrofibre-reinforced concrete, if it is properly air entrained, can have an excellent frost resistance. The presence of macrofibres, however, cannot protect non-air-entrained concrete against frost action. Little is known of the de-icer salt scaling resistance of macrofibrereinforced concrete, but it seems clear that air entrainment is also necessary for good scaling resistance.

The use of microfibres could perhaps enhance the frost and de-icer salt scaling resistance of concrete, but there are no significant data in the literature on this subject.

5.3 FROST BEHAVIOUR OF COARSE AGGREGATES

Aggregates can influence the frost resistance of concrete in two ways. First, unsound aggregates can be deteriorated by the repeated action of freezing and thawing cycles (this deterioration can even lead to the complete disintegration of the aggregate particles disrupted by the freezing of water in their internal pore structure). Second, even sound aggregates (i.e. those which are not intrinsically frost susceptible) can contribute to the deterioration of the structure of the concrete by expelling water into the surrounding cement paste during the freezing period.

Apart from their chemical and mineralogical composition, the frost behaviour of aggregates is mainly related to their pore structure which determines their permeability, the amount of freezable water, and the degree of saturation that can be achieved in given exposure conditions. The size of the particles is another parameter of great importance which will be discussed in the following pages.

5.3.1 Frost Susceptibility of Aggregates

The aggregates that are used for making of concrete, just like cement paste, are porous and can be deteriorated by the action of frost if their internal pores are filled with water. However the pores of aggregates are usually much coarser than those of cement paste. Experimental data suggest that, most of the time, the mechanism of frost action in aggregate particles is in good agreement with that proposed in Powers' hydraulic pressure theory as described in Chapter 2 (Powers, 1955; Larson and Cady, 1969). According to this theory, the 9% increase in volume which accompanies the formation of ice forces the aggregate particles to expand (to accommodate the increase in volume) or to expel the excess water outside the particles. In both cases disruptive pressures are generated inside the aggregate particles and damage occurs when these pressures exceed the tensile strength of the material. These two mechanisms of deterioration point to three basic aggregate properties related to their frost resistance: their **elastic accommodation,** their **critical size** and their **critical degree of saturation**.

Osmotic and thermodynamic effects have also been suggested as possible mechanisms of deterioration (Hudec, 1987). Osmotic pressures and swelling can be generated when de-icing salts have penetrated the aggregate, and water from outside is attracted to the salt water in the pores. This mechanism, however, is not directly related to freezing, and probably only applies to certain types of rocks with very small pores. The flow of unfrozen adsorbed water to the sites of ice formation (a desorption phenomenon very similar to that proposed by Litvan to explain the action of frost in cement paste (Chapter 2)) could explain part of the damage to rock particles. This second mechanism, however, similarly to the hydraulic pressure theory, involves tensile stresses due to the movement of water, and also probably only applies to certain types of rocks with very small pores.

Consider the freezing of water in a closed vessel. Assuming that this vessel is completely filled with water, watertight, and infinitely rigid, the pressure generated in the vessel can reach a value as high as 200 MPa to constrain the expansion of ice when the temperature falls below the freezing point (Cordon, 1966). If it is assumed that the pore water in an aggregate particle is trapped inside and cannot be expelled, this aggregate particle can be considered as a closed vessel which is not, however, infinitely rigid. Part of the pressure caused by the formation of ice will thus be relieved by the elastic deformation of the particle which increases the total volume available to ice. This phenomenon is known as **elastic accommodation**. The pressure associated with ice formation P can then be expressed as a function of both the total amount of freezable water W_f and the elastic properties of the aggregate (E and μ) in the following way (Verbeck and Landgren, 1960):

$$P = \frac{0.09\ W_f E}{3(1 - 2\mu)} \tag{5.1}$$

where P is the internal ice pressure in the aggregate, W_f is the volumetric fraction of freezable water contained in the aggregate, E is the modulus of elasticity of the aggregate, and μ is Poisson's ratio of the aggregate.

Disruption of the aggregate occurs when the pressure due to ice formation P exceeds the tensile strength of the rock. Equation (5.1) is particularly relevant to the case of instantaneous freezing of a completely saturated aggregate. In such a case, water has no time to escape outside and the pressure of the ice can only be relieved by the elastic deformation of the aggregate. For that particular case, the total absorption capacity of the aggregate is of paramount importance since it determines the amount of freezable water when the aggregate is saturated. Verbeck and Landgren have calculated theoretically the ice pressures for three common aggregates with various absorptions. Their calculations indicate that, for a quartzite aggregate with a very low absorption (0.1%), the pressure due to the growth of ice is relatively small (5.4 MPa) and can be accommodated since it remains lower than the tensile strength of the aggregate. However these pressures can reach 117 MPa for chert (with a 2.1% absorption) and 241 MPa for dolomite (with a 6.7% absorption), and thus well exceed the tensile strength of the aggregate (of the order of 10 MPa) and cause its fracture.

Instantaneous freezing is an extreme condition and, of course, the rate of cooling is never infinite. When freezing is more gradual, the expulsion of water outside the aggregate can also contribute significantly to the relaxation of the pressures caused by the growth of ice crystals. The forced expulsion of water outside the aggregate induces internal hydraulic pressures in accordance with Darcy's law on the flow of liquid through a porous continuum (Powers, 1949). The magnitude of these pressures is a function of the total porosity, the degree of saturation, the permeability and the size of the aggregate particle. Assuming, for simplicity, that both the propagation of freezing and the expulsion of water are unidirectional (i.e. the formation of ice on one side of the particle forces the water to travel through the particle towards the other side as shown in Figure 5.3), the maximum hydraulic pressure inside a fully saturated aggregate particle is then given by the following relationship (Verbeck and Landgren, 1960):

$$P_{\max} = \frac{0.09\,L}{K}\,\frac{\partial W_{\mathrm{f}}}{\partial t} \times (\mathrm{constant}) \tag{5.2}$$

where $P_{\max}$ is the maximum hydraulic pressure inside the aggregate, L is the dimension of the aggregate (in the direction of freezing), K is the coefficient of permeability, and $\partial W_{\mathrm{f}/\partial t}$ is the rate of freezing of water, i.e. the total pore volume multiplied by the rate of linear propagation of freezing. Disruption occurs when the hydraulic pressure exceeds the tensile strength of the aggregate.

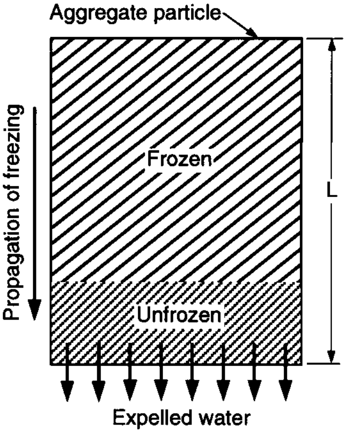


Figure 5.3 Schematic illustration of the internal hydraulic pressures caused by the forced movement of freezable water through aggregate particles during freezing (after Verbeck and Landgren, 1960).

Equation (5.2) indicates that the hydraulic pressure generated is directly proportional to the dimension of the particle (this dimension represents the maximum distance that water must travel to be expelled from the aggregate particle). Since failure only occurs when the hydraulic pressure exceeds the tensile strength of the aggregate, it is possible to define a **critical size of particle** below which the aggregate will be frost resistant. On the contrary, particles larger than the critical size will suffer severe deterioration when exposed to freezing and thawing cycles while fully saturated. Assuming that the aggregate is unconfined (i.e. that expulsion of water from the aggregate is not restricted), this critical size can be estimated by rearranging (5.2) (Verbeck and Landgren, 1960):

$$L_{\max} = \frac{K\,T}{0.09\,\dfrac{\partial W_{\mathrm{f}}}{\partial t}} \times \frac{1}{\mathrm{constant}} \tag{5.3}$$

where $L_{\max}$ is the maximum permissible size of the particles, and T is the tensile strength of the aggregate.

The critical size L_{max} is thus a function of the permeability K and the tensile strength of the aggregate T, of the amount of freezable water W_f, and of the rate of cooling. The results of theoretical computations by Verbeck and Landgren for a chert-type aggregate (with a 2.1% absorption and a coefficient of permeability of 1×10^{-10} cm/s) and a dolomite(with a 6.7% absorption and a coefficient of permeability of 300×10^{-10} cm/s) assuming a freezing rate of about 4 cm/h (which is similar to the maximum freezing rate occurring in nature) indicate that chert particles larger than 1.2 cm are frost susceptible, while the dolomite is immune to frost action even for particles as large as 85 cm. Although its total porosity is about three times larger than that of chert (6.7% compared to 2.1%), the dolomite is less frost susceptible because its permeability is about 300 times larger which significantly reduces the internal hydraulic pressures. This illustrates very clearly that the frost durability of an aggregate particle is not only a function of its total porosity (which determines the amount of freezable water) but also of its permeability. The concept of the critical size is supported by experimental evidence. From a practical point of view, it is particularly useful since it determines, for each aggregate, the maximum size of particle that can safely be used for making concrete.

It will be remembered that, in the hydraulic pressure theory (Chapter 2), the freezing rate is in degrees per hour and not in centimetres per hour. This basically stems from the fact that the pores of the aggregates are usually much larger than those of the cement paste. Water therefore freezes in the pores of the aggregates as soon as the temperature falls below the freezing point. In the paste, however, the formation of ice increases only gradually with the decrease in temperature, both because the water in the paste contains dissolved chemicals and because surface forces are important and restrict ice formation. In the hydraulic pressure theory as it is applied to cement paste, it is therefore considered that, at a given point in the paste, the formation of ice increases with the decrease in temperature, and that the amount of water expelled from the capillary pores is related to the rate at which the temperature decreases. In aggregates, since water freezes almost immediately when the temperature drops below freezing point, it is the rate at which frost penetrates that is important. This is why the rate of freezing is in centimetres per hour.

In the previous discussion it was assumed that water can freely be expelled outside the aggregate particles during freezing but, in concrete, the movement of this water is restricted by the confining effect of the surrounding cement paste (or mortar). In these conditions the rate of water expulsion is governed by the freezing rate and the porosity of the aggregate (which determines the amount of freezable water), as well as by the permeability of the cement paste (more permeable pastes allowing an easier expulsion of water) and the presence of escape boundaries (usually air voids) that accommodate the volume of expelled water in the mortar fraction. Empty capillary pores and cracks can also act as escape boundaries but, in a fully saturated concrete, the air voids are usually the only spaces available to expelled water. When both the permeability of the cement paste and the number of escape boundaries are small, the hydraulic pressures built up inside the aggregate particles tend to be higher because the expulsion of water is restricted. This means that an aggregate which is frost resistant when exposed to unconfined freezing can be deleterious when used in making concrete. On the other hand, the use of air entrainment and of more permeable pastes has a positive influence on the frost resistance of aggregates in concrete (although, as will be seen later, more permeable pastes facilitate the saturation of the aggregate particles). The size of the aggregate particles is also important because larger particles expel a larger amount of water per unit area of escape surface which increases the water flow and thus the associated hydraulic pressures.

Of course, the expulsion of water induces disruptive stresses in the surrounding cement paste also, and damage to the concrete body due to freezing and thawing cycles can occur even if the aggregate itself is frost resistant. To assess roughly the distance that expelled water must travel into the surrounding paste, consider a cubic aggregate particle subjected to unidirectional freezing perpendicular to the concrete surface exposed to frost (Figure 5.4). Assuming that the air voids are uniformly distributed in the cement paste and that equal amounts of water are expelled from the other five surfaces of the cube, the required distance can be obtained from the following equation on the basis of simple volumetric considerations (Verbeck and Landgren, 1960):

$$\Delta L = \frac{0.09\, W_f L}{5\, A} \tag{5.4}$$

where ΔL is the distance required for volumetric accommodation, L is the dimension of the aggregate cube, W_f is the total amount of freezable water, and A is the air content of the cement paste (fractional).

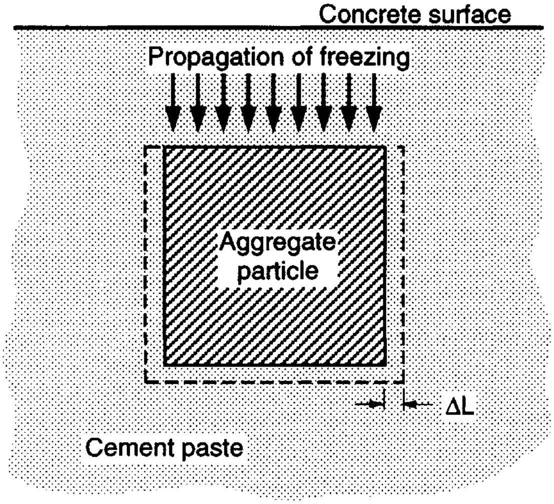


Figure 5.4 Schematic illustration of a cubic aggregate particle subjected to unidirectional freezing perpendicular to the concrete surface exposed to frost (after Verbeck and Landgren, 1960).

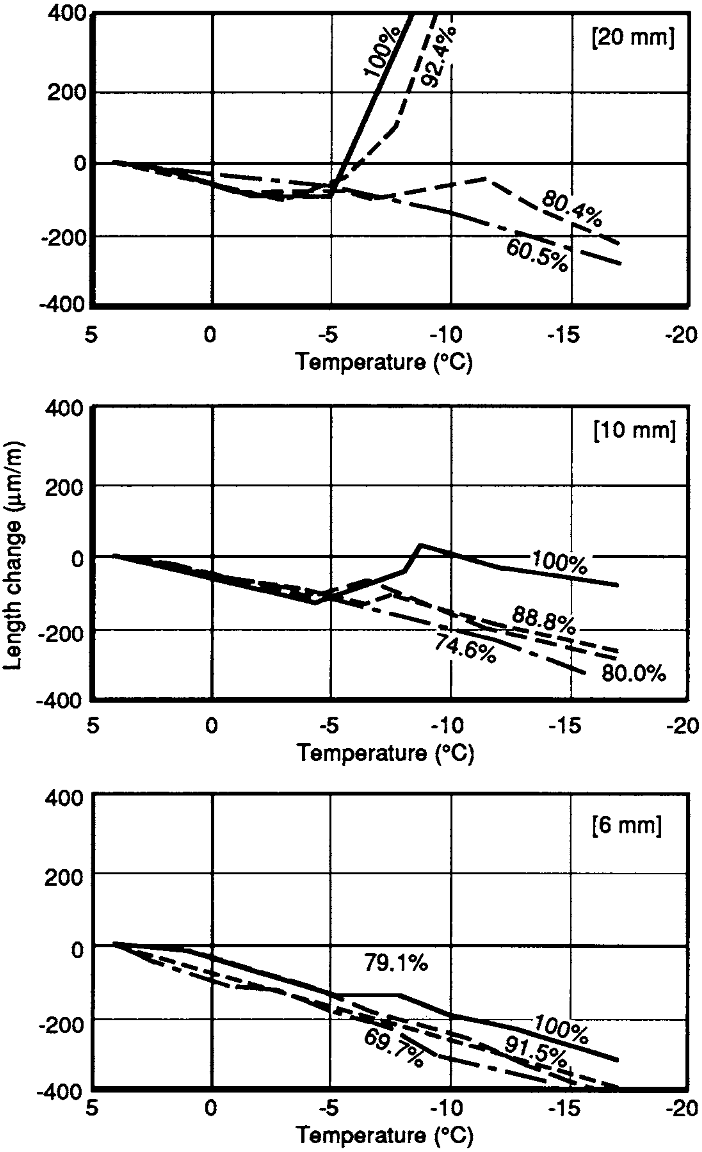


Figure 5.5 Influence of the maximum size of aggregates and of the degree of saturation (%) on the length change of a 0.5 water/cement ratio concrete during freezing, (after Maclnnis and Lau, 1971).

Verbeck and Landgren have calculated the required expulsion distance ΔL for various sizes of chert and dolomite aggregates. For small particles of the chert aggregate having an intermediate porosity (2.1% absorption), ΔL ranges from about 40 µm (for a 6 mm cube) to 150 μm (for a 25 mm cube) if it is assumed that 18% of the cement paste volume is occupied by air voids. These values are relatively small and remain below the limit of 200–250 μm usually recommended for the protection of cement paste against frost action (although, as previously explained, failure can occur for chert particles larger than 1.2 cm solely due to the internal hydraulic pressures produced at a 4 cm/h freezing rate). However, for the dolomite aggregate with a high porosity (6.7% absorption), the value of ΔL ranges from 100 μm (for a 6 mm cube) to 400 μm (for a 25 mm cube) which is not negligible and can possibly contribute to the deterioration of the cement paste. These considerations on the confining effect of cement paste clearly indicate that the maximum allowable size of an aggregate is not only a function of the characteristics of the aggregate itself, but also of the characteristics of the confining cement paste (Figure 5.5).

In the above discussion it was assumed, for simplicity, that the aggregates were fully saturated or nearly so. The magnitude of the hydraulic pressures, the required expulsion distance in the cement paste and the critical size of the aggregates are of course different when the aggregates are not fully saturated at the time of freezing. Theoretically, the aggregates should be immune to frost when the degree of saturation is below 91.7% because, in this case, the pore system contains enough empty spaces to accommodate the increase in volume of the water due to the formation of ice. In the relatively few cases where the disruptive stresses do not primarily originate from ice formation but from thermodynamic disequilibrium (as sometimes happens for very fine-grained aggregates for which the surface forces inside the pore system are predominant), these stresses can exist even for degrees of saturation smaller than 91.7%. For a given aggregate, with a given maximum nominal size, embedded in a given cement paste (with a given permeability and air content) and exposed to a given rate of cooling, a **critical degree of saturation** can be defined below which this aggregate can be considered to be frost resistant. The durability of a concrete made with this aggregate will be strongly related to the ability of this aggregate to maintain a degree of saturation smaller than the critical level **under natural exposure conditions**. The durability of an aggregate is therefore not an intrinsic property, but is a function of many parameters other than those related to the aggregate itself (pore structure, permeability, mechanical properties, size of particles etc.), such as the characteristics of the cementitious matrix (porosity, permeability, air content etc.), and the exposure conditions (relative humidity, rate of cooling etc.).

5.3.2 Influence of the Porosity of Aggregates

The porosity of aggregates is, without a doubt, one of their most important characteristics. Many studies have shown that the frost behaviour of aggregates is mainly related to the characteristics of their pore system. In the past, the frost durability of coarse aggregates was generally considered to be related mainly to their total absorption (or total porosity), but it is now commonly agreed that this durability is strongly dependent on pore-size distribution and not only on total pore volume. Howe (1910) was the first to suggest that the size of pores was more important than total porosity. Since then, many investigators have found that aggregates containing a large volume of pores smaller than approximately 4–5 μm generally have a poor frost resistance (Schaffer, 1932; Sweet, 1948; Blanks, 1949; Fears, 1950; Lewis *et al.,* 1953).

The detrimental influence of small pores can be explained in part by the fact that, according to Kelvin's law (Chapter 2), the natural ability of an aggregate to achieve a high degree of saturation is a function of the mean pore size. Figure 5.6 shows the relationship between relative humidity and degree of saturation for four different aggregates. Clearly, aggregates having fine pores, such as the traprock, can achieve a high degree of saturation at a relatively low relative humidity level, but the degree of saturation of aggregates with a relatively coarse pore system, such as the dolomite, decreases very rapidly with a decrease in relative humidity. Part of the detrimental influence of small pores is also due to the fact that aggregates with small pores usually have a low permeability. This means that the hydraulic pressures generated when water is expelled from the aggregate are higher.

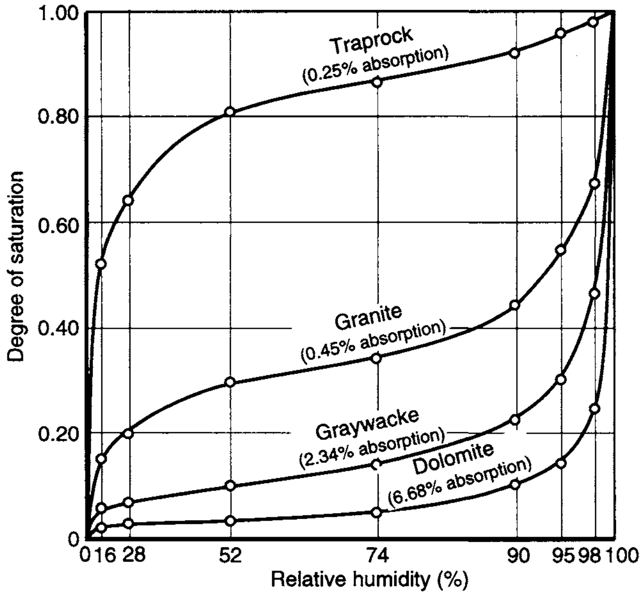


Figure 5.6 Relationship between the relative humidity and the degree of saturation for four different types of aggregates (after Verbeck and Landgren, 1960).

The rate at which an aggregate can absorb water is inversely proportional to the size of the pores (and it can be shown that this is particularly significant when the relative humidity is high). Practically, this means that aggregates containing small pores become more easily saturated, under field conditions, than those containing coarser pores which is, of course, detrimental to their frost resistance. Hudec (1989), for instance, has demonstrated that a carbonate limestone aggregate with a fine-grained pore system absorbs water approximately two times faster than a similar aggregate with a coarser pore-size distribution.

Aggregates differ not only in their pore-size distribution but also in their total porosity (or absorption). For a given pore-size distribution, the time required to reach a critical degree of saturation is directly proportional to the total porosity. For example, an aggregate having a 15% porosity would require three times as long to increase the internal humidity as a similar aggregate having the same pore-size distribution but a 5% porosity. This could be significant because, if an aggregate having a 5% porosity requires 3 months to achieve a critical degree of saturation, an aggregate with a 15% porosity would then require 9 months to reach the same level. If the additional 6 months were sufficient to take the concrete through the critical wetting season, the aggregate could never in these conditions reach the critical degree of saturation and a satisfactory performance could be expected. From a practical point of view, however, one would generally prefer an aggregate with a low absorption in order to limit the amount of water expelled from the aggregate into the paste during freezing.

The influence of the porosity of aggregates on the frost resistance of concrete was particularly well demonstrated by Kaneuji *et al.* (1980) who made concretes with 14 different types of aggregates and subjected these concretes to 300 rapid cycles of freezing and thawing in water according to ASTM Standard C 666. These aggregates were carefully chosen to cover a wide range of pore characteristics. Figure 5.7 shows different pore-size distribution curves with the corresponding durability factors obtained from the freezing and thawing tests (the higher the durability factor, the better the frost resistance). The data indicate that for aggregates having a similar total pore volume, those with the finer pore systems are generally less durable: the durability factor ranges from 3.4% for the finer-grained aggregate to 27.2% for the coarser one. Concurrently, the data in Figure 5.8 confirm that, for aggregates having approximately the same pore-size distribution, those having a higher total porosity are less durable.

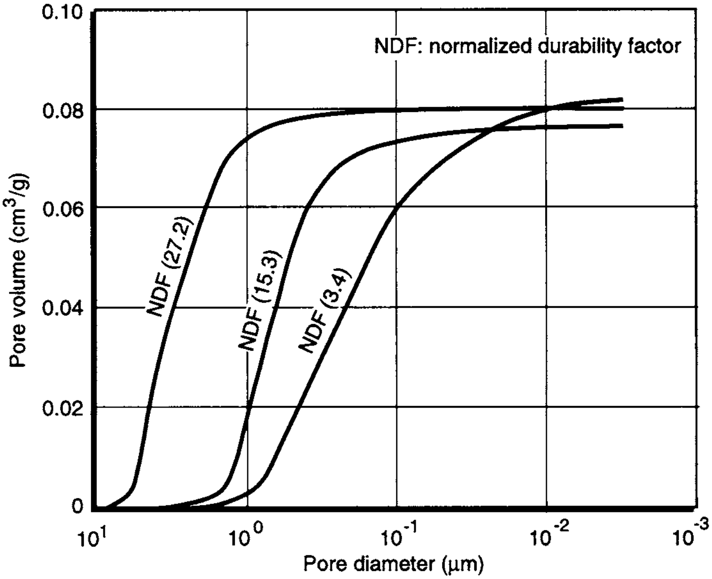


Figure 5.7 Test results showing the improvement in concrete frost durability (NDF) with the increase in the average aggregate pore size for a constant value of the total aggregate porosity (each curve represents the pore-size distribution of a given aggregate) (after Kaneuji *et al.,* 1980).

Based on their results, Kaneuji *et al.* have proposed the ‘expected durability factor’ concept to assess the frost durability of coarse aggregates. This factor can be calculated from the known values of the total pore volume and of the median pore diameter by using the relationship

$$\mathrm{EDF} = \frac{0.579}{\mathrm{PV}} + 6.12\ \mathrm{MD} + 3.04 \tag{5.5}$$

where EDF is the expected durability factor of concrete, PV is the total pore volume of coarse aggregate (in cm^3/g), and MD is the median diameter of the pores contained in the coarse aggregate (in μm).

The testing of approximately 30 different aggregates taken from existing structures showing different levels of deterioration led the authors to consider that an aggregate will not be harmful to the frost resistance of concrete when EDF is greater than 40. Figure 5.9 indicates, on the basis of this criterion, the various possible combinations of total pore volume and median pore diameter for durable as well as non-durable aggregates. It also shows that aggregates generally do not affect the frost resistance of concrete when the total pore volume is lower than approximately 0.015 cm3/g (i.e. when the total absorption is less than 1.5%).

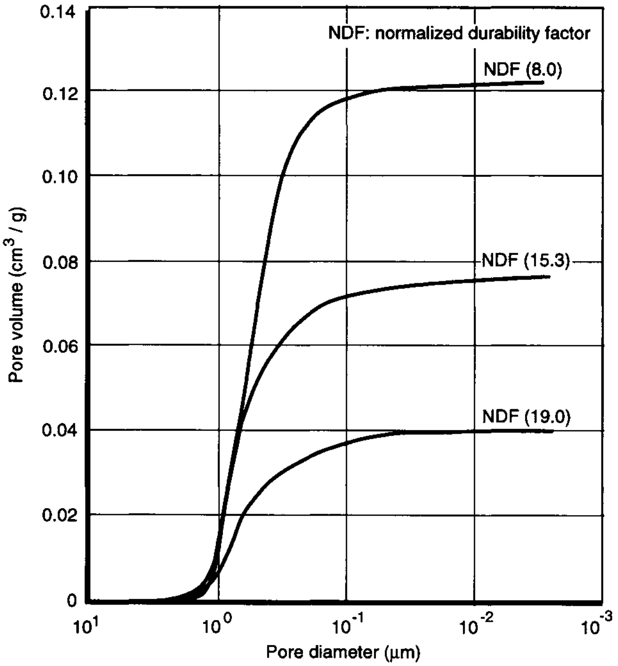


Figure 5.8 Test results showing the improvement in concrete frost durability (NDF) with the decrease in the total aggregate porosity for a constant value of the average poresize; each curve represents the pore-size distribution of a given aggregate (after Kaneuji *et al.*, 1980).

The influence of the porosity of coarse aggregates on the frost resistance of concrete can be summarized by dividing the aggregates into three categories. The first category contains **aggregates with a very low porosity**. These aggregates are generally highly frost resistant because, even when they are fully saturated, they only contain a negligible amount of freezable water which is not sufficient to develop significant stresses inside the particle or in the surrounding cement paste.

The second category contains **highly porous aggregates**. When these aggregates are tested in the laboratory under severe conditions (i.e. fully saturated or nearly so), they may show a poor frost resistance because they contain a large amount of freezable water (Walker and Hsieh, 1968). But they do not necessarily break upon freezing because they often have the ability to expel water easily without generating excessive hydraulic pressures (Verbeck and Landgren, 1960). However, when these aggregates (with a high degree of saturation) are used to make concrete in the laboratory, the concretes are often found to be non-durable because the cement paste does not contain enough air voids to accommodate properly the large amount of water expelled from the rock particles (Schuster, 1961). Nevertheless, field experience has demonstrated that, most of the time, these aggregates have a good service record simply because they usually never become critically saturated under field conditions. This can be explained by the fact that highly porous aggregates generally have a

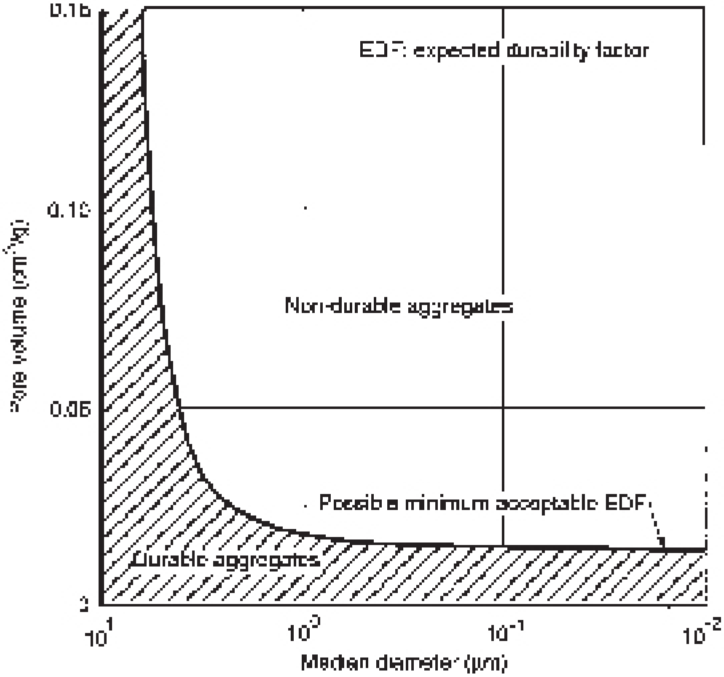


Figure 5.9 Diagram of the median aggregate pore diameter versus the total pore volume of the aggregate showing the limit between durable and nondurable aggregates (after Kaneuji *et al.,* 1980).

coarse-textured pore system which is easily drained as soon as the relative humidity decreases below 100%. It is also difficult to resaturate these highly porous aggregates because, considering the low permeability of cement paste and the large volume occupied by these pores, the time required to achieve a high degree of saturation can be longer than the period of time during which concrete will be exposed to the moist environment.

The third category contains a large variety of aggregates with an **intermediate porosity**. Most of the aggregates which have a very poor frost resistance generally fall into this last category. These frost-susceptible aggregates often contain pores which are large enough to permit water to enter but not large enough to allow an easy drainage when ice crystals are formed in their inner pore structure. Their frost durability is, as previously mentioned, strongly related to their ability to become critically saturated under field exposure and, of course, also depends on the characteristics of the surrounding mortar. These characteristics are particularly important for the performance of the aggregates of intermediate porosity. The pores in the aggregates are usually much larger than the capillary pores in the cement paste, and self-desiccation due to cement hydration always creates empty spaces which tend to be filled by the water contained in the aggregate pore system (this can occur even with concrete made with saturated aggregates and kept in a moist environment). When the mortar is dense and has a low permeability, water from outside cannot easily resaturate the aggregates. Furthermore, any decrease of the ambiant relative humidity will first reduce the degree of saturation of the aggregate pores which are larger than those of the cement paste. However, if the aggregates do become saturated, the lower permeability of the cement paste will increase the hydraulic pressures. In this case, air entrainment can help to relieve the pressures to a certain extent, but it will be remembered that only the air voids close to the aggregate—paste interface can be of help since the distance that water can travel in the cement paste is relatively small.

5.3.3 Surface Deterioration due to Aggregates and D-Line Cracking

In addition to pop-outs (described in Chapter 3) which are due to the presence of soft or laminated aggregates such as shale close to the surface of the concrete, another form of deterioration due to frost action is directly related to the presence of aggregates near the finished surface of concrete. This common phenomenon (referred to as type II pop-outs in Chapter 3) can occur when a saturated aggregate particle located just a few millimetres below the surface is subjected to freezing. In this case, the water expelled from the aggregate towards the surface creates disruptive pressures inside the thin layer of mortar above the aggregate particle. If these disruptive pressures are large enough, the mortar layer will break away leaving a shallow depression over the particle as illustrated in Figure 3.4. Even if it does not affect the structural integrity of the concrete, this type of deterioration damages the appearance of the concrete. This phenomenon is related to the characteristics of the inner pore structure of the aggregates, and also to the characteristics of the transition zone between the paste and the aggregates. Aggregates having a high porosity are the most likely to cause type II pop-outs because they can expel a relatively high amount of water. The size of the aggregate particles is also important. The use of smaller particles reduces the risks involved because the amount of water expelled per unit surface area is correspondingly reduced.

The occurrence of this type of deterioration (type II pop-outs) is not only related to the characteristics of the aggregate itself but also to the characteristics of the mortar cover. The use of a low water/cement ratio significantly reduces the permeability of cement paste and correspondingly reduces the probability that the aggregate particle will become critically saturated under natural exposure conditions. An increase of the cover thickness will have the same effect. Table 5.1 shows the results obtained by Verbeck and Landgren (1960) for the same dolomite aggregate (with a 6.68% absorption) used in the making of two concrete mixtures (with water/cement ratios of 0.70 and 0.45) and three different mortar cover thicknesses (3, 6 and 9 mm). The table gives the number of days of wetting required to produce failure of the mortar cover when subjected to freezing. This number ranges from 111 days (for a 0.70 water/cement ratio and a 3 mm mortar cover) to 980 days (for a 0.45 water/cement ratio and a 9 mm mortar cover). The differences are significant and are of practical importance because deterioration will occur only if, under field conditions, the concrete is kept at a high humidity level for a period sufficiently long for the aggregates to become critically saturated. Of course, it is not really possible to control the mortar cover in practice, but the data in Table 5.1 indicate that the water/cement ratio exerts a great influence, especially for the smaller cover thicknesses (for a 3 mm mortar cover, the period of wetting before failure moves from 111 days for a 0.70 water/cement ratio to 477 days for a 0.45 water/cement ratio). However, the use of a low water/cement ratio cannot prevent a really poor aggregate from creating frost damage.

Table 5.1 Number of days required for a dolomite aggregate to reach the degree of saturation which will cause failure of the mortar cover during freezing, as a function of the water/cement ratio and the thickness of the mortar cover (after Verbeck and Landgren, 1960).

Water/cement ratio (by mass)	Permeability ($\times 10^{-9}$ cm/s)	Days of wetting sustained before failure (pop-out) at various thicknesses of mortar cover		
		3 mm	6 mm	9 mm
0.70	3000	111	879	792
0.45	1	477	885	980

Another type of deterioration often related to coarse aggregates is D-line cracking. D-line cracking (briefly described in Chapter 3) is defined by the *ACI Manual of Concrete Practice* as ‘a series of cracks in concrete near and roughly parallel to joints, edges and structural cracks’ (Figure 3.1). D-line cracking, which is not merely a surface problem but, most of the time, goes through the entire thickness of the concrete slab, very often results from the volume change of coarse aggregates (or the expulsion of water at the aggregate–paste interface) during freezing. The increased volume of the aggregate during freezing (due to ice formation in the inner pore system), or the expulsion of water, creates disruptive stresses in the surrounding cement paste which produce microcracks. The repetition of freezing and thawing cycles causes the propagation of these microcracks which progressively coalesce to form macrocracks and then become apparent at the surface of the concrete slab. The phenomenon is generally very slow, and sometimes more than 15 years will be required for macrocracking to be observed at the surface of the concrete. D-line cracking is generally observed near gutters, joints, and edges or structural cracks, simply because these locations usually provide a higher level of relative humidity. Concrete structures which are frequently exposed to wetting, such as roads and airfields, are thus particularly affected by this type of deterioration.

The use of low water/cement ratios can be helpful in preventing D-line cracking, because the saturation of aggregates is more difficult when the paste is less permeable. Calcareous and siliceous sedimentary rocks are generally considered as the types of aggregates most likely to cause D-line cracking. With certain aggregates, D-line cracking may even occur without any freezing and thawing cycles, since the volume changes of the particles due to wetting and drying cycles are sufficient to initiate microcracks. If they are present in sufficient number, aggregate particles that cause pop-outs can also be expected to cause D-line cracking, but particles that cause D-line cracking do not necessarily cause pop-outs. D-line cracking is less likely to occur with smaller particles, because the total amount of water expelled from the particle per unit area (and thus the disruptive stresses generated into the mortar fraction) is lower.

5.3.4 Petrographic Nature of Aggregates

The vast majority of aggregates likely to cause problems when exposed to freezing and thawing cycles are in the family of sedimentary rocks. Very few igneous or metamorphic rocks have been found to be significantly affected by the action of frost, most probably because these rocks usually have a very low porosity. Granites, basalts and marbles are good examples of rocks which are generally highly frost resistant. However, the frost susceptibility of an aggregate can be related to the presence of only a relatively small number of frost-susceptible particles (often less than 20%). Sometimes, 5–10% of deleterious particles in the aggregate is sufficient to cause significant damage (Larson and Cady, 1969).

Non-durable aggregates are usually characterized by a low bulk specific gravity, a high porosity (or absorptivity), and a large number of small pores, and they can achieve a high degree of saturation relatively easily under field conditions. Cherts are often mentioned as one of the most common unsound aggregates. Their poor behaviour is mainly due to the combination of a relatively high porosity (often larger than 4%), a fine-grained pore structure and a low permeability. Pop-outs and D-line cracking are frequent when chert is present. It is therefore generally agreed that chert should be avoided as much as possible in the making of concrete subjected to freezing and thawing cycles (Lewis *et al.,* 1953; Schuster, 1961; Larson and Cady, 1969; Walker *et al.,* 1969). Unsound aggregates also include a variety of shales, limestones (and especially limestones with laminae of expansive clay), sandstones and dolomites (Cordon, 1966). Aggregates containing clay minerals, particularly of the montmorillonite or illite group, can also be deleterious because they have a high swelling potential during the wetting period. For example a dolomite has been found to produce a 0.06% volume expansion during wetting and drying cycles, and concrete containing such an aggregate would certainly not be able to withstand freezing and thawing cycles (Neville, 1983). The presence of organic impurities, coal, wood and soft particles can also cause pitting and scaling, even when they are present in small quantities, mainly because these particles are very absorptive and have a high swelling potential. It is recommended to limit these particles to 1% of the total mass of the aggregate. The number of unsound particles in the aggregate is limited in many codes of practice. ASTM Standard C 33, for instance, limits the total amount of clay lumps, friable particles, and chert to values ranging from 3% to 10%, as a function of the type of structure and the degree of exposure. These unsound particles are usually found in natural aggregate deposits, and are much less frequently encountered in crushed aggregates.

5.4 INFLUENCE OF MIX COMPOSITION

5.4.1 Water/cement ratio

The overall quality of cement paste is strongly dependent upon its water/cement ratio and, like most of its other properties, the freezing and thawing durability of concrete is greatly influenced by this value. Basically, the water/cement ratio determines the characteristics of the capillary pore system, i.e. not only the volume, but also the size distribution of the pores. For high values of water/cement ratio, the cement grains are relatively distant from one another, and some of the space located at mid-distance between the grains will never be filled by hydration products. For smaller values, however, the cement grains are closer together, and the volume occupied by the larger pores is very significantly reduced, while the size distribution of the very small capillaries remains much the same (Mehta and Manmohan, 1980). The porosity of cement paste, and particularly the size distribution of the capillary pores, significantly influences the resistance of concrete against internal cracking due to freezing and thawing cycles. The reduction of the water/cement ratio decreases the amount of freezable water, as well as the permeability of the paste, and increases the mechanical resistance. The reduction in freezable water content and the increase in strength both contribute to the enhanced frost resistance of concrete. However, the reduction in permeability is harmful, since the paste offers a greater resistance to the flow of the water being forced out of the capillaries during freezing, and the internal disruptive pressures caused by this flow are thus increased (Chapter 2). The resulting effect of a reduction of the water/cement ratio then depends on the relative importance of the positive influence of the reduced amount of freezable water (and increased mechanical resistance) compared to the negative influence of the reduced permeability.

As an example, consider the critical spacing factor $\bar{L}_{\mathrm{crit}}$ values in Table 3.1 for the ordinary Portland cement concretes (subjected to 300 rapid freezing and thawing cycles in water after an initial moist curing period of 14 days). In this particular case, the reduction of the water/cement ratio from 0.5 to 0.3 was slightly detrimental to the frost durability since $\bar{L}_{\mathrm{crit}}$ was decreased from 500 to 400 μm, which means that the air voids had to be more closely spaced to protect the cement paste against internal microcracking caused by freezing and thawing cycles. This can be explained by the fact that the decrease in permeability had more influence than the reduction of the freezable water content; but when the water/cement ratio was lowered to 0.25, $\bar{L}_{\mathrm{crit}}$ increased to 750 μm, i.e. the paste became less sensitive to frost action. In this case, the reduction of the freezable water content had a much more significant effect than the decrease in permeability. If the water/cement ratio is sufficiently low, the amount of freezable water can become so small that the concrete can be frost resistant even without air entrainment. This is the case for certain very high-strength concretes (section 5.5).

The preceding remarks relate mainly to the protection of concrete against internal microcracking, but the concepts discussed are still valid when surface scaling is considered. However, contrary to the case of internal microcracking, a lower permeability is not necessarily detrimental to the scaling resistance, and can even be helpful in preventing the ingress of water and dissolved de-icer salts into the concrete. Permeability increases rapidly with the water/cement ratio. A high water/cement ratio can therefore be very harmful because it not only facilitates the ingress of dissolved salts, but also the saturation of the surface layers. The high degree of saturation of these layers can be particularly harmful if the concrete contains aggregates that are frost susceptible and can cause pop-outs or other scaling problems when they are saturated. The water/cement ratio is limited by many codes of practice to a maximum value of 0.45 for concretes exposed to scaling in the presence of de-icing chemicals. A relatively low water/cement ratio also ensures a good mechanical resistance.

5.4.2 Mixture proportions

With the exception of the water/cement ratio, the relative proportions of the constituents (cement, fine and coarse aggregates) generally do not have any significant influence on the frost resistance of properly designed concrete mixtures. The frost resistance could, however, be detrimentally affected by any deficiency in the composition which causes non-homogeneity of the mixture such as segregation, or excessive bleeding. Poor compaction, or any other flaw resulting in the production of poor quality concrete, can also be harmful. Although cement content itself does not really influence the frost behaviour of concrete, it is generally considered good practice to specify a minimum cement content to provide a reasonable assurance that the concrete will have a proper quality.

5.5 HIGH-STRENGTH CONCRETE

Since the mid-1980s, the use of high-strength concrete has become one of the most promising developments in the field of concrete technology. High compressive strengths (60 MPa and over) are normally achieved with the use of very low water/cement ratios, which requires large amounts of superplasticizer. It is also common to use silica fume (or other mineral additives) as partial replacement for Portland cement. In 1975, a 60 MPa concrete was used for the construction of the Water Tower Place in Chicago. In 1988, a 70-storey concrete building was constructed in Toronto using a concrete with an average strength of 85 MPa at 28 days (Aïtcin and Laplante, 1992). In 1989, the concrete delivered for the construction of a high rise building in Seattle had a measured 28 day compressive strength of 131 MPa. It is believed that, in the near future, it will be possible to produce a 150 MPa concrete using conventional concrete plants and standard rotating drum ready-mix trucks. In the laboratory, although under special conditions almost impossible to reproduce in the field at the present time, 200–800 MPa concretes have already been produced (Richard and Cheyrezy, 1994).

There is no clear distinction between normal concretes and so-called high-strength concretes. Nevertheless, the line can be roughly drawn at about 60 MPa, which generally corresponds to a water/cement ratio of approximately 0.35. Concretes with a compressive strength greater than about 100 MPa are often called ultra high-strength concretes. These concretes are generally obtained with water/cement ratios lower than 0.25. At the present time, it is not possible to define an absolute minimum value for the water/cement (or water/binder) ratio. It can be said, however, that, although high-strength concrete will probably become a common construction material over the next few years, ultra high-strength concrete will only be used for very special applications.

The freezing and thawing behaviour of high-strength concretes is still disputed, but, basically, their frost durability is related mainly to their low water/cement ratio. If the water/cement ratio is sufficiently low, the amount of freezable water can be so small that the concrete will be immune to frost action even if it is not air entrained. The real question for these concretes, then, is to determine if air entrainment is still required as a protection against internal microcracking due to cycles of freezing and thawing. In addition, the resistance against de-icer salt scaling must also be verified.

A number of investigations have been conducted to study the frost resistance of high-strength concretes. Okada *et al.* (1981) have subjected concrete mixtures with different water/cement ratios and various values of the spacing factor to 300 rapid freezing and thawing cycles in water according to the ASTM C 666 (procedure A) test method. The results obtained are shown in Figure 5.10. The line gives the value of the critical spacing factor as a function of the water/cement ratio, considering that concretes with a durability factor higher than 90% are frost resistant. Clearly, the critical spacing factor increases rapidly with the reduction of the water/cement ratio. All concretes with a water/cement ratio lower than 0.35 (and a compressive strength higher than 80 MPa) can be considered frost resistant, including non-air-entrained concretes with spacing factors greater than 900 μm.

In another study, non-air-entrained concretes having a water/binder ratio of 0.25 and containing up to 30% silica fume as partial replacement for Portland cement were found to be frost resistant, even for spacing factors greater than 750 μm (Yamato *et al.,* 1988). However the same study concluded that air entrainment was still required for water/cement ratios higher than 0.35. Kobayashi *et al.* (1981) tested a large number of concretes having different water/cement ratios (0.27, 0.32, 0.42 and 0.55) and different spacing factors. Their results are summarized in Figure 5.11, which shows the relationship between the critical spacing factor and the water/cement ratio. These results are in relatively good agreement with those obtained by Foy *et al.* (1988) who measured a critical spacing factor of 750 μm for a 0.25 water/cement ratio concrete, and those obtained by Gagné *et al.* (1990) who concluded that the critical spacing factor was higher than 800 μm for similar concretes made with a high early strength Portland cement. All these results indicate that air entrainment is not required when the water/cement ratio is smaller than 0.25.

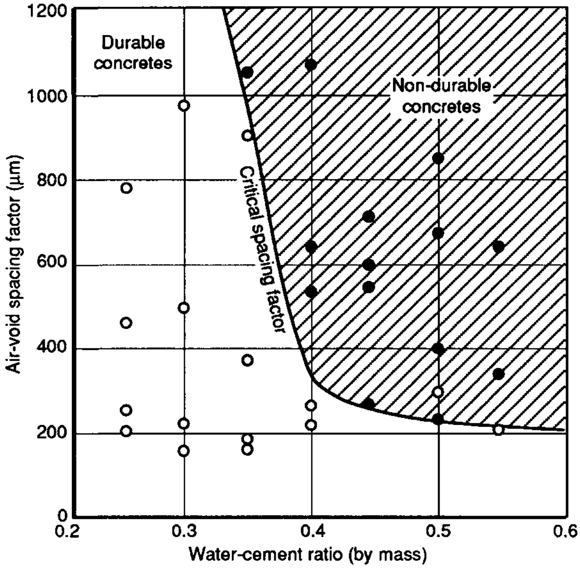


Figure 5.10 Relationship between the air-void spacing factor and the water/cement ratio. The white points represent the concrete mixtures which have satisfactorily sustained 300 rapid freezing and thawing cycles (ASTM C 666) while the black points represent the concrete mixtures which were damaged by the same test procedure (after Okada *et al.,* 1981).

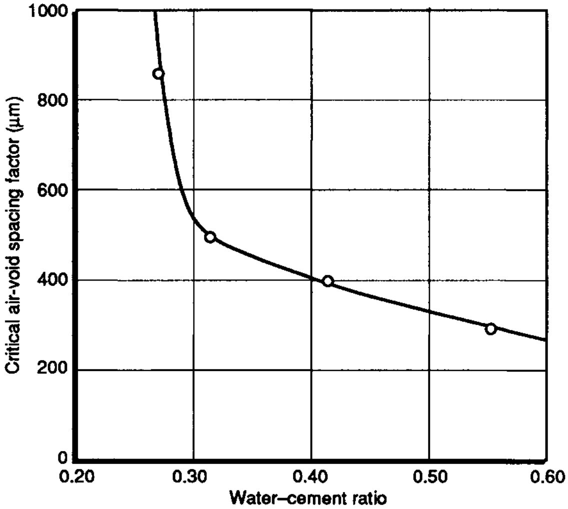


Figure 5.11 Relationship between the critical air-void spacing factor and the water/cement ratio (after Kobayashi *et al.,* 1981).

In 1987, Malhotra *et al.* studied the frost durability of concretes having water/cement ratios ranging from 0.25 to 0.35, and concluded that air entrainment was still required to protect these concretes against freezing. Whiting (1987) also observed poor frost resistance for non-air-entrained concretes containing 10–20% fly ash with water/binder ratios ranging from 0.26 to 0.36. These concretes had compressive strengths in the 50–70 MPa range. Hammer and Sellevold (1990) found that a very high-strength concrete (110 MPa) with a water/cement ratio of 0.26 could be severely damaged by frost.

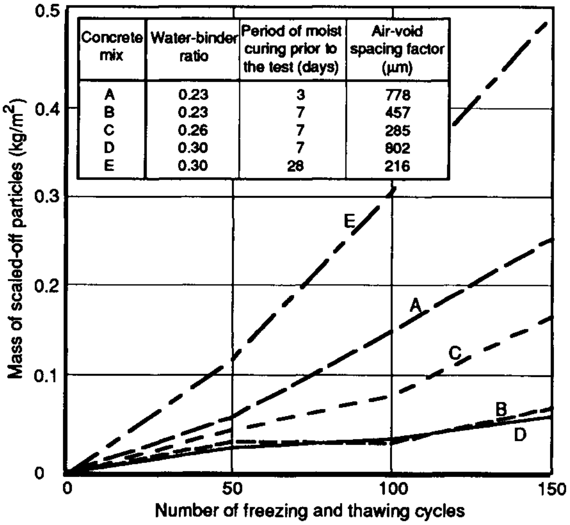
Thus, from the data available at the present time, it can be tentatively concluded that air entrainment is generally not required for high-strength concretes having a water/binder ratio smaller than about 0.25 (except when fly ash or slag is used as partial Portland cement replacement, particularly since there is not enough data available in this case). These concretes generally have a critical spacing factor higher than the spacing factor usually obtained without air entrainment. However, care must be taken for highly optimized concrete mixtures which could have very low air contents and exceptionally high spacing factors. It also seems very clear that air entrainment is needed for concretes having a water/cement ratio higher than 0.35.

For concretes having water/cement ratios in the 0.25–0.35 range, no clear conclusions can be drawn, and tests are needed to determine if air entrainment is required. In this range of water/cement ratios, it seems that the characteristics of the cement are particularly important. With certain cements, the paste has a finer porosity, which seems to influence significantly the frost behaviour of concrete. Often, a higher compressive strength is obtained with these cements (Gagné *et al.,* 1990). It also seems that, in this range of water/cement (or water/binder) ratios, the use of silica fume, fly ash, and blastfurnace slag can have a significant influence on the frost resistance because it has a large influence on the characteristics of the capillary pore system. Although the compressive strength does give a good indication of the overall quality of concrete, it cannot generally be used as a criterion for frost resistance because many parameters that have no influence on the frost resistance can influence strength (Bruno *et al.,* 1991).

Investigations have also been carried out to assess the resistance of high-strength concrete to de-icer salt scaling. Non-air-entrained concretes with a water/cement ratio of 0.25 and moist cured for 14 days were found to have a good scaling resistance when subjected to the ASTM C 672 scaling test method, even after 150 daily cycles of freezing and thawing (Foy *et al.,* 1988). Gagné *et al.* (1990, 1991) fabricated a large number of concretes with and without silica fume at different water/binder ratios (0.23, 0.26 and 0.30). These concretes were tested according to ASTM Standard C 672 after various periods of moist curing. All concretes, regardless of the spacing factor, had a particularly good performance, since the mass of scaled-off particles was in all cases well below the commonly accepted limit of 1 kg/m after 50 cycles. Figure 5.12 shows the relationship between the mass of scaled-off particles and the number of freezing and thawing cycles for some of the concretes tested by Gagné *et al.* Hammer and Sellevold (1990) also observed good scaling resistance for a non-air-entrained concrete having a water/cement ratio of 0.37 and exposed to 150 cycles of freezing and thawing according to the Böras method (Swedish Standard SS 13 72 44).

It thus seems that non-air-entrained high-strength concretes generally have a good scaling resistance, and that the main concern about these concretes is their resistance to internal microcracking. The limiting values of the water/cement ratio that were mentioned above concerning the use of air entrainment to protect high-strength concrete against internal microcracking can threrefore be safely applied to de-icer salt scaling, again with the exception of concretes containing fly ash or slag. The small amount of data that is available indicates that the use of fly ash and slag in high-strength concrete can cause scaling problems, and the reasons behind these problems remain to be investigated.

The use of high-strength concrete is relatively recent, and no significant field data have been published on their frost and de-icer salt scaling resistance. The available information almost entirely comes from laboratory testing, and thus caution is recommended in the use of these new materials until more about their frost resistance under field conditions is known.



Concrete mix	Water-binder ratio	Period of moist curing prior to the test (days)	Air-void spacing factor (µm)
A	0.23	3	778
B	0.23	7	457
C	0.26	7	285
D	0.30	7	802
E	0.30	28	216

Figure 5.12 Mass of scaled-off particles versus number of freezing and thawing cycles for a number of high perormance concretes subjected to the ASTM C 672 de-icer salt scaling test (after Gagné *et al.,* 1991).

It is generally more difficult to entrain air voids in high-strength concretes, mainly because of the high cohesiveness of the cement paste. However, when air entrainment is needed, it is generally possible to obtain an adequate air-void system by using a high dosage of the air-entraining admixture. The use of a more efficient mixer (which provides a higher mixing energy) can also be useful. Often, the entrained air voids are significantly smaller in high-strength concretes than those in normal concretes. This is advantageous because a smaller air content is then required to obtain a satisfactory spacing factor.

5.6 SPECIAL PRODUCTS

Non-air-entrained concrete can be protected from frost action by the use of certain finely divided solid materials. These materials do not become saturated when they are added to the fresh mixture, but nevertheless represent areas in the hardened concrete where ice can form without creating significant internal pressures. Some of these products are small particles of expanded clay aggregates (Litvan and Sereda, 1978), and others are microscopic hollow spheres. For various reasons, these products are not commonly used in industry, although laboratory tests tend to show they can be effective as a protection against frost action. The use of pulverized rubber particules has also been tested, but the data that exist are not conclusive.

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Chapter 6
Air Entrainment

Air entrainment, except perhaps for certain high performance concretes, is necessary to protect concrete against frost action. In North America, the admixtures required to entrain air in concrete, the air-entraining agents, have been in use for more than 40 years. Although air entrainment is influenced by a very large number of parameters, all of these admixtures, if used correctly, can provide almost any standard concrete mix with a sufficiently closely spaced system of air voids.

6.1 BASIC PRINCIPLES

Air is entrained in the fresh concrete by the mixing process, the role of air-entraining admixtures generally being to facilitate this process and, most important, to stabilize the air bubbles in the mix. To understand the mechanisms which explain the action of air-entraining agents, the concept of **surface energy** must first be addressed.

A certain amount of energy is necessarily associated with any surface in any material. This surface energy is equal to the surface tension of the material multiplied by the surface area. Thus, any air void in fresh concrete has associated with it a certain amount of energy, equal to the surface tension of water multiplied by the surface area of the void. When concrete is mixed in a laboratory pan-type mixer, or in a large drum-type mixer in a concrete plant, air is entrapped during the process. This can be either due to concrete falling on itself (a process known as kneading, typical of drum-type mixers) or to the stirring action (in pan-type mixers) which draws air into the mix by means of a vortex action (Powers, 1964). This of course requires energy, since air bubbles form. To subdivide these bubbles into smaller bubbles, further energy is required because, for a given volume, two voids have a larger total surface than a single void. If, for example, during mixing, a 1-mm bubble is split into 50-µm bubbles, there will be 8000 of these 50-µm bubbles and their total surface (as well as the corresponding energy) will be 400 times larger than that of the 1-mm bubble.

Most air-entraining agents are surface-active agents (surfactants) that reduce the surface tension of water as they concentrate at the air-paste interface. This reduction can be of the order of 30% (and perhaps more) at the concentrations normally used (Backstrom *et al.,* 1958a). These admixtures are long organic molecules with a hydrophilic end and a hydrophobic end, which explains why they concentrate at the interface. The reduction of the surface tension is important because it not only reduces the energy required to form the voids but it also reduces the energy required to break them down into smaller voids.

The process of mixing (due either to the shearing action of the mixer blades or to that of the aggregate particles which are violently agitated) tends to shear the larger voids, thus producing smaller voids. For a given air volume, smaller voids have a lower spacing factor than larger voids, and it will be recalled that the protection against frost action increases as the spacing of air voids decreases. The distinction between the entrained air voids (those present when an air-entraining admixture is used) and the entrapped air voids (normally present in any mix) is very often made, but it is obvious from what has just been said that there is no clear cut distinction between the two.

Air-entraining agents must do more than facilitate air entrainment. They must also stabilize the small air voids produced by the action of mixing. Because any system tends toward its lowest value of free energy, the natural tendency of small air bubbles is to coalesce to form larger bubbles. Larger bubbles, from a spacing factor point of view, are much less useful, and such large voids are more easily expelled from the mix because the hydrostatic pressure that pushes them upwards becomes more important than the friction forces (that are a function of the surface). In concrete that is not air entrained, the voids coalesce and are expelled more easily than in air-entrained concretes, which explains why the air content of these concretes is usually lower (and the spacing factor higher).

There are various ways by which small air voids in concrete can be stabilized. The air-entraining admixtures that are surfactants (that reduce surface tension by concentrating at the air-paste interface) form an elastic film around the air bubbles. This film reduces the risk of air-void coalescence when collisions during mixing occur (Powers, 1964). Very often, the hydrophilic end of the admixture molecules is negatively charged. These molecules therefore tend to become adsorbed to the cement grains, thereby effectively binding the air voids to the cement grains as shown in Figure 6.1 (Kriejger, 1967).

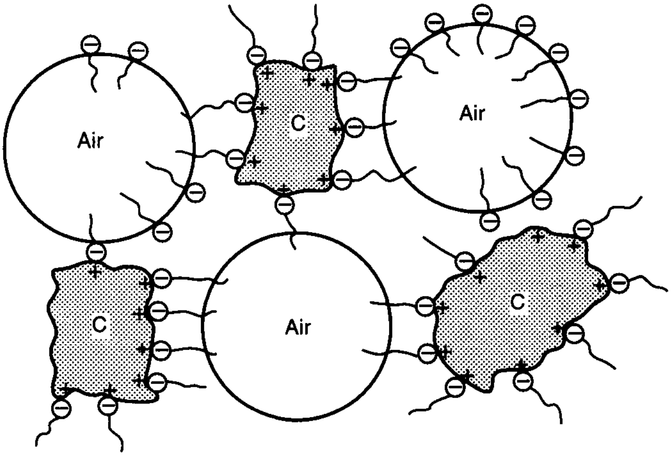

Figure 6.1 Air bubbles tied to Portland cement grains by ionic air-entraining admixture molecules (after Kriejger, 1967).

Some air-entraining agents reduce only slightly the surface tension of water but are nevertheless effective in stabilizing the air voids. These admixtures react with the calcium hydroxide (that is liberated when cement comes into contact with water) to form a gelatinous and water repellent membrane around the air voids. As with surfactants, this membrane reduces the risk of coalescence when collisions occur (Mielenz *et al.,* 1958).

According to Mielenz and his associates, an air-entraining agent should

- form an elastic film at the air-water interface;
- reduce surface tension;
- prevent the transmission of air through the interface;
- not deteriorate with time;
- bind the air voids to the cement grains;
- not modify significantly the properties of the concrete.

When air voids (in hardened concrete) are seen under the scanning electron microscope, the paste around the voids often appears to be denser than elsewhere (Figure 6.2). This is particularly evident in hardened pastes with a relatively low degree of hydration where the shell of paste surrounding the air voids can be observed quite clearly (Pigeon, 1984). This tends to confirm observations by Bruere (1967) and Mielenz *et al.* (1958) that air voids in fresh concrete are bound to the paste since cement particles appear to be attracted to the voids.

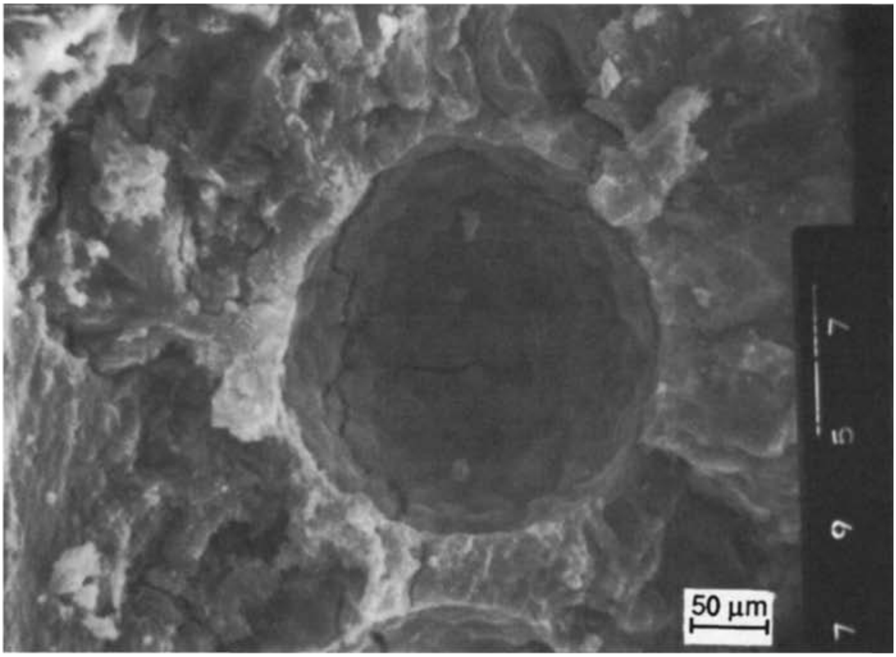

Figure 6.2 Air void seen under a scanning electron microscope.

The **viscosity** of cement paste is an extremely important parameter as regards air entrainment. As the viscosity of the paste increases, the movement of all air voids in the paste becomes difficult. This reduces the risk of coalescence, and also helps to keep the bubbles in the mix. Of course, more energy is required to stir or shear a more viscous paste (or a stiffer concrete) and this also influences air entrainment. If a paste is more viscous, it is normally because it contains more solid particles (or finer particles) for a given amount of water. Since all solid surfaces need to be covered with water, the formation of air bubbles, which also requires water, becomes more difficult as the surface area of the solid particles increases with respect to the water content.

6.2 CHEMICALS USED AS AIR-ENTRAINING AGENTS

A very large number of chemicals can be used as air-entraining agents. Most of them are recycled byproducts of various chemical industries (pulp and paper, petroleum or others). The number of commercial products available is extremely large and many products are mixtures of various chemicals. It is thus very difficult to give a complete list of products or chemicals. The most commonly used chemicals are

- sodium salts of wood resin (neutralized Vinsol resin)
- salts of fatty acids
- salts of sulphonated hydrocarbon
- alkyl-benzyl sulphonates.

The concentration of solids in the commercially available products is variable and usually relatively low (very often less than 10% by weight). The normal dosage of these commercial products required to obtain a satisfactory air-void system ranges approximately between 0.2 and 1.0 mL/kg of cement (i.e. between 50 and 400 mL/m^3 of fresh concrete for standard mixtures).

6.3 CHARACTERISTICS OF THE AIR-VOID SYSTEM IN HARDENED CONCRETE

The three basic parameters used to describe the characteristics of the air-void system in hardened concrete, as outlined in Chapter 4, are

- the air content
- the specific surface of the air voids (related to the average size of the voids)
- the spacing factor of the air voids.

These characteristics are measured on polished hardened concrete sections examined under an optical microscope at a magnification ranging between 50 and 120×. At 120× magnification, all voids larger than about 10 μm can be detected. ASTM Standard C 457 recognizes two methods to measure these characteristics, the ‘linear traverse’ method, and the ‘modified pointcount’ method (Chapter 4).

As can be seen in Figure 1.4, which shows a polished section of air-entrained concrete at 10× magnification, air voids cover a large range of sizes. Most air voids in air-entrained concrete are in the 10–100 μm range, but they can be as large as a few millimetres. Data published a few years ago indicate that the number of air voids smaller than 10 μm is not very important (Pleau *et al.,* 1990). Hover (1988) has calculated that, theoretically, air voids smaller than 10 μm cannot exist because in such voids the internal pressure (that, in effect, balances the surface tension) becomes higher than the pressure required to dissolve the air in water. Recent results, however, suggest that, in dry concretes, such as dry-mix shotcrete or concrete paving blocks, the number of these micro air voids (<10 μm) could be quite significant, probably because very high dosages of air-entraining admixtures are sometimes used in these types of concrete (Lamontagne, 1993).

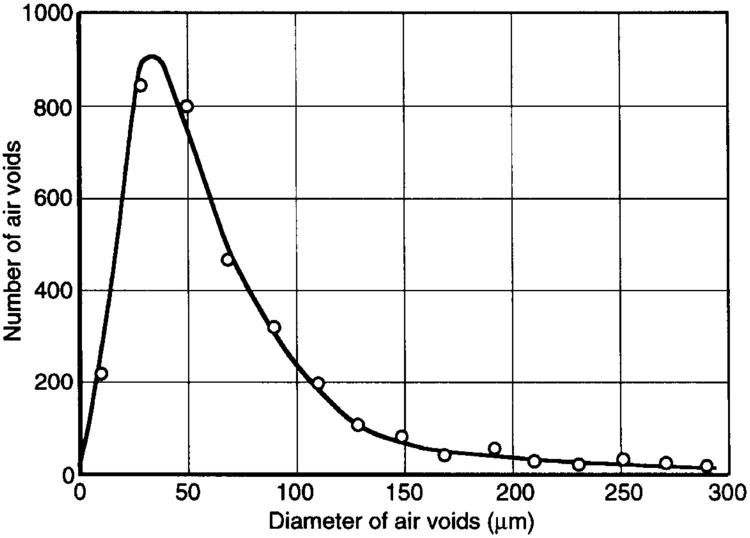

Figure 6.3 Size distribution of the diameter of air voids observed on a polished concrete section for a typical air-entrained concrete (after Pleau *et al.,* 1990).

Figure 6.3 shows the distribution of air-void sizes in a typical air-entrained concrete. This distribution was obtained by measuring the diameters of the intercepted air voids on a polished concrete section. It does not, however, represent exactly the real distribution of air-void sizes because statistically the larger voids are more likely to be intercepted than the smaller ones. The figure shows clearly that the average size of air voids in air-entrained concrete is of the order of 50 μm.

Figure 6.4 shows the distribution of the 'chord intercepts' (obtained with the linear traverse method of ASTM Standard C 457) for a typical air-entrained concrete. These chord intercepts are measured along a line of traverse on a polished concrete section. They do not therefore represent exactly the distribution of the diameters of the air voids intercepted on the section, since the line of traverse does not necessarily cross the void in the middle.

The air content of the fresh concrete is usually measured by the pressure method (ASTM Standard C 231), and, in most countries, that value of the air content serves as an acceptance criterion for concrete. If the value is lower or higher than the specified range (generally 5–7% for concrete with 20 mm nominal size aggregate), it is rejected. Figure 6.5 shows the relationship between the air content measured on the fresh concrete and that subsequently measured in the hardened concrete for a large number of laboratory and field mixes. These test results indicate that in the normal range of air contents (2–10%), these two values are

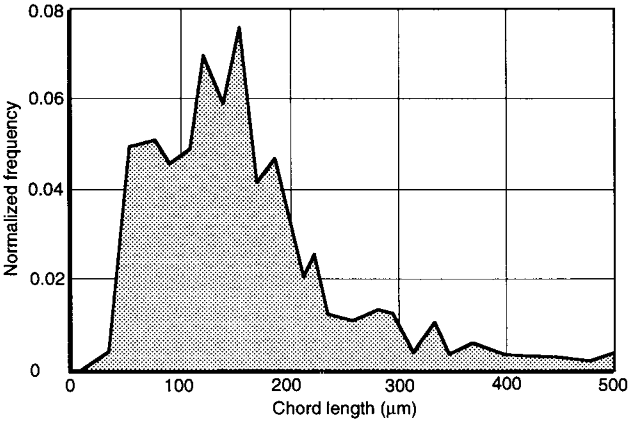

Figure 6.4 Size distribution of the chords intercepted in the air voids by a line of traverse of a typical air-entrained concrete (after Roberts and Scheiner, 1981).

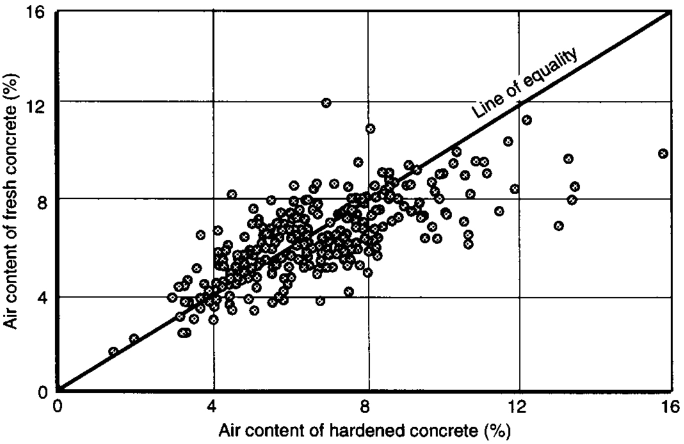

Figure 6.5 Relationship between the air content measured on fresh concrete (using the ASTM C 231 pressure test method) and the air content measured on hardened concrete (using the ASTM C 457 microscopical examination) (after Saucier *et al.,* 1991).

generally in good agreement. The differences that do occur can be due to numerous causes (Hover, 1989; Saucier *et al.,* 1991):

- there are normal statistical variations due to concrete heterogeneity;
- concrete in the pressure meter is not necessarily compacted in the same way as the specimens used for the microscopical examinations;
- air voids in these specimens can collapse before setting, or the air in the smaller voids can be dissolved in water;
- the hypothesis on which the pressure method is based is not necessarily always valid.

As regards frost resistance, it is the spacing factor which is most important, not the air content. It is therefore important to evaluate whether the air content measured in the fresh concrete can provide a reasonable estimate of the value of the spacing factor. As can be seen in Figure 6.6 (which shows the relationship between the air content measured in the fresh concrete and the spacing factor measured on the hardened concrete for the same samples as in Figure 6.5), the value of the spacing factor for a given air content can be quite variable. At an air content of 6% for instance, spacing factor values range between 100 and 400 μm approximately (depending on the specific surface or the average size of the air voids).

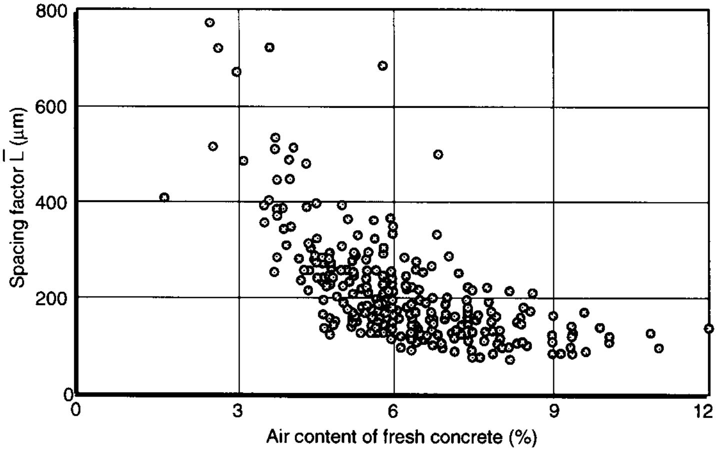

Figure 6.6 Relationship between the air content measured on fresh concrete and the air void spacing factor (measured on hardened concrete) (after Saucier *et al.,* 1991).

6.4 PRODUCTION AND STABILITY OF THE AIR-VOID SYSTEM

Concrete is not always cast immediately after mixing. Very often, it is mixed at the plant and transported to the site in rotating drum-type trucks. Concrete can thus be cast as late as 90 min after mixing (the maximum length of this period is usually specified in the codes of practice). It is therefore essential to assess the influence of the continuous agitation and of the reactions that take place during this time on the physical properties of the cement paste, such as viscosity. This question is extremely important, particularly since in most laboratory tests the performance of air-entraining admixtures is based on testing specimens which are cast approximately 15 min after the initial water-cement contact was achieved (these specimens are left to harden and later sliced up to examine the air-void system in the hardened concrete). It is thus often useful to consider separately the production of the air-void system in fresh concrete (i.e. the air-void system in specimens cast over a period ranging between 5 and 10 min after initial water-cement contact) and the subsequent stability of the air-void system during transportation and agitation (i.e. the air-void system in specimens cast much later on). In this respect, as will be shown later, there may be differences between laboratory test results and the actual situation on site.

Extensive studies at the Portland Cement Association (more than 30 years ago) have been carried out to analyse the various parameters that affect the stability of the air content in fresh concrete (usually called air loss since this is considered by many to be the fundamental stability problem). However, only relatively recently has the problem of air-void spacing factor stability been investigated in depth (Gebler and Klieger, 1983; Pigeon *et al.,* 1989), probably because many concrete producers have only recently realized that, very often, the air-void spacing factor of cast-in-place concrete is much higher than the recommended values, even though the air content of the fresh concrete was within the specified limits.

6.5 PARAMETERS AFFECTING AIR ENTRAINMENT

The parameters that can significantly affect air-void production and stability are numerous. It is thus simpler to consider them separately. At first the influence of the various materials that make up the concrete will be considered, and then the influence of the mix composition and characteristics, and finally the influence of external conditions such as mixing and placing techniques will be discussed.

6.5.1 Cement and Mineral Additives

The influence of cement on air entrainment can be physical as well as chemical. The physical effect of the cement is mainly related to its fineness (Bruere, 1974). In a finer cement, there are more surfaces that need to be covered with water. This means that less water is available for air-void formation, and air entrainment becomes more difficult. The viscosity of the paste increases and this also makes the entrainment of air bubbles more difficult.

The physical effect of mineral additives (condensed silica fume, ground granulated blastfurnace slag, fly ash, natural pozzolans, limestone and other fillers) is similar to that of cement, i.e. it is related to the fineness. This is particularly the case for silica fume (which is approximately 100 times finer than normal Portland cement) when it is used in normal strength concrete without large dosages of superplasticizers (Gagné, 1986).

Some chemical substances in cement react very rapidly upon contact with water. These are mostly tricalcium aluminate, gypsum and soluble alkalies (generally in the form of sulphates), and, therefore, they can be expected to influence the process of air entrainment. Tricalcium aluminate, gypsum and alkali sulphates react to form a product known as ettringite. The ettringite molecule contains 31 molecules of water and is needle-shaped. Its formation thus increases the viscosity of the paste in a chemical as well as a physical way. If the formation of ettringite is relatively rapid, the production of the air-void system will be influenced by the increased viscosity. If it is relatively slow (or if the primary short needles of ettringite are transformed gradually during the dormant period of cement into long needles of secondary ettringite (Regourd, 1982)), then stability problems may occur because of the gradual change in the viscosity of the paste.

It has been known for a long time that alkalies in cement influence air entrainment. The exact nature of this influence has been studied by many investigators and is still a subject of dispute. Many researchers have found that the system of air voids is coarser when the alkali content of the cement is higher. In many cases, this is probably simply due to the fact that alkalies are generally in the form of sulphates that promote the formation of ettringite.

According to Mielenz *et al.* (1958) and Farkas (1964), the presence of alkalies reduces the amount of calcium in the solution and correspondingly reduces the amount of air-entraining agent that precipitates to form the membrane around the air voids. There is thus more of the admixture left to form more membranes (and the air content tends to be higher), but the air voids are less stable. This could explain why larger voids are observed since coalescence becomes easier. This mechanism can of course only be valid when membrane-forming air-entraining admixtures such as neutralized Vinsol resin are used.

Plante (1989) has recently published an in-depth study of the influence of alkalies. As have many others, he has noted that the system of air voids is coarser at the beginning when alkali sulphates are added to the mix. He has also studied the air-void system in specimens cast as late as 90 min after initial water-cement contact, and come to the conclusion that alkalies mostly promote air-void stability (Pigeon *et al.,* 1992). This is probably due to ionic bridging between the cement particles in the shell of paste surrounding the air voids (Pigeon and Plante, 1990). Since this shell is more solid, air-void coalescence is more difficult. Figure 6.7 shows a micrograph of a polished section of paste that indicates that alkalies (in this case potassium) tend to concentrate around air voids, perhaps due to the ionic nature of the air-entraining agent.

Fly ash is a byproduct of power plants that burn coal, and it can contain a significant amount of carbon. Silica fume can also contain carbon. The presence of carbon in fresh concrete can create severe air-void production and stability problems, because carbon slowly inhibits the air-entraining admixtures and thus gradually reduces the amount available for air entrainment (Gebler and Klieger, 1983).

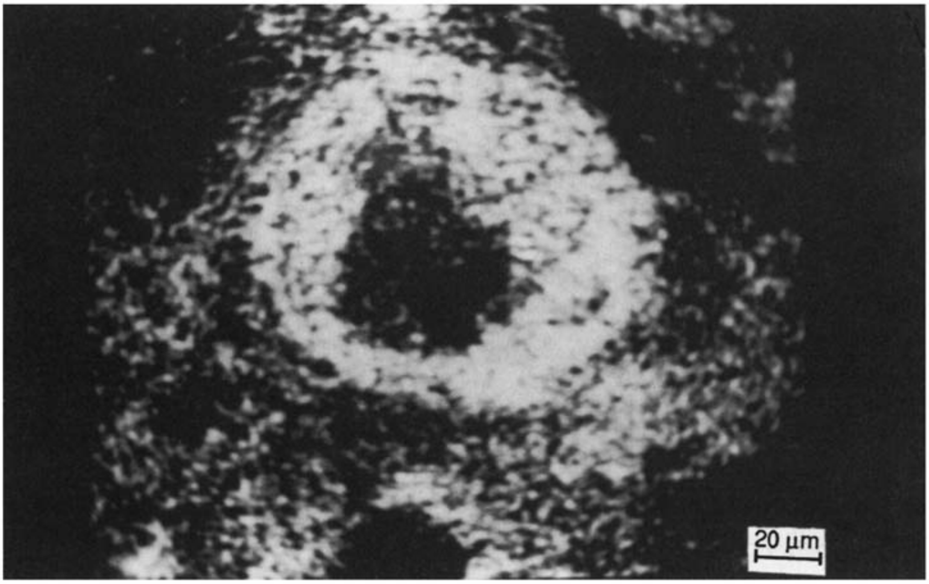

Figure 6.7 Micrograph of a polished section of cement paste (obtained with an electron microprobe) showing the concentration of potassium around an air void (after Pigeon and Plante, 1990).

6.5.2 Aggregates

Coarse aggregate *per se* has little influence on air entrainment. However, the quantity of aggregate affects the stiffness of the mix and can thus, indirectly, affect the air-void system. Mixes that contain larger aggregates usually have a lower paste content and the air content of these concretes is generally lower.

Fine aggregate, in addition to its influence on viscosity (which can be relatively important if, for instance, the quantity of very fine particles is large), has a 'grid effect' and prevents air voids from escaping the mix (Powers, 1964). This effect is related to the grading of the sand, but no consensus exists as to the sizes of the sand particles that are the most important (Whiting and Stark, 1983). It seems that the air content tends to decrease as the sand becomes finer, but the exact influence of the fine aggregate on the air-void system is not very clear. In a properly air-entrained mix, it is probable that the grading of the sand is not very important.

6.5.3 Admixtures

In addition to air-entraining agents, the most common admixtures are water reducers, superplasticizers, retarding agents and accelerators. Almost all the concrete sold in North America today contains a water reducer. Basically, less cement paste is required to obtain a given slump and concretes containing such an admixture are more economical. They also have lower creep and shrinkage and a somewhat higher strength due to the better dispersion of the cement grains. Some water reducers (such as calcium lignosulphonates) are surfactants and thus help to entrain air (Vénuat, 1971), but the air voids entrained by lignosulphonates are not very stable. Since all water reducers increase the fluidity of the paste, all of them tend to enhance the air-entraining effect of air-entraining agents. They do not, however, increase the stabilizing effect.

At normal dosages, the use of water reducers does not generally seem to create any special problems. However, if the dosage is increased (as is common when the temperature is high because they usually also have a retarding effect), stability problems can occur because the dosage of the air-entraining agent has to be reduced to prevent excessive air content increases (Plante *et al.,* 1989a).

Superplasticizers can affect the air-void system in two ways. First, they increase the paste fluidity which can facilitate air-void coalescence. Second, they increase the repulsive forces between the cement grains and can thus weaken the shell of cement paste that protects the air voids from coalescence.

The influence of superplasticizers on the air-void system has been studied by a large number of investigators in recent years (Mielenz and Sprouse, 1978; Tognon and Cangiano, 1982; MacInnis and Racic, 1986; Plante *et al.,* 1989b; Saucier *et al.,* 1990). With a few exceptions, all have concluded that adding a melamine or naphthalene-based superplasticizer to a standard mix to increase slump tends to cause an increase in the spacing factor, a decrease in the specific surface and a loss of air. The results obtained, however, are quite variable, and seem to depend on the characteristics of the cement, the type of air-entraining agent and the other admixtures in the mix. The influence of cement, for instance, is illustrated in Figure 6.8 where the variation of the spacing factor with the time of casting is shown for two groups of laboratory mixes containing various superplasticizers and air-entraining agents. In the first group of mixes, all made with cement A, the spacing factor stays approximately constant throughout the 90-min period, whereas there is a significant increase in the spacing factor immediately after the addition of the superplasticizer (at 15 min) for the group of concretes made with cement B. Cement A has a higher soluble alkali content than cement B, which may account for the better stability of the air voids in the mixes containing cement A.

In field tests, Saucier *et al.* (1990) found that superplasticizers generally had little effect on air-void stability, probably in part because the dosages of the superplasticizers were reduced by about 40% to avoid problems during the placement operations. Figure 6.9 shows the variation of the spacing factor with time for two groups of field mixes made with the same cements A and B as those in Figure 6.8 and containing various superplasticizers and air-entraining agents. In most cases, there is no increase in the spacing factor after the addition of the superplasticizer (at 15min).

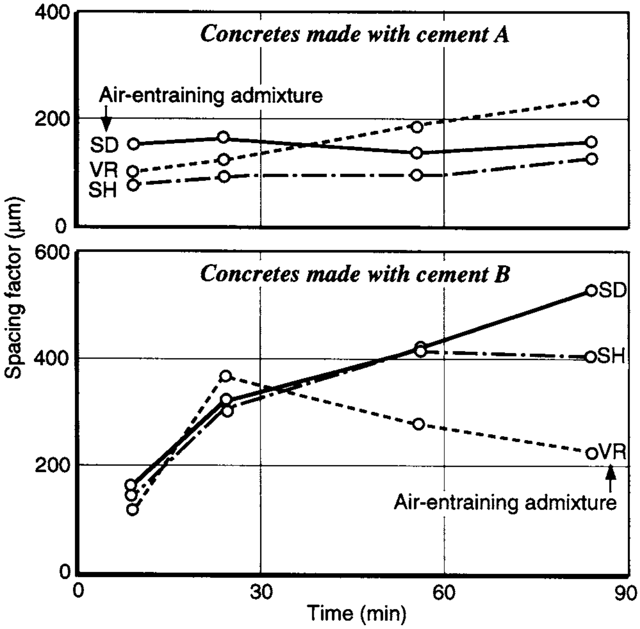

Figure 6.8 Variation of the air-void spacing factor with the time of casting for superplasticized laboratory concretes made with two different cements and three different air-entraining admixtures (after Pigeon *et al.,* 1989).

Figure 6.10 shows the size distribution of the air voids in a normal air-entrained concrete (with a spacing factor of 134 μm) and in a superplasticized air-entrained concrete (with a spacing factor of 387 μm). The two distributions are similar, which indicates that superplasticizers can simply reduce the number of entrained air voids without affecting the size distribution.

There are no data in the literature concerning the stability of the air-void system in air-entrained high-strength concretes made with high superplasticizer dosages. It is probable, however, that the high viscosity of the paste in these concretes helps to prevent air-void coalescence.

Retarding agents do not seem to have a very significant influence on air entrainment. Mielenz (1968) considers that these admixtures simply increase the length of time (after the placement operations) during which the air-void system can change, for instance by diffusion of the air in the very small voids to the larger ones. It is probable, however, that the air-void system after casting does not change very significantly because there is no energy input into the system. Coalescence is always possible, but this cannot easily be verified.

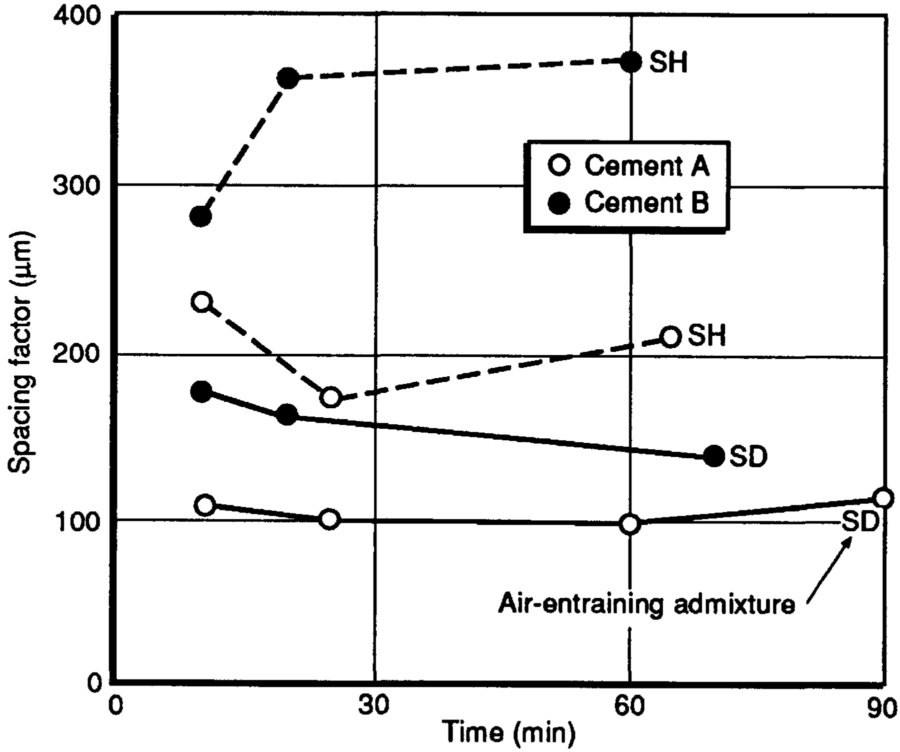

Figure 6.9 Variation of the air-void spacing factor with the time of casting for superplasticized field concretes made with two different cements and two different air-entraining admixtures (after Saucier *et al.*, 1990).

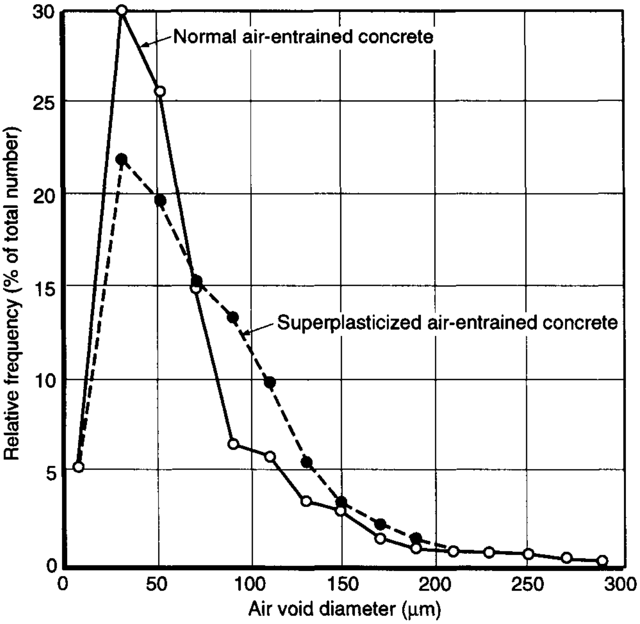

Figure 6.10 Size distribution of the diameter of the air voids observed on a polished concrete section for a normal air-entrained concrete (with a spacing factor of 134 μm) and a superplasticized air-entrained concrete (with a spacing factor of 387 μm) (after Pleau *et al.,* 1990).

Little information is available on the effect of accelerators and other admixtures, such as, for instance, pumping aids. It is clear, however, that the influence of any admixture on any given mix is very difficult to predict and that, for any combination of admixtures (air-entraining agent, water reducer etc.) and cement, tests are needed to verify the production and stability of the air-void system.

Certain admixtures, usually called defoamers, are sometimes utilized to reduce the air content in fresh concrete. There is little information available on the mechanisms that are responsible for the decrease in air content when defoamers are used, nor on the influence that these admixtures have on the characteristics of the air-void system other than the air content.

Air-entraining agents are commercial products, and it is not possible to find in the technical literature clear indications as to the type of air-entrain-ing admixture which would yield the best results in a given situation. Therefore, although there are publications in which the air-void systems obtained with various air-entraining agents are compared, the authors have decided not to discuss the test results obtained with various types of air-entraining agents, particularly in view of the fact that the most important factor is probably the compatibility of the admixtures and the cement. The fact that compatibility problems are extremely important can be seen, for instance, in Figure 6.11 which shows the variation of the air content as a function of the water-reducer dosage for various combinations of types of water reducer and cement.

6.5.4 Water

It is generally considered that drinking water is suitable for making concrete. Although no clear test results are available, it seems that air entrainment can be affected by certain mineral substances dissolved in normal drinking water. Calcium carbonates, in particular, which are known to reduce the capacity of water to dissolve soaps and detergents, could affect air entrainment. This is, however, disputed (Whiting and Stark, 1983), but it again indicates the importance of tests to verify the capacity of any air-entraining agent to give a correct and stable air-void system in any given concrete.

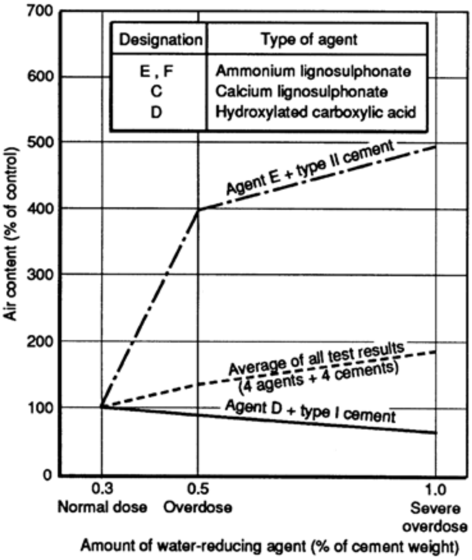

Figure 6.11 Variation of the air content with the dosage of the water-reducing admixture for different combinations of type of water-reducer and cement (after Wallace and Ore, 1959).

6.5.5 Mix Composition and Characteristics

The single most important parameter related to mix composition that can influence air entrainment is obviously the water/cement ratio. The other parameters, such as paste or aggregate content, only have an indirect effect. They influence the stiffness of the mix and can thus increase or decrease the energy required to entrain air.

The importance of the water/cement ratio, as stated clearly by Backstrom *et al.* (1958b), is directly related to the viscosity of the paste. This is illustrated in Figure 6.12 where the air-void grading for three different water/cement ratios is shown. It can be seen that the size of the air voids decreases with the water/cement ratio, probably because the movement of air voids is more difficult in a more viscous paste and thus the risk of air-void coalescence is reduced. Backstrom *et al.* (1958b) have also shown that a higher dosage of the air-entraining agent is needed to obtain a normal volume of air if the water/cement ratio is low. In such a case, however, because the average size of the voids is smaller, the value of the spacing factor is lower (Figure 6.13).

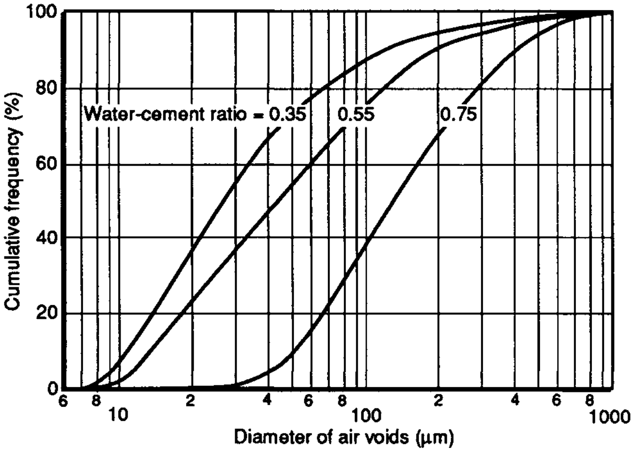

Figure 6.12 Size distribution of the air vtoids for three concretes with different water/cement ratios (after Backstrom *et al.,* 1956).

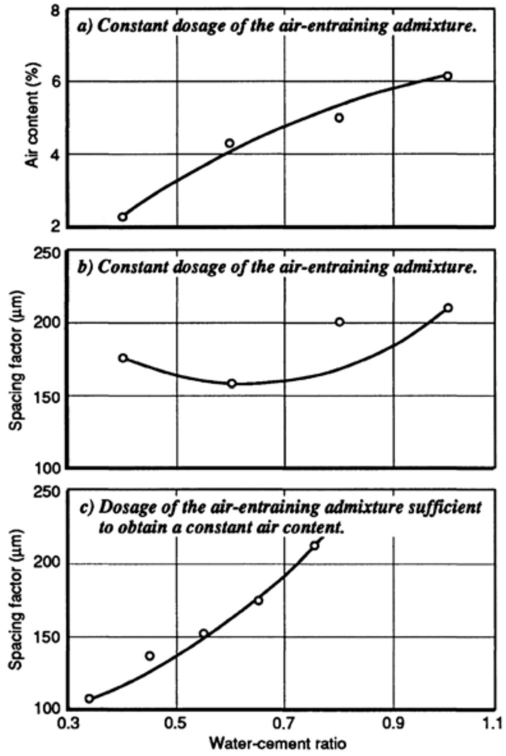

Figure 6.13 Relationship between the air content and the air-void spacing factor, and the water/cement ratio (after Backstrom *et al.,* 1958b).

It is possible to entrain air in high performance concretes with water/cement ratios as low as 0.25 (Gagné *et al.,* 1990). Such concretes contain large quantities of superplasticizer. The required dosage of the air-entraining agent can be as much as ten times the normal dosage, but it remains extremely difficult to obtain spacing factors lower than about 200 μm when the water/cement ratio is that low. In a recent field test with a 0.3 water/binder ratio, silica fume concrete, an average spacing factor of 180 μm was obtained using approximately double the dosage of a common air-entraining admixture (Aïtcin *et al.,* 1993).

Slump is often mentioned as an important parameter controlling air entrainment. As previously mentioned, air entrainment is more difficult in stiffer mixes. On the other hand, in more fluid mixes, the risk of air-void coalescence increases. The influence of slump *per se* is difficult to assess because slump variations are necessarily related to variations in mix composition (water content, water/cement ratio etc.), but field experience tends to indicate that the spacing factor increases with the slump.

The temperature of the fresh concrete, as most concrete producers know, directly affects the air content (Gay, 1985). For a given dosage of the air-entraining agent, the air content is generally higher in colder mixes. Producers therefore tend to reduce the dosage of the admixture during the winter months. Unfortunately, this results in air-void systems with higher spacing factors (Gay, 1983). In fact, temperature only affects the air content, not the spacing factor obtained with a given dosage of the air-entraining agent (Saucier *et al.,* 1990).

6.5.6 Mixing, Placing and Finishing Techniques

It is the stirring or kneading process during mixing that entrains the air in fresh concrete. It is evident, intuitively, that the time of mixing must be sufficiently long to ensure a homogeneous product. This is particularly important for air entrainment because, as Powers (1964) stated:

> *Circulation causes a given bubble to enter the region of high stress repeatedly, and thus the probability of its becoming divided depends partly on the duration of the stirring period. Since at any given moment only a fraction of the batch is being subjected to the highest shear stress, and in successive moments different fractions of the batch are brought to this region, a certain amount of time is required for practically all the batch to have been subjected to maximum shear rate.*

This means that, normally, the mixing time should be increased for larger batches in a given mixer. Some mixers are obviously more ‘energetic’ than others. For instance, pug mill-type mixers with blades turning around a horizontal axis are more efficient than large drum-type mixers. However, in most practical cases, the lower efficiency of a mixer can at least be partly compensated for by an increase in the length of the mixing period, since there are always certain points in the mixer where higher shear stresses are developed.

When only small quantities of concrete are needed, such as for concrete repairs, trucks known in North America as ‘concrete mobiles’ are often used (Figure 6.14). These trucks have three separate containers for cement, coarse and fine aggregate, and the required amount of concrete is simply mixed progressively with a double screw system. Tests have shown that this mixing technique is not very efficient and that a correct spacing of air voids will only be obtained if the air content is relatively high (Larose and Pigeon, 1988).

Agitation in mixer trucks during transportation or waiting periods has no significant influence on air entrainment other than increasing the time during which chemical and physical changes in the paste can occur (which in turn can sometimes, as we have seen, cause instability problems). Loss of air during transportation is often observed but, in correctly air-entrained concrete, it is probable that this reduction in air content is mostly due to the loss of large air voids and has little influence on the value of the spacing factor (Pigeon *et al.,* 1987). Pumping and conveying over long distances can be harmful to the air-void system (Whiting and Stark, 1983), but there are no data on the exact influence of these techniques on the value of the spacing factor. When they are used, air-void stability tests should be made.

Retempering, i.e. adding water to the mix to increase the slump, or adding air-entraining agent to increase the air content, are very common practices. If the quantity of added water is not very high, it seems that this has little effect on the value of the spacing factor (Burg, 1983; Pigeon *et al.,* 1990). However, if the fluidity of the mix is increased to a very large extent, air-void coalescence will become easier and this could affect the stability of the air-void system.

Figure 6.14 Typical concrete mobile truck.

If the air content of concrete when it arrives on site is significantly lower than the specified minimum value, the concrete should generally be rejected. Retempering to increase the air content is therefore usually carried out only to increase the air content by about 1% and, in such cases, only a small amount of air-entraining agent dissolved in water is added. This increases the air content, but has no significant influence on the value of the spacing factor (Langan and Ward, 1976). The increase in air content is probably due in this situation only to the remixing of a more fluid mix. To decrease significantly the value of the spacing factor, large quantities (of the same order of magnitude as the original dosage) must be added (Pigeon *et al.,* 1990).

The process of compaction or consolidation means, by definition, the removal of unwanted air voids. When concrete is vibrated, air is expelled. Fortunately, according to Backstrom *et al.* (1958b), the spacing factor of properly air-entrained concrete is little affected by normal vibration because it is mostly the larger air bubbles and the entrapped air pockets that are expelled (Figure 6.15). This has been confirmed recently by Simon *et al.* (1992).

Little information is available on the influence of finishing operations on the air-void system near the surface. It is well known, however, that surfaces exposed to freezing and thawing cycles in the presence of de-icer salts should only be lightly finished (if possible with a wooden trowel) in order not to disturb the air-void system. Overworking of the surface, particularly with steel trowels, can significantly decrease the scaling resistance.

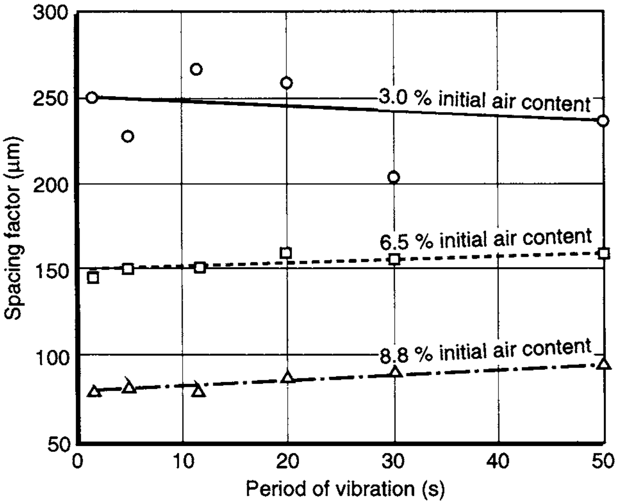

Figure 6.15 Relationship between the air-void spacing factor and the vibration time (after Backstrom *et al.,* 1958b).

6.6 PRACTICAL CONSIDERATIONS

The purpose of air entrainment is to protect concrete from frost action by providing it with a closely spaced system of air voids. The commonly used limit of 200 µm for the spacing factor can be considered as a safe design value although, depending on the exposure conditions, some field and laboratory concretes can be frost resistant when the air-void spacing factor is significantly higher than 200 µm, as has already been described.

Considering the large number of parameters that affect air-void production and stability, and considering also the compatibility of the various admixtures between themselves as well as with the cement, it must be emphasized again that testing is the only way to verify whether the use of a particular air-entraining admixture in a given mix will yield a system of closely spaced air voids (with a spacing factor of approximately 200 μm), which will stay stable until the concrete has set.

Field tests are much more preferable than laboratory tests. Laboratory testing involves relatively small amounts of concrete where heat of hydration effects, for instance, can be very different from those in large volumes of concrete. Many laboratory mixers are more energetic than field or plant mixers, and tend to overestimate the stability problems since they tend to increase the production of smaller voids at the beginning when the concrete is more fluid. Some of these voids gradually disappear as the concrete which is continually agitated stiffens, and the spacing factor increases. Figure 6.16 illustrates the variation of the spacing factor with the time of casting for a typical laboratory mix with an insufficient dosage of the air-entraining agent.

When field tests are carried out, samples for the determination of the air-void characteristics of the concrete should be taken after a sufficiently long period (one hour or more) in order that stability problems, if any, will be observed. If the air-void system after such a period is correct, it can safely be assumed that it was also correct immediately after initial mixing, although tests to verify this should also be carried out. These tests will also serve to verify if the initial mixing period is sufficiently long. If a superplasticizer is to be added to the mix on site to increase the slump, samples should be taken immediately before and after the concrete has been remixed with the superplasticizer, in order to determine the effect of the superplasticizer on the air-void stability.

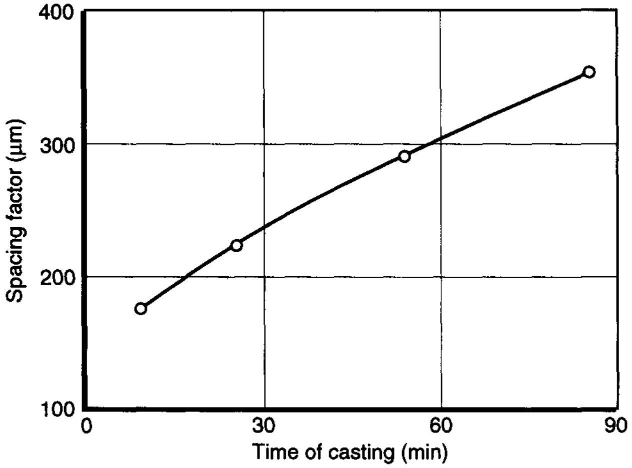

Figure 6.16 Variation of the air-void spacing factor with the time of casting for a typical laboratory air-entrained concrete with an insufficient dosage of the air-entraining admixture (after Pigeon *et al.,* 1990).

Once the dosage of the air-entraining agent required to obtain a correct spacing factor in a mix is determined, it should not be changed significantly because it is almost certain that reducing the dosage will result in a higher spacing factor even if the air content stays constant. Figure 6.17 shows the relationship between the dosage and the spacing factor for a large number of superplasticized and non-superplasticized concretes containing various air-entraining agents and cements. Even if, for a given dosage, there is a wide range of spacing factor values, the trend is clear: the higher the dosage, the lower the spacing factor. Air-entraining agents, it will be recalled, concentrate at the surface of the air voids and help to stabilize them. The higher the amount of admixture available, the larger the amount of surface area that can be stabilized. Large surface areas mean smaller voids and smaller voids correspond to lower spacing factors.

The spacing factor for a given air content, due to the importance of the specific surface, can be quite variable (Figure 6.6). It has been shown that air content variations, particularly when superplasticizers are used, are not necessarily a very good indication of the variation of the spacing factor, unless these air content variations are large (Saucier *et al.,* 1991). The use of total air content variations to predict spacing factor variations should therefore be accompanied as much as possible by measurements of the spacing factor in hardened concrete samples.

It is possible that, in certain mixes, the air content needed to obtain a correct spacing factor will be unacceptably high. This is more likely to occur in mixes with water/cement ratios higher than 0.45 which, in North America, is the upper limit for concrete exposed to freezing and thawing cycles in the presence of de-icer salts. This phenomenon can be considered as a compatibility problem, and other types of admixtures should be tried. Fortunately, the number of commercial products available is large, and it should be possible in most cases to find an admixture (or a combination of admixtures: air-entraining agent and water reducer) that will be compatible with the cement and aggregates used.

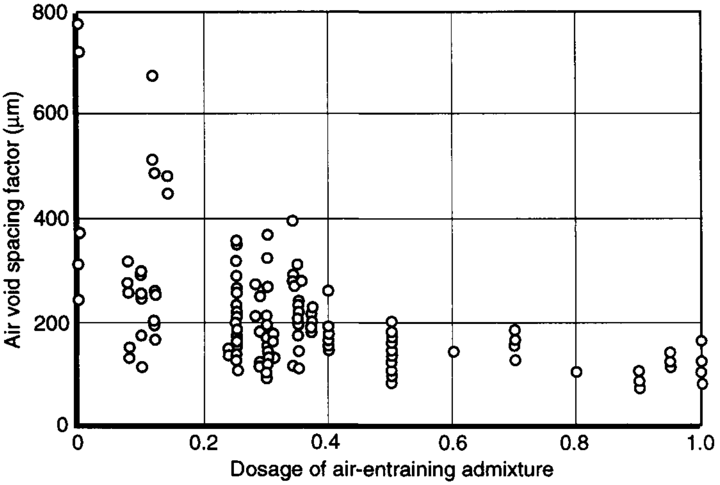

Figure 6.17 Relationship between the dosage of air-entraining admixture and the air-void spacing factor for superplasticized and non-superplasticized concretes containing various cements and air-entraining admixtures (after Saucier *et al.,* 1991).

It is also possible, and this is a more delicate problem, that in certain mixes there will be unpredictable increases of the air content even if the dosage of the air-entraining admixture is kept constant. These increases can be due to temperature variations for instance, or to changes in the grading of the sand, or even to variations in the quality of the mixing water. Reducing the content of air-entraining agent to solve this problem is not desirable considering that any decrease in the dosage of the air-entraining agent can cause an increase in the spacing factor. There is no simple answer to this problem, and research is still needed to understand the factors that influence air content (i.e. the factors that influence the production of large entrapped air bubbles as opposed to small entrained air bubbles). In a brochure published by the Association Technique de l'Industrie des Liants Hydrauliques (the French equivalent of the Portland Cement Association in North America), a solution to this problem is suggested. Since a decrease in the water/cement ratio tends to decrease the average size of the air voids, but has little influence on the spacing factor for a given dosage of the air-entraining agent (Backstrom *et al.,* 1958b), it is simply suggested to increase the cement content of the mix. This should reduce the production of unwanted large bubbles and also increase strength (which is necessary to compensate for the reduction due to the increase in air content).

Recently, Saucier *et al.* (1991) have suggested the use of a 'performance index' to characterize the air-void system in concrete. This index incorporates the spacing factor and the air content in a single parameter. It is based on the assumption that spacing factors lower than approximately 200 μm do not significantly increase the frost resistance of concrete, and that analysis of field concretes often shows little frost damage in concretes with a spacing factor lower than about 300 μm (Fournier *et al.,* 1987). It also takes into consideration the fact that air content *per se* does not influence the resistance to freezing and thawing cycles, but affects significantly the strength, which is an important concern for producers.

Isocurves that can be used to calculate the performance index are shown in Figure 6.18. Saucier *et al.* (1991) consider 80% as the lower limit for an acceptable air-void system. It corresponds to a spacing factor of 200 μm at an air content of 8% (a good air-entraining agent should yield such a spacing factor with no more than 8% air) and to a spacing factor of 300 μm at an air content of 2%. The value of 300 μm is the upper limit for frost resistance; it was verified in more than 1000 field and laboratory mixes that this value cannot be practically obtained with an air content lower than 2%. It can be seen in Figure 6.18 that a spacing factor of 200 μm at an air content of 5% (which Saucier *et al.* consider a very good 'performance') corresponds to a performance index of 100%. Values higher than 100% are of course always possible.

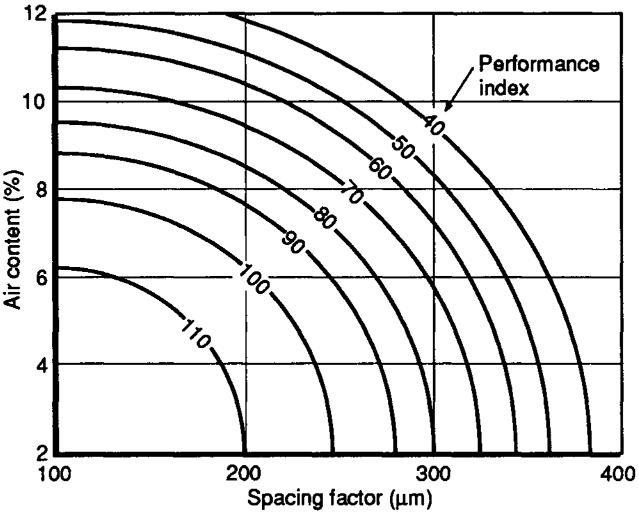

Figure 6.18 Isocurves used in the computation of the performance index (after Saucier *et al.,* 1991).

The performance index could be very useful for concrete producers faced with difficult decisions when, for instance, unforeseeable variations in the air content occur.

6.7 OTHER EFFECTS OF AIR ENTRAINMENT

In addition to protecting concrete against frost action, air entrainment also has other significant effects on concrete. The presence of air voids in the paste increases the workability of the fresh mix, but it obviously reduces the strength of the hardened concrete. It also decreases the permeability and thus increases the resistance to various forms of chemical attack.

In standard Portland cement mixes designed for frost resistance (with water/cement ratios of 0.45 to 0.50), the use of air entrainment has a relatively small influence on the cement content, and thus on the cost of the mixes. Because the presence of the small air voids increases the workability of the mix, the water content can be reduced. It is thus possible, with about the same cement content (or just a little more), to obtain the same compressive strength for an air-entrained as for a non-air-entrained mix, because the air-entrained mix has a lower water content and thus a lower water/cement ratio. In high-strength concretes, however, this is not the case; the decrease in compressive strength due to air entrainment is generally significant and cannot be compensated for without adding significantly to the cost of the mixes.

The influence of air entrainment on permeability and resistance to chemical attack is related to a number of factors. In addition to the fact that air-entrained concretes generally have a lower water/cement ratio, and thus a lower capillary porosity, the use of air entrainment tends to reduce segregation and, most important, bleeding. In pavements, slabs and other horizontal structures, bleeding creates a network of capillary channels from the bottom to the top. The presence of these channels increases permeability and facilitates the penetration of salts and other aggressive chemicals. Some authors also consider that the spherical air voids (which are much larger than the capillary pores and where water has less tendency to penetrate) tend to slow down the movement of water. In the same way as ice, which can form in the air voids without creating any significant stresses, the expansive products due to certain chemical reactions can also in part form in the air voids, and this can reduce the damage due to the formation of these products.

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Chapter 7
Exposure Conditions and Field Performance

The previous chapters have examined the different theories and concepts related to the action of frost on concrete, as well as the various parameters which influence the frost resistance of concrete and the laboratory tests used to determine this resistance. Although in many instances the natural exposure conditions which the tests are intended to simulate were mentioned, and some of the differences between the laboratory tests and the natural field conditions were pointed out, no general discussion of the frost durability of concrete under natural conditions of exposure has yet been presented. In this chapter, the differences between laboratory and field conditions are presented and analysed, with a view to determining which have the most significance concerning frost resistance. The results of a number of field tests and case histories are then described, and the relationships between field performance and the theories and concepts presented in the previous chapters, as well as the importance of the parameters normally expected to influence the frost resistance, are discussed.

7.1 EXPOSURE CONDITIONS

The characteristics of the freezing and thawing cycles are certainly the most obvious, if not the most important, of the possible differences between laboratory and field exposure. These characteristics are basically the freezing rate, the minimum temperature and the length of the freezing period. The most important difference (besides the number of cycles which, in laboratory tests, is generally fixed at 300) is probably the **variability** of the natural cycles as compared to that of any standardized cycle. Consider as an example the cycles shown in Figure 7.1. Each curve represents the variation of the outdoor temperature in the Québec city area on a given 3-day period. In certain cases the temperature varies only between +1 °C and −1 °C, but in other cases it drops from +4 °C to −13 °C in 10 h. Of course, the temperature of any portion of a concrete element exposed to natural cycles does not necessarily directly follow the variation of the air temperature, particularly the surface layer of such elements. As explained in Chapter 2, Hudec *et al.* (1986) have observed that, due to alternate sunny and cloudy periods on cold winter days, the surface layer can be subjected to several freezing and thawing cycles per day. Freezing rates of more than 12 °C/h were noted in certain cases (Moukwa and Adkins, 1988).

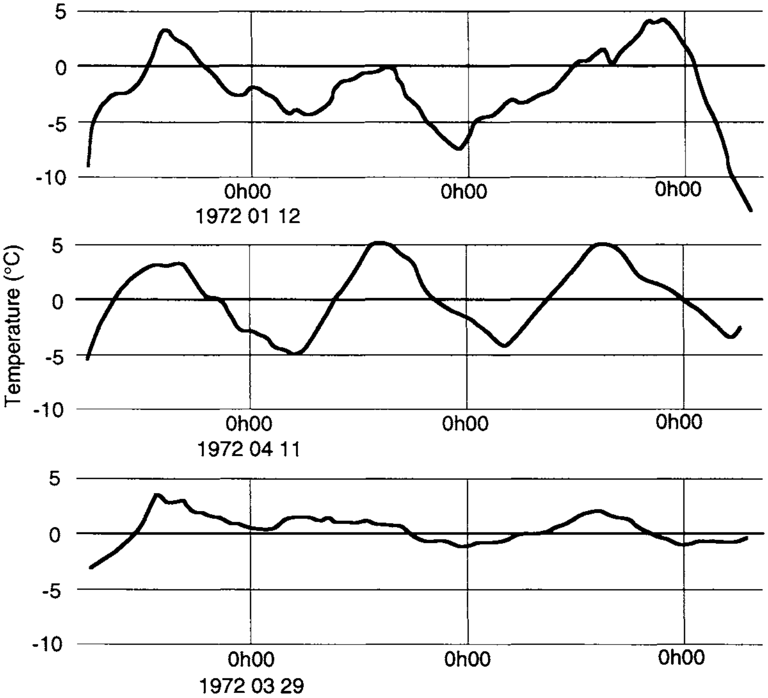

Figure 7.1 Typical freezing and thawing cycles in Québec city.

In most freezing and thawing cycle tests, the freezing rate in the body of the specimen is higher than the natural rates which are typically of the order of 0.5 °C/h–2 °C/h, perhaps 3 °C/h at the most (Pigeon, 1989; Cordon, 1966). In the standard test of ASTM C 666, the minimum rate of freezing that is allowed is about 8 °C/h and the maximum 16 °C/h. Laboratory tests, as well as theoretical considerations (Pigeon *et al.,* 1985; Litvan, 1980), clearly indicate that such rapid temperature decreases create internal stresses which will rarely be experienced under field conditions. Furthermore, the minimum temperature during most natural daily cycles is generally significantly higher than the usual −18 °C (0 °F). Although the exact influence of the minimum temperature is still disputed, lower values are surely more damaging than higher values. In addition, because of time limitations, laboratory freezing and thawing cycle tests generally do not include any holding time at the minimum temperature, i.e. the temperature starts to increase as soon as the minimum is reached. As explained in Chapter 2, time is required for ice accretion in the capillary pores because water cannot move rapidly in the paste. The lack of such holding periods at the minimum temperature therefore reduces the severity of laboratory freezing and thawing cycle tests and, although the exact influence of these periods is also still a matter of dispute, it is probable that it compensates in part for the effect of the higher freezing rate. Recent results by Stark (1989) have confirmed the influence of the length of the freezing period.

The resistance of concrete to de-icer salt scaling is generally determined with a minimum of 50 daily cycles of freezing and thawing, the surface of the specimen being covered at all times with a de-icer salt solution. For many reasons, these tests are generally considered to be very severe, as well as closer to natural exposure conditions. First, although the rate of freezing is usually somewhat lower than in freezing and thawing cycle tests such as ASTM C 666 (Figure 4.4), the long freezing periods (approximately 4–8 hours at a minimum temperature of −18 °C or −20 °C) allow much more time for ice accretion in the capillary pores. Secondly, as Sellevold and Farstad (1991) have shown, the concrete surface can be weakened by the drying period before the test, probably because drying can increase the permeability and the freezable water content. While it seems that an increase in permeability has a positive influence on the resistance of concrete to freezing and thawing cycles because it facilitates the movement of water to the air voids (Wong *et al.,* 1973), it probably has a negative influence on the resistance to scaling because it can facilitate the saturation of the surface, perhaps even that of the air voids (recent information suggests that, as observed by Verbeck and Klieger (1957), moderate drying can have a positive influence). Thirdly, contrary to ASTM C 666 which is mostly meant to determine the resistance of the body of the specimens to internal stresses due to freezing, this test is meant to measure the resistance of the surface to scaling. However, while it is evident that no concrete specimen can be completely saturated throughout during freezing, this is not the case for the surface which is covered with a de-icer salt solution at all times and thus is fully saturated during freezing. Lastly, the concentration of the de-icer salt solution that covers the concrete surface during the tests is always the most damaging (i.e. approximately 3–4%). This, of course, is not necessarily the case in the field. The concentration of the de-icer salt solution covering the surface controls in good part that of the solution in the capillary pores of the surface layer of concrete. If the concentration on top is much lower than 3%, this will tend to reduce the concentration in the capillary pores and thus reduce the osmotic pressures. If it is much higher, the concentration in the capillary pores will also be higher and ice formation will be reduced.

The importance of the minimum temperature of the cycle was studied by Sellevold and Farstad (1991), in connection with the resistance to de-icer salt scaling. They found that increasing the minimum temperature from −20 °C to −10 °C could reduce very significantly the amount of surface deterioration. In certain cases, the mass of scaled-off particles after 56 cycles decreased from more than 2 kg/m^2 to less than 0.25 kg/m^2. Low temperature calorimetry (as well as theoretical considerations) indicates that the major peak of ice formation, which generally occurs between −2 °C and −10 °C (Figure 3.6), is displaced towards the lower temperatures when the salt concentration in the pore water is high. If the minimum temperature during a de-icer salt scaling test is increased from −20 °C to −10 °C, it is thus probable that ice formation is significantly lower.

The question of the degree of saturation is certainly the most important difference between laboratory tests and natural exposure conditions. It is an undisputed fact that concrete needs to be relatively close to a full saturation state in order to be damaged by frost. Very often, in cities such as Québec and Montréal where frost damage is unfortunately quite frequent, it is evident that concrete is only significantly deteriorated in the areas where it has easy access to moisture (Figure 7.2). **To protect any concrete from frost damage, the most important thing is therefore to design properly the structure to ensure that no significant part of the concrete will be kept humid most of the time.** This, of course, is not always possible, and this is why so many precautions are necessary to ensure good frost and salt scaling resistance of pavements, curbs, sidewalks and similar structures.

Apart from the work done by Fagerlund (1971) and by Litvan (1973), there are not many test results reported in the technical literature on the influence of the degree of saturation. The main reason for this is probably that it is difficult to define exactly and to determine a degree of saturation. MacInnis and Beaudoin (1968) studied the influence of the degree of saturation on the frost resistance of mortars, the degree of saturation being defined as the weight of evaporable water contained in the specimen at the time of freezing divided by the weight of evaporable water required for full saturation (from the oven-dry state to a constant weight state under vacuum saturation). They found that a degree of saturation of more than 90% was required for frost damage to occur in non-air-entrained 0.40–0.50 water/cement ratio concretes. The results of these tests clearly confirm the necessity of a high degree of saturation for frost damage. They do not, however, provide information which can be of any direct use, particularly since the drying process modifies the microstructure of concrete and because the extent to which the gel and the capillary pores can become completely filled with water after drying is not known.

Figure 7.2 Frost damage on a part of a concrete structure with easy access to moisture.

As mentioned previously, deterioration due to frost is most likely to occur in practice in pavements, sidewalks, curbs, highway barriers and similar structures, because they are more likely to freeze in a saturated state and are subjected to direct salt applications. Other structures or parts of structures, however, can also be seriously deteriorated by frost action because they are placed in such a way that salt water can be splashed on them, or because salt brine (due to trucks passing on a wet salted pavement) can be sprayed on them (Figure 7.3). Although laboratory tests indicate that the most damaging de-icer salt concentration is of the order of 3–4% (for sodium and calcium chloride (Figure 2.6)), field observations indicate that deterioration generally increases with the amount of de-icer salts used. This is probably simply due to the fact that the penetration of chloride ions is a relatively slow process in good quality concrete, and mostly that rainfall periodically washes away some of the salt from the concrete surface. The salt concentration in the pore water of field concrete therefore does not normally reach the most damaging value of 3–4% (Cady and Weyers, 1983).

Figure 7.3 Concretre highway structure exposed to splashing of water containing de-icer salts.

In the laboratory, concrete freezes with a salt solution of a given concentration on the surface of the specimen. In the field, however, concrete pavements, for instance, will be frequently sprayed with de-icer salts and the surface will freeze in a close to saturated state but with little water on it. Highway barriers, such as those studied by Moukwa and Adkins (1988), can also suffer severe de-icer salt scaling problems without freezing in the presence of a salt solution. At the end of a cold and sunny day, the surface layer can freeze and trap a lens of unfrozen water beneath it. This mechanism, according to Moukwa and Adkins, can create large tensile stresses.

Early freezing, before concrete has had time to set, or during setting, can cause very serious damage. When concrete freezes before setting, small ice lenses are formed in the paste. The areas in which these lenses are located do not become filled with hydration products when the concrete is heated and the hydration process starts again. This causes a permanent loss of compressive strength that can reach 50% of the strength of the same concrete cured normally. These large pores, however, do not seem to become filled easily with water again, and could thus act as micro air voids to help protect concrete against frost damage (Lacroix and Houde, 1991). Freezing during setting, as is well known, also significantly reduces the compressive strength that can be obtained when concrete is heated again to reactivate the hydration process. It is therefore always advisable to protect concrete from early freezing because it usually leads to permanent damage, and air entrainment does not offer a good protection against this phenomenon of ice lens formation.

7.2 FIELD PERFORMANCE

To determine the most important parameters affecting the resistance of concrete to freezing and thawing cycles and to scaling due to de-icer salts, the best method is obviously to analyse the performance of concrete subjected to natural exposure conditions, since, regardless of all theoretical considerations and laboratory test data, field performance is what really counts. There are two basic ways to study field performance: field tests and case histories. These two methods are in fact quite similar. The only difference between them is that, in field tests, the characteristics of the concrete mixes and the exposure sites are chosen in advance and the placement and curing operations are controlled by competent staff. However, if the original mix composition and details of the placement and curing operations can be found, case histories provide information that can be as useful as that of field tests, since in both cases the final analysis is based on the actual field performance of the material.

Over the last 50 years, even if there are still some engineers and technicians who are not fully convinced of this fact, the field performance of concrete in a large number of locations throughout Europe and North America has proven beyond any doubt the importance of air entrainment for good frost resistance. In the USA, the Portland Cement Association has published extensive data on this subject (Klieger, 1980). As part of their research programme ‘Long-Time Study of Cement Performance in Concrete’, concrete boxes were exposed for more than 25 years in a test plot located in Naperville, Illinois. As stated by Klieger, the results obtained show clearly the ‘overwhelming effect of air entrainment’.

At Treat Island, Maine, an exposure station operated by the US Army Corps of Engineers, where concrete specimens are placed in racks at midtide level and are subjected to an average of 100 cycles of freezing and thawing each year, numerous test projects have confirmed the importance of air entrainment for concretes exposed to freezing and thawing cycles (Malhotra *et al.,* 1987).

The benefits of air entrainment for protection against de-icer salt scaling were also demonstrated clearly by field tests carried out by the Portland Cement Association. Figure 7.4 shows, for instance, the excellent correlation between the number of air voids per unit of traverse (measured according to ASTM Standard C 457) and the actual field performance (in terms of the intensity of surface scaling) of a concrete pavement subjected to freezing and de-icer salts (in the state of New York). Sommer (1979) reported the results of a field study carried out in West Germany which also showed clearly the importance of correct air entrainment for good de-icer salt scaling resistance of concrete pavements.

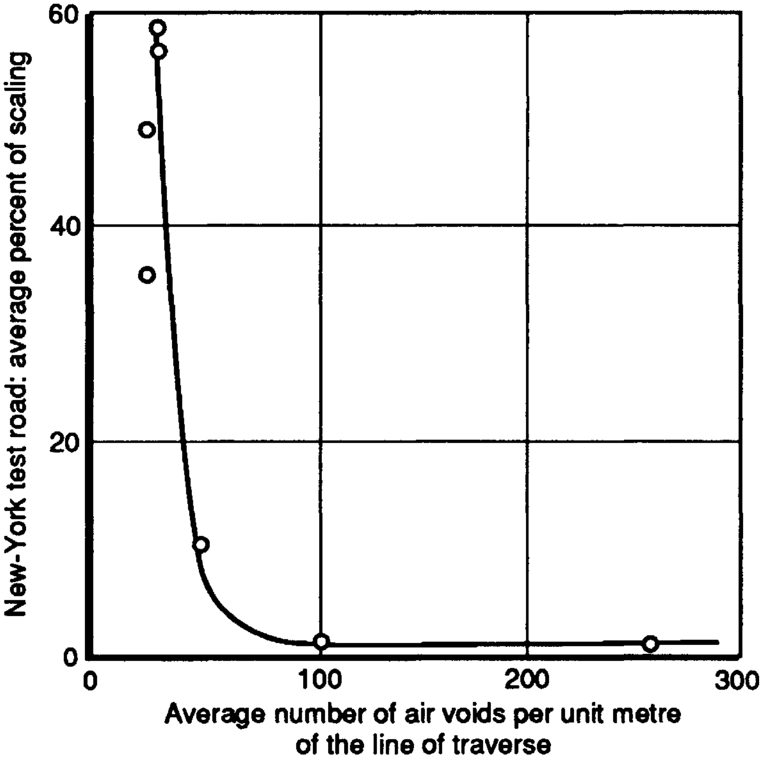

Figure 7.4 Relationship between surface scaling and number of air voids per unit length of traverse for a pavement in the state of New York (after Klieger, 1980).

In Canada, and especially in the provinces of Ontario and Québec, exposure conditions for concrete structures are considered to be particularly severe: snow is frequent (and often also freezing rain), the number of freezing and thawing cycles per year is high, the minimum temperatures can be very low, and large amounts of de-icer salts are used. In the province of Québec, more than 20 metric tons of sodium chloride per kilometre of road are poured on the highways every year (Fournier *et al.,* 1987). In a field survey carried out in 1985 on a large number of structures in the Québec city area, scaling was only observed on the surface of concretes with an air-void spacing factor higher than 300 μm (Figure 7.5). In the city of Montreal, 20 experimental sidewalks were built in 1955. After 4 years, all non-air-entrained concretes were severely scaled and all air-entrained concretes were in a very good condition (Hode Keyser, 1968). The performance of more than 100 km of sidewalk in Montréal was also monitored for many years (Weaver and Isabelle, 1968). This study yielded similar conclusions.

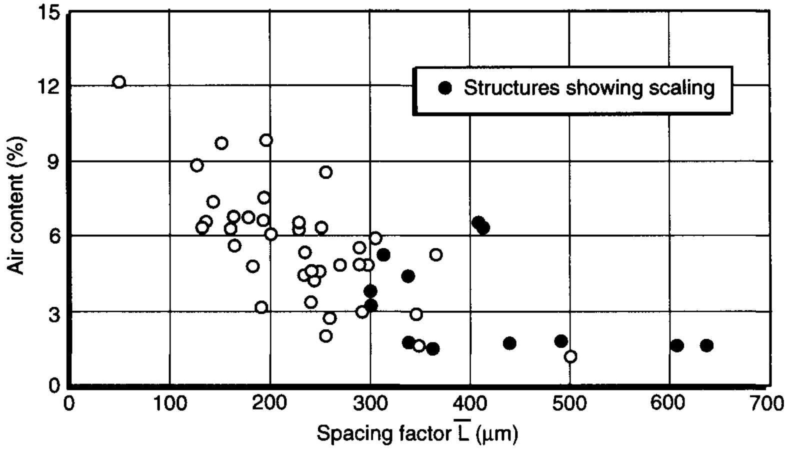

Figure 7.5 Relationship between air content and spacing factor for various concrete structures in the Québec city area (from Fournier *et al.,* 1987).

Although air entrainment is necessary to protect normal concretes against freezing and thawing cycles and de-icer salts, it cannot always prevent surface deterioration. If the concrete is of poor quality, or has not been sufficiently cured, scaling will eventually occur, even if the air-void spacing factor is below the usual 200 μm limit. This is illustrated in Figure 3.11 which shows the relation between the spacing factor and the intensity of scaling rated from 0 (no scaling) to 5 (very severe scaling) for a series of four-year-old sidewalk sections. In spite of the scatter of the data which is normal for field conditions, it is quite clear from this graph that the resistance to scaling is always very poor at high values of the spacing factor, but can range from good to very poor at low values.

It is evident, from what was said at the beginning of this chapter, that field exposure conditions are very different from laboratory exposure conditions. As a rule, engineers tend to prefer tests that are severe because it is considered preferable to reject some concretes that could be durable under field conditions than risk accepting even a small number of concretes that would not be durable under field conditions. In laboratory freezing and thawing tests, concrete is therefore generally subjected to exposure conditions that are more severe than most natural conditions. This fact came out clearly, for instance, from a series of field tests carried out in Canada from 1972 to 1977 (Litvan *et al.,* 1980). Litvan even concluded from these results obtained for precast concrete elements that

> *conventional laboratory tests, under conditions prevailing in the present programme, yielded predictions which show little, if any, agreement with actual field performance.*

Recent tests on field concretes, however, have indicated that the ASTM C 672 is perhaps not as severe as was previously considered, and that it is still a very useful tool to predict field performance (Laroche *et al.,* 1993).

In addition to pointing out the importance of many basic parameters such as air entrainment and the generally better durability of concrete exposed to field conditions as opposed to laboratory conditions, field studies can provide useful information on many other aspects of frost durability. Aïtcin and Pigeon (1986), for instance, carried out a series of field tests on the performance of silica fume concretes used for pavements and sidewalks and concluded that, contrary to the results of certain laboratory tests (Pigeon, 1987), the de-icer salt scaling resistance of these concretes could be quite satisfactory if they had a proper air-void system. Whiting and Schmitt (1989) analysed the performance of twelve structures built with concretes incorporating a superplasticizer located in Canada and the Northern part of the United States. The observation of these 4- to 12-year-old structures revealed that scaling had developed in less than 4% of the total surface, even if many concretes did not have a proper air-void system according to generally accepted standards. The main conclusion of this field study was that good scaling resistance was possible with marginal spacing factors if the water/cement ratio of the concretes was below 0.40 and there was a sufficient air content in the surface layers of the concretes.

Numerous laboratory research projects, but only a small number of field studies, have been carried out on the frost durability of aggregates in concrete. Kaneuji *et al.* (1980), after having determined the relationship between the aggregate pore characteristics and the laboratory frost resistance of concrete (made with saturated aggregates) examined the pore characteristics of aggregates from approximately 30 different concrete structures exposed to freezing and thawing cycles. On the basis of the observed field performance of these structures, they concluded that, as in the laboratory tests, the aggregates with a relatively high and fine porosity were the most deleterious (Chapter 5). The importance of the size of the aggregate particles (Chapter 5) was confirmed by field observations of cracking in pavements in Ohio.

Sometimes, field observations can yield results that are quite unexpected. Stark (1986) noticed that freeze-thaw scaling had developed on a pavement surface in the paths followed by the vibrator heads of the paving machine, and therefore studied in the laboratory the effect of vibration on the air-void system and the frost resistance of concrete. He found that, in 0.40 and 0.50 water/cement ratio concretes, a 20 s vibration period at frequencies higher than 8000 vpm (vibrations per minute) resulted in significant increases of the air-void spacing factor, and concluded that excessive vibration during the placement operations of the pavement had probably adversely affected the air-void system in the areas near to the vibrators. In a report submitted to the Canadian Department of Transportation, Pigeon *et al.* (1990) similarly concluded that longitudinal cracks had developed in an airport runway because the vibrators of the paving machine had locally reduced the air content significantly. The concrete near the vibrators had therefore become frost susceptible, whereas the rest of the concrete had a sufficient air content. On the runway, the cracks had developed almost exactly along the paths followed by the vibrators.

Apart from the fact that the durability of concrete under field conditions is often much better than the durability measured in the laboratory, most field studies tend to confirm that the fundamental mechanisms of frost action as described by Powers, Helmuth and Litvan are valid and that most of the basic information obtained from laboratory testing is correct. The importance of air entrainment to protect the cement paste against frost action has been demonstrated a very large number of times. The increase in durability with the decrease of the water/cement ratio has also been well documented, and the relationship between the characteristics of the aggregate pore system (as well as the maximum size of the particles) and the resistance of concrete to freezing and thawing cycles has been clearly established. When the results of field tests (or of field observations) are not in agreement with those of laboratory tests, it is often because laboratory tests are more severe. Poor laboratory performance and good field performance is quite common, but good laboratory performance and poor field performance, apart from a few odd cases generally related to de-icer salt scaling, is rare.

The most important difference between laboratory tests and field exposure is probably, as mentioned at the beginning of this chapter, the degree of saturation. This is clearly illustrated in Figures 7.6 and 7.7. The degree of deterioration of a large number of bridge structures in Japan was found to be completely unrelated to the number of freezing and thawing cycles per year (Figure 7.6). However, a very clear relationship was found between the degree of deterioration and the product of the number of cycles multiplied by a saturation factor taking into account the amount of rainfall (Figure 7.7). If all concretes were always fully saturated during freezing, frost durability would not always be good, because experience unfortunately shows that concrete does not always have an air-void system with the required characteristics (Pigeon, 1989). Vanderhorst and Janssen (1990) measured the degree of saturation in various concrete pavements in the United States at different moments during the year and found values ranging approximately from 80% to 95%. So called D-line cracking likely occurs near to joints and corners because this is where concrete has easy access to moisture (Cordon, 1966).

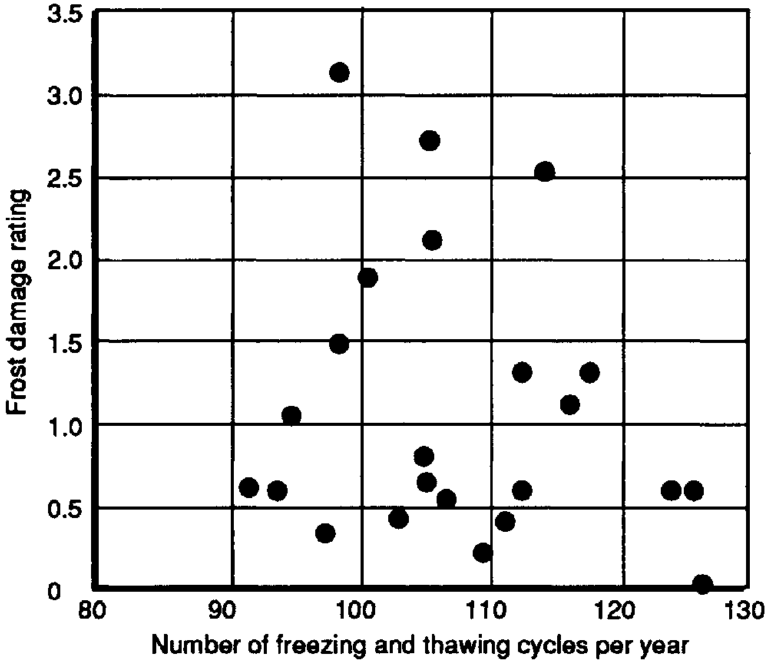

Figure 7.6 Frost damage versus number of freezing and thawing cycles per year for various concrete structures in Japan (after Fujiwara, 1987).

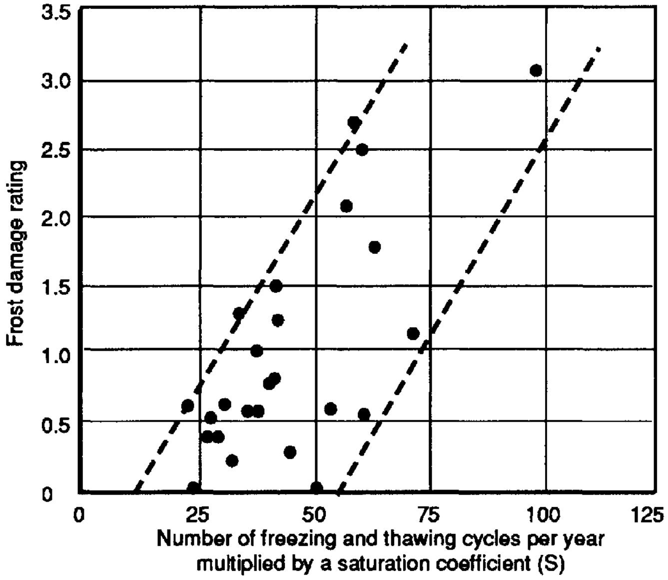

Figure 7.7 Frost damage versus number of freezing and thawing cycles per year multiplied by a saturation coefficient *S* for various concrete structures in Japan (after Fujiwara, 1987).

In laboratory de-icer salt scaling tests (ASTM C 672), the surface of the specimen is covered with salt water at all times. This, as previously pointed out, is not representative of field conditions and probably accounts in good part for the severity of the salt scaling test. Drying is also an important parameter, and recent results clearly show that long drying periods or high drying temperatures are particularly harmful (probably because they increase the thickness of the layers that are affected). Normal Portland cement concrete with a 0.45 water/cement ratio and a correct spacing factor that has dried for three days at 40 °C has a weight loss higher than the usual limit of 1 kg/m^2 after 50 cycles of freezing in the presence of de-icer salts (Pigeon, 1990). It is thus difficult, to say the least, to predict the service life of a given concrete from the results of de-icer salt scaling tests, particularly since there is no information available from field concretes as regards the effect of natural drying on the microstructure of the surface layers. It is clear, however, that the drying condition of laboratory specimens should be very carefully controlled.

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Chapter 8
Frost Durability of Dry Concretes

The theories described in Chapter 2 are applicable to normal cast-in-place concretes which have sufficient fluidity at the time of casting to be considered relatively homogeneous. Unless special problems occur, the coarse as well as the fine aggregate particles in normal concretes are completely surrounded by cement paste in which the cement grains (and thus the capillary cavities containing the freezable water) are relatively well dispersed. Air voids are present, even when the concrete is not air entrained, but they are almost all spherical in shape and fairly well distributed in the paste. Internal bleed water or very large air voids can sometimes be trapped underneath aggregate particles and this, together with certain phenomena occurring at the aggregate-paste interface, can reduce the homogeneity of the hardened concrete. In such concretes, the average size of the pores which contain the freezable water is at least 100 times smaller than the size of the air voids. Under normal conditions the air voids never become saturated and can always act as escape areas in which water can freeze without creating any internal pressure. Each air void can therefore be considered to protect a certain volume of paste with a certain freezable water content. The distance between the air voids determines the volume of paste that each void must protect and thus the largest distance that water must travel to reach an air void (hence the spacing factor concept).

Dry concretes, such as roller-compacted concrete, can have an internal structure very different from that of normal concretes; it is not clear that the theories related to frost action which are valid for normal concretes are also applicable to dry concretes. In this chapter, after a brief description of the different types of dry concretes, their internal structure is examined and compared to that of normal concretes, and the differences which are important concerning frost resistance are identified. Since the early 1980s, a limited number of investigations have been carried out to determine the frost durability of certain types of dry concrete, to analyse the main parameters which affect this durability and, in certain cases, to study the problem of air entrainment in dry concretes. This information is also presented and discussed.

8.1 THE DIFFERENT TYPES OF DRY CONCRETES

Generally speaking, dry concretes can be defined as concretes in which the amount of water or cement paste in the mix is significantly lower than that in normal concretes. Some form of pressure is thus required during the placement operations to obtain a reasonable degree of compaction.

Roller-compacted concrete is used mainly for dams and also for certain types of pavements. In the case of dam construction, its main advantage is, of course, the lower cement content of the mix which reduces the problems due to the heat of hydration of cement. In the case of pavements, its advantages are mainly economical: the cost of the concrete is lower due to the lower cement content, the concrete can be transported to the site in dump trucks instead of the usual ready-mix trucks, and it can be placed with the same equipment as asphalt (Figures 8.1 and 8.2).

Many concrete elements that are fabricated in plants are made of dry concrete. Typical examples are prefabricated concrete curbs, and concrete paving blocks. Manufactured concrete pipes are generally made of dry concrete, but, in this case, frost durability is not considered to be an important problem. Some parts of the drainage system in city streets, however, which are often manufactured with dry concrete (the top portion of concrete manholes for instance) can be exposed to freezing and thawing cycles in a saturated state, and this should not be neglected.

Shotcreting is a very convenient technique for concrete repairs in many situations. Wet-process shotcrete is similar to normal concrete, but dry-process shotcrete (where water is added at the nozzle only) has an internal structure probably closer to that of dry concrete, although, in part because of the rebound phenomenon, its coarse aggregegate content is generally quite low.

These different types of dry concrete all have one very important common feature: the amount of water that they contain must be controlled precisely because the stiffness of the mix in all cases plays an extremely important role during the placement operations. In roller-compacted concrete, for instance, the mix must be stiff enough to support a five- or ten-ton roller. In the manufacture of paving blocks, the blocks are demolded immediately after they are compacted, and shotcrete must stick to the underlying material. The mix therefore should not contain too much water, but, on the other hand, if it is too dry, the right degree of compaction simply cannot be attained.

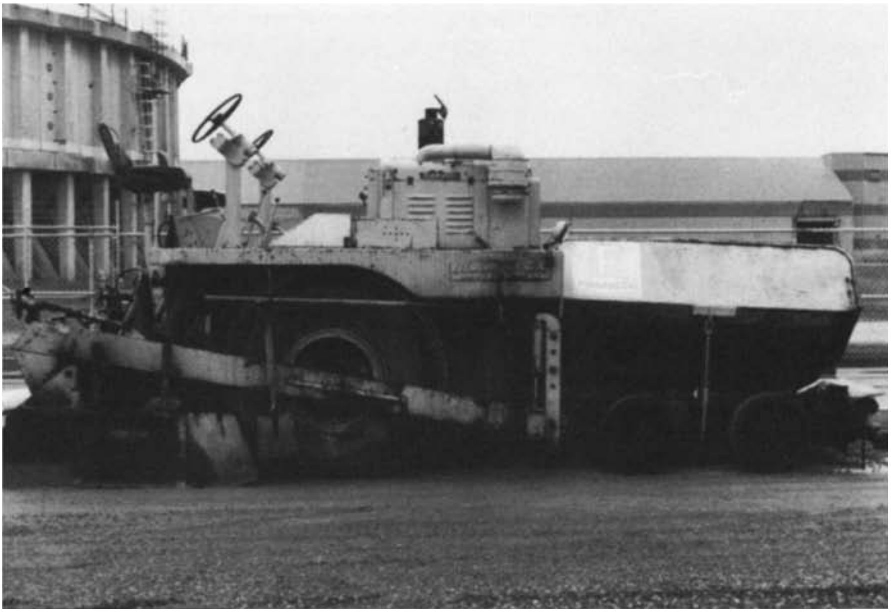

Figure 8.1 Asphalt paver used to place roller-compacted concrete.

Figure 8.2 Dump truck used for the transportation of concrete during the construction of a roller-compacted concrete pavement.

8.2 INTERNAL STRUCTURE OF DRY CONCRETES

The easiest way to visualize the internal structure of any dry concrete (with the exception of dry-process shotcrete) is to consider it as a mass of coarse and fine aggregate particles which are covered with a thin layer of cement paste and then compacted together. This is represented schematically in Figure 8.3. Neglecting the possibility that these concretes are air entrained (this topic is discussed in the next section), it can be seen that the air voids in dry concrete are not spherical in shape as in normal concrete, but are irregularly shaped (Figure 8.4 shows a polished section of a paving block at an original magnification of 30×). These air voids are called compaction voids because they are formed during the compaction process. They are inevitable because the dry mixes generally do not contain enough paste to fill all the spaces left between the aggregate particles. The total volume of compaction voids in any dry concrete should, of course, be as small as possible. In this respect, the grading of all solid particles, including coarse and fine aggregates as well as cement and mineral additives, is particularly important.

It would be easy to jump to the simple conclusion that dry concretes are naturally air entrained, apply the procedure described in ASTM C 457 to determine the air-void spacing factor (taking into account all compaction voids) and consider that the concrete will be frost resistant if the air-void spacing factor is smaller than 200 μm. However, this would be too easy, and most probably incorrect in many cases, for two main reasons. The first one is that the possibility that these voids are interconnected is not negligible. In normal concrete, the air content forms a discontinuous network of voids separated from each other by cement paste with a relatively low permeability (at least in good quality concrete). This explains why, in most circumstances, these voids are never saturated and can act as ‘safety valves’. If the compaction air voids are not discontinuous, they will become saturated if enough water is available and their influence on frost resistance will be negative instead of positive.

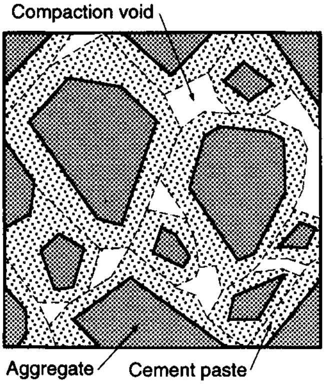

Figure 8.3 Schematic representation of the structure of roller-compacted concrete.

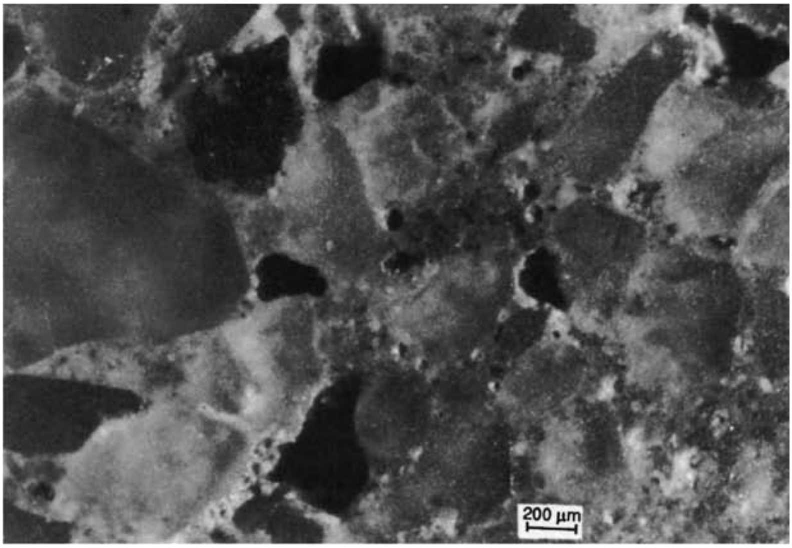

Figure 8.4 Typical compaction air voids in a concrete paving block (polished section examined under an optical microscope at an original magnification of 30×).

The second reason for being cautious in applying to dry concretes the concepts that are valid for normal concretes is the possibility that the paste in such concretes has a lower degree of homogeneity. It is much more difficult to disperse the cement grains properly in a low water/cement ratio paste (such as is often the case in dry concrete) and proper paste mixing is certainly much more difficult to achieve when most of the paste simply forms a thin coating on the aggregate particles. This was verified recently by Marchand *et al.* (1993), who also found, however, that the use of fly ash or silica fume could increase the degree of homogeneity of the paste.

If the paste is less homogeneous, it will contain more large or macro capillary pores where water can freeze at temperatures just below 0 °C. It will also be more permeable than the paste in normal concrete, which means that it will become saturated more easily and that the compaction air voids, even if they are discontinuous, will also have more chance of becoming saturated. But even if the compaction air voids do not become saturated, the presence of a higher number of large capillary pores can clearly reduce very significantly the frost resistance of dry concretes simply because of the increase in the freezable water content and the higher probability that the concrete will be more saturated at the time of freezing.

Apart from the presence of the compaction voids and the greater difficulty in obtaining a relatively homogeneous paste, there is another possible significant distinction between the internal structure of dry concretes and that of normal concretes. Due to the compaction process and the high aggregate content, dry concretes (again with the exception of dry-process shotcrete) have a very rigid skeleton of aggregate particles. It is thus possible that shrinkage in the paste creates much more cracking than in normal concretes due to the higher restraining effect of the aggregate. While this has not been definitely proven, it represents another illustration of the possible structural differences between normal and dry concretes.

The possibility that the compaction voids help to reduce the internal pressures due to freezing of course exists. This will be discussed below.

The coarse aggregate content of dry-process shotcrete, as previously mentioned, is generally quite low. This material thus contains only a limited number of compaction voids. Its cement paste, however, is probably less homogeneous than that of normal concrete.

8.3 AIR ENTRAINMENT IN DRY CONCRETES

Is it possible to entrain air in dry concretes? The answer to this question is yes, but in most cases it involves a more complicated procedure than simply adding an air-entraining admixture to the concrete in the mixer.

Powers (1964) has described clearly the mechanisms of air entrainment in concrete. He pointed out that the formation of air bubbles is only possible if a sufficient amount of water is available, because there has to be a film of water around the bubbles. As the water/cement ratio decreases, not only does the viscosity of the paste increase (which in turns increases the required mixing energy), but the amount of water available for bubble formation decreases because there are more solid surfaces that must be covered with water.

The stiffness (or dryness) of a mix increases with the amount of aggregate because the solid surfaces of the aggregates, like the surfaces of the cement particles, must be covered with water. Entraining air in dry concrete is therefore generally only possible if the mixing sequence is modified in such a way as first to mix the cement, the water and the air-entraining agent with only a fraction of the aggregate. Once the action of mixing has allowed the formation of a sufficient volume of air voids, then the rest of the aggregates can be added. Andersson (1987) has succesfully used this type of procedure for roller-compacted concrete mixes. In his tests, the cement, the water and the air-entraining admixture were first mixed with the fine aggregate (a small amount of superplasticizer was used to increase the fluidity and the homogeneity of the paste), and the coarse aggregate was added only after this first period of mixing.

Since air entrainment in dry concrete is difficult, it is of course particularly important to use the most powerful air-entraining agent available. The type of mixer also obviously plays an important role. Boisvert *et al.* (1992) found that air bubbles could be entrained in a dry mix (prepared for fabricating paving blocks) without modifying the mixing sequence. This was apparently due to the very energetic mixer used (a horizontal cylinder-type mixer with blades rotating around a horizontal axis). Other investigators, using very efficient laboratory mixers (Figure 8.5), have also succeeded in entraining spherical air voids in various types of dry concretes (Delagrave *et al.,* 1994; Guiraud, 1995).

In a recent series of field tests, Marchand *et al.* (1992) have found that it is extremely difficult to entrain air bubbles in roller-compacted concrete (with a water/cement ratio of approximately 0.35), even when the cement paste (containing the air-entraining agent) is first mixed with only half the total amount of both coarse and fine aggregates. These field concretes, however, were mixed in a drum-type plant mixer where the mixing action is mostly due to concrete falling on itself. Table 8.1 gives the characteristics of some of the mixes tested by Marchand *et al.,* as well as the results of the determination of the air-void characteristics of the hardened concretes, the spherical air voids being considered separately from the compaction voids for the determination of the air content.

In dry-process shotcrete, recent investigations have shown that it is possible to reduce significantly the air-void spacing factor by using very large dosages of an air-entraining agent in the water that is added under pressure at the nozzle (Lamontagne, 1993). The general applicability of such a procedure, however, has yet to be demonstrated.

Figure 8.5 Typical concrete mixer used in the laboratory.

Table 8.1 Air void characteristics of various roller-compacted concretes (after Marchand *et al.,* 1993).

Mixture No.	Spherical air void content (%)	Total air void content (%)	Specific surface (mm^{-1})	Spacing factor (μm)
1	0.7	9.9	15	130
2	0.4	4.2	20	240
3	0.1	9.4	9	220
4	0.1	6.0	13	340
5	0.1	6.1	17	220
6	1.2	7.9	20	110
7	0.3	6.1	18	220
8	0.2	7.3	11	260

8.4 FROST RESISTANCE

Dry concretes, like all other types of concrete, can be subjected to two types of deterioration due to frost: internal cracking and surface scaling. Although, as previously pointed out, both types of damage can occur separately, in certain cases both occur together, and it is difficult to distinguish between the two effects. This seems to be particularly the case with paving blocks. Some blocks which are subjected to natural freezing and thawing cycles and frequent de-icer salt applications are sometimes damaged so badly that it is not possible to determine the main cause of the damage, i.e. very intensive surface scaling, internal disruption or both. As can be seen in Figure 8.6, it seems that individual paving blocks are either frost resistant or not. It is not common to find areas where all blocks exhibit similar deterioration.

Ragan (1986) has studied the frost durability of a large number of roller-compacted concrete pavements made between 1976 and 1985 in the United States. Specimens were sawn from the various pavements and subjected to freezing and thawing cycles in accordance with ASTM Standard C 666, procedure A (freezing and thawing in water). The air-void characteristics of all concretes were also determined. The main conclusion of this study was that the frost durability was directly related to the air-void spacing factor, the value required for good durability being approximately 250 μm. Since none of these concretes was fabricated with an air-entraining agent, these tests indicate that the compaction air-void system in dry concretes can offer, in certain cases, the same protection against frost action as entrained air voids.

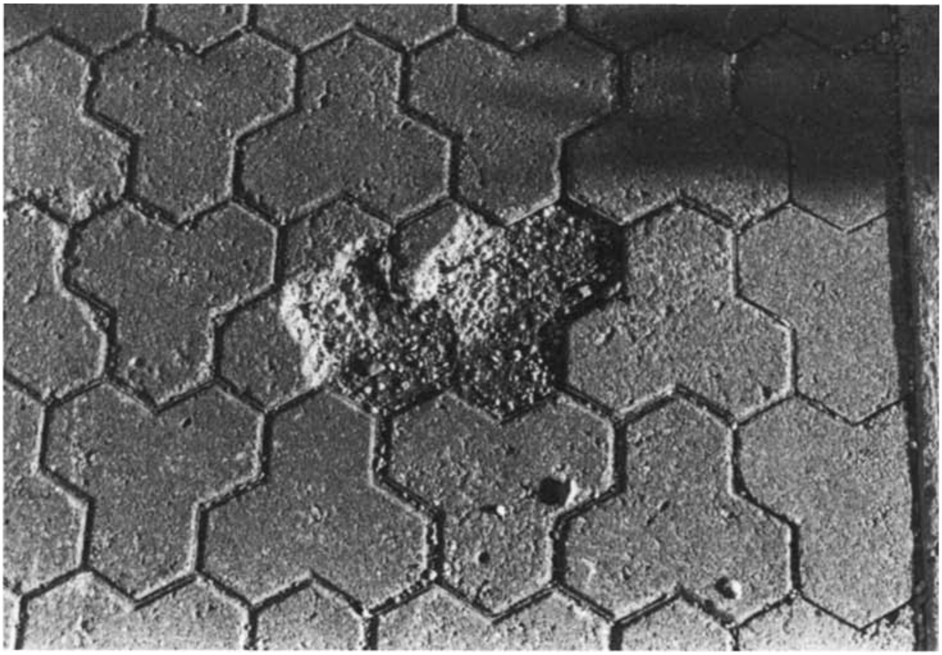

Figure 8.6 Typical deterioration on a section of a pavement made of concrete paving blocks.

The frost durability of various roller-compacted concretes used for constructing a pavement test section was recently investigated by Pigeon and Marchand (1993), using the same test methods as Ragan. Although some of the concretes had been made with an air-entraining agent, only two contained a significant number of spherical air voids. It was found that the frost durability of these concretes was quite variable, and that it was not related to the air-void spacing factor. Some of the results, however, indicate that the use of air-entraining agents often had a positive influence, even if no spherical air voids were seen during the optical microscope examinations. It was also noted by Pigeon and Marchand that the frost resistance was related to the degree of compaction, well compacted concretes generally having a better frost resistance. In certain cases, significant deterioration was noted only after a very large number of cycles. The ASTM Standard requires 300 cycles when the dynamic modulus of elasticity does not decrease by more than 40% during the test (Chapter 4), but a number of specimens tested by Pigeon and Marchand were subjected to 1000 cycles.

The results of the tests by Ragan and by Pigeon and Marchand tend to demonstrate that, at least as regards the resistance to internal cracking, the compaction voids can offer the same protection as the air bubbles in normal air-entrained concrete. It is further possible that the higher permeability of the dry concretes has a positive effect because it helps to reduce the internal pressures due to the movement of water to the air voids during freezing. However, the compaction voids do not always offer a sufficient protection. Furthermore, some concretes can resist 300 cycles, but not 1000. This is in contrast to normal concretes which are usually either frost susceptible or frost durable; if they are frost durable, the number of cycles they can withstand is very large. Of course, freezing cycles in water tend to increase the degree of saturation of any concrete, but this is probably much more important in the relatively more permeable dry concretes. One of the possible causes of the lack of resistance of some dry concretes to a large number of cycles could therefore be the gradual filling up of all the very large capillary pores (which are not necessarily all filled with water at the time of testing) and of some of the compaction voids.

The problem that can be created by the presence of a number of fully saturated compaction voids, even if the paste contains empty air voids or bubbles, is illustrated in Figure 8.7. In normal air-entrained concrete, the freezable water is contained in capillary pores that are small compared to the size of the air bubbles, and one air void serves as a safety valve for all of the freezable water contained in the capillary pores situated within the sphere of influence of the void, the thickness of this sphere determining the maximum distance that water must travel and hence the intensity of the pressure due to the flow. Considering, however, a dry concrete with a compaction void filled with water, it can be seen that the situation is in effect reversed. There is a large reservoir filled with water that is surrounded by empty air voids. As ice forms, water must move from this void to the others (i.e. a distance equivalent to twice the value of the spacing factor), and it is only those air voids that are close that can offer escape routes for the water. In addition, in such a case, the flow of water in the paste in the localized area around the void filled with water is much higher than the flow from the small capillary pores to the air bubbles in normal concrete.

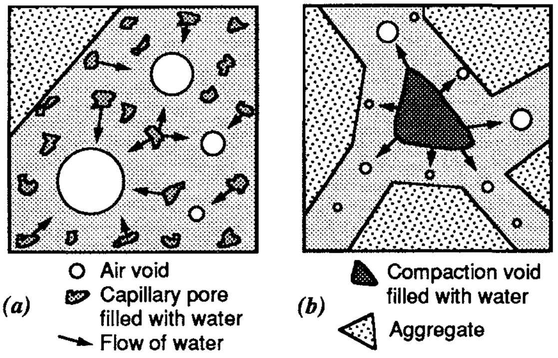

Figure 8.7 Schematic representation of: (a) the influence of water-filled capillary pores on the frost resistance of normal concrete; (b) the influence of a water-filled compaction void on the frost resistance of a dry concrete.

As previously described, dry-process shotcrete contains only a small number of compaction air voids. It is therefore probable that its frost resistance is directly related to the air-void spacing factor. Many investigators have found that dry-process shotcrete could have an excellent frost resistance (Morgan, 1989), and recent studies have indicated that its air-void spacing factor is generally of the order of 300 μm (Lamontagne, 1993).

The de-icer salt scaling resistance of dry concretes is, in a way, a problem that is simpler than the resistance to internal cracking. It is clear from what has just been said that if the compaction voids can easily be filled with water, the frost durability will be very low. This is of course particularly true for de-icer salt scaling because saturation of the surface is much more rapid than the saturation of the body of the specimen. A good de-icer salt resistance will therefore only be possible if the concrete has a very low permeability. The test results obtained by Clark (1980) and those obtained by Boisvert *et al.* (1992) tend to confirm this hypothesis. These investigators have studied the de-icer salt scaling resistance of many different dry concretes used to fabricate paving blocks, and, basically, they have come to the same conclusion. Clark, who tested a large number of different non-air-entrained concretes concluded that the salt scaling resistance varied significantly with only one of the parameters investigated, the water/cement ratio. Boisvert *et al.* concluded that all factors which tended to decrease the permeability of the concrete (the use of silica fume, for instance) had a positive influence on the salt scaling resistance. Clark and Boisvert *et al.* used the same type of test (daily freezing and thawing cycles with a saline solution on top of the test specimen), and they found that a satisfactory performance was possible. Recent results by Pigeon and Marchand (1993) tend to confirm this hypothesis on the influence of permeability. They have observed that satisfactory de-icer salt scaling resistance could be obtained only if roller-compacted concrete contained supplementary cementing materials (such as fly ash and silica fume) to enhance the paste homogeneity.

Information on the de-icer salt scaling resistance of dry-process shotcrete is scarce. Recent results tend to show that, under certain conditions (air entrainment being one of them), this type of concrete can be resistant to scaling (Lamontagne, 1993). According to a survey by Morgan (1990), scaling is not a very common type of deterioration for this type of material, probably in good part because it is not used for the most severely exposed parts of concrete structures (such as slabs and curbs).

8.5 SUMMARY

More research is obviously needed before the problem of the frost durability of dry concretes can be fully understood. It is clear, at least theoretically, that the compaction voids must be discontinuous. However, many questions remain unanswered. The role of air entrainment, for instance, is still not clear. Good frost durability appears to be possible without air entrainment, but future research will be necessary to evaluate how the use of air entrainment can increase the resistance to freezing and thawing cycles as well as to de-icer salt scaling. Research will also be required to determine how the ASTM C 457 test method can be applied to concretes containing compaction voids (which do not necessarily have the same size distribution as the air bubbles in normal concrete), and to concretes containing both spherical air voids and compaction voids. Only then will it be possible to establish the limiting values of the spacing factor that are required for good frost resistance in dry concretes.

The resistance to de-icer salt scaling definitely seems to be related to permeability. A low surface permeability is needed for good scaling resistance, in order to reduce the possible saturation of the compaction voids and of the large capillary pores in the surface layers. Many problems remain to be solved, however, particularly in the case of roller-compacted concretes in which the structure of the surface layer can be affected very significantly by the compaction process. The influence of drying must also be investigated.

Finally, more research is needed to understand clearly the internal structure of all types of dry concretes, and especially the factors which cause this structure to vary and the influence that this variation can have on frost durability. Can water reducers and superplasticizers be used to increase significantly the homogeneity of the paste, and thus perhaps the frost durability? What are the conditions under which supplementary cementitious materials should be used in order to enhance the homogeneity of the paste? Is there a minimum cement or paste content required to obtain a sufficiently compact and durable internal structure? This is particularly important in the case of dams built with roller-compacted concrete where heat of hydration is a very significant parameter.

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Chapter 9
How to Make a Durable Concrete

It is possible, on the basis of the concepts and of the laboratory and field data presented in the previous chapters, to formulate a series of recommendations regarding the fabrication and production of durable concrete. These recommendations concern the choice of the materials and of the mixture characteristics, the mixing, transportation, placing, finishing and curing techniques, as well as the design of concrete structures exposed to frost. Many of these recommendations have already been discussed and this chapter is essentially a summary of the preceding chapters.

9.1 CHOICE OF MATERIALS

The making of durable concretes implies a careful choice of aggregates. Of course, frost-susceptible aggregates, i.e. aggregates which can be rapidly destroyed by repeated cycles of freezing and thawing, must be avoided. These generally have a relatively high total porosity but a fine pore structure. In fact, all aggregates with a high porosity (with a 24 h absorption of more than approximately 2%) should be avoided as much as possible, mostly because, when they are saturated, they can expel a significant amount of water into the surrounding paste and thus amplify the disruptive pressures due to frost action. D-line cracking (Chapter 5) is often considered to be due to frost action in aggregates which are not necessarily frost susceptible but which can create internal pressures due to the expulsion of water on freezing. Soft and laminated aggregates, such as shale, should also obviously never be used. Since the frost susceptibility of aggregates is a function of particle size (Chapter 5), caution must also be exercised when exceptionally large aggregates are used.

It is difficult to predict safely the frost behaviour of an aggregate since this behaviour is a function of both its intrinsic properties and the freezing environment. Petrographic examinations (ASTM C 295) can be very helpful to observe the macropore structure of the aggregates and to detect the presence of minerals known to be frost susceptible (such as chert for example) or of other internal weaknesses. However, this test cannot identify all aggregates which are frost sensitive, and it should only be performed by an experienced petrographer familiar with the problem of frost durability of concrete.

The ASTM C 88 sulphate soundness test is often used to assess the frost resistance of aggregate. In this test the growth of magnesium sulphate ($MgSO_4$) crystals inside the pores of the aggregate causes an internal pressure considered similar to that due to freezing water. Unfortunately, the mechanisms involved are significantly different from those occurring in a freezing and thawing environment and the results obtained are not really satisfactory.

The critical dilation test (ASTM C 682) or the usual rapid freezing and thawing test (ASTM C 666) are probably the most reliable, since the aggregates to be tested are used to make concrete specimens which are subjected to freezing and thawing cycles in the laboratory. Even if the freezing and thawing cycles produced in the laboratory are not perfectly representative of the real conditions to which concrete will be exposed, these tests can nevertheless give extremely useful indications, not only on the frost resistance of the aggregates themselves, but also on their influence on the frost resistance of concrete.

The problem of surface scaling can also be, in certain cases, related to the aggregates. Even though it is not specifically designed for this purpose, the ASTM C 672 surface scaling test can provide useful indications in this respect. Pop-outs represent a very common type of deterioration, which is due to the presence of weak or porous particles close to the surface. This type of deterioration can therefore only be prevented by selecting aggregates in which the number of such particles is very low. When available, the past service record of an aggregate probably remains the best guarantee of its durability.

Generally, the characteristics of the cement that is used have little influence on the resistance of concrete to internal cracking due to frost action (although type III Portland cement was found to give better results than type I for very high-strength concretes, as discussed in Chapter 5). The use of mineral additives, such as blastfurnace slag, fly ash and other natural pozzolans, can modify significantly the characteristics of the cement paste: first, because the reaction rate of these products is generally slower than that of Portland cement and, secondly, because they usually create a refinement of the pore structure. Most of the time, however, provided proper curing procedures are used to ensure that the cement paste will be of good quality at the time of freezing (this can be particularly relevant if the concrete is cast late in the fall), their use does not significantly influence the resistance to internal cracking, although it is often considered to reduce the resistance to de-icer salt scaling. This, of course, is a function of the amount that is used, and more research is needed before guidelines for the use of such admixtures in concrete exposed to de-icer salts can be defined.

Silica fume is a very special pozzolan, first because its mean particle size is much smaller than that of Portland cement and, secondly, because its rate of reaction is much higher than that of most mineral additives. Silica fume, when used for the making of high-strength concrete, has been found to have a positive effect on frost and de-icer salt scaling resistance. In normal concrete, however, the use of high amounts of silica fume has been found to reduce the value of the critical spacing factor, and many agencies recommend to limit the amount that is used to 8–10% of the mass of cementitious material. In such amounts, the effect on the resistance to internal cracking as well as on the de-icer salt scaling resistance (even if this subject is still disputed) is considered not to be very significant.

As indicated in Chapter 6, the influence that the characteristics of the cement (especially its alkali content) can have on the production and stability of the air-void system is not negligible. The use of pozzolanic admixtures, particularly, can increase the amount of air-entraining admixture required to produce a satisfactory air-void system (this effect being mainly related to their carbon content) and ASTM C 618 and C 311 Standards provide a test method to assess this effect. These standards also provide uniformity requirements to ensure that the variability of the physical and chemical properties of a fly ash (or a natural pozzolan) will not significantly influence the dosage of the air-entraining admixture. Clearly, special care must be exercised when mineral additives are used for making concrete exposed to frost action.

When selecting admixtures for the making of concrete exposed to freezing and thawing cycles and de-icer salts, the most important question is obviously the influence that these admixtures can have on air entrainment. The next section of this chapter addresses this extremely important question, and additional information can be found in Chapter 6. Admixtures can also, of course, have an influence on the overall quality of the mixture, but this is not specifically related to the problem of frost action. Concrete exposed to frost, like any other concrete, should be good quality, homogeneous, and dense concrete, and the admixtures that are used should be chosen keeping this in mind.

One aspect of the problem of frost action perhaps more directly related to the use of admixtures is bleeding. Certain water-reducing admixtures also act as retarding agents and this can increase bleeding because setting is delayed. Bleeding tends to create small vertical channels from the body of the concrete to the surface, and these do not necessarily become filled during hydration. The presence of these channels can increase the chloride ion permeability of concrete and thus make it more susceptible to salt scaling. Bleeding can also increase the water/cement ratio of the surface layers. These phenomena have not yet been clearly demonstrated but, considering the available information, and since excessive bleeding is known to increase permeability, the use of retarding agents in concrete mixtures designed for sidewalks and similar structures exposed to de-icing salts should be carefully controlled.

9.2 CHARACTERISTICS OF THE AIR-VOID SYSTEM

Air entrainment is, for almost all types of concrete except perhaps certain very high-strength concretes, an essential condition to ensure good frost resistance. As discussed in the previous chapters, this resistance is closely related to the mean spacing of air voids, and it is generally accepted that a spacing factor of approximately 200 µm is required to ensure that concrete in a severe freezing environment will be well protected. Although recent studies have demonstrated that concretes with much higher values of the spacing factor can be properly protected against internal microcracking, even in very severe laboratory testing conditions, laboratory as well as field experience shows that a low spacing factor is a necessary (but not sufficient) condition to protect concrete against scaling due to freezing in the presence of de-icer salts. **A spacing factor of 200 µm can thus generally be considered as a safe design value.**

Although the spacing factor is the parameter of the air-void system that is the most closely related to the frost resistance of concrete, the quality of the air-void system is usually assessed by measuring the total air content in concrete. The air content has the great advantage of being easy to measure directly on the job site, and unsatisfactory concretes can thus be rejected before casting. Unfortunately, the relationship between air content and spacing factor is quite scattered (Figure 6.6) and, although a higher air content generally corresponds to a lower spacing factor, a wide range of spacing factors can be obtained for a given air content. For example, Figure 6.6 indicates that the spacing factor can range from 100 µm to 400 µm for a 5% air content (the minimum value usually required for normal concretes exposed to severe freezing conditions). **An adequate air content does not**

therefore necessarily guarantee an adequate spacing factor. Experience indicates that concretes which are severely deteriorated in service, even if the air content measured on the fresh concrete was considered correct, very often have an inadequate air-void system with a high spacing factor. The aim of producers should thus be the production of concretes with a closely spaced air-void system as well as with a minimum air content.

Basically, the large scatter observed in the relationship between air content and spacing factor is due to the fact that the air content is a function of the volume of the air voids while the spacing factor is mainly a function of their number. For a given air content it is then preferable to produce a large number of small air voids instead of a smaller number of larger air voids, as schematically illustrated in Figure 9.1. It must also be remembered that the air voids in concrete cover a wide range of sizes (their diameters ranging from 10 μm to more than 1 mm which is roughly a ratio of 1:100). Since the volume of a sphere is proportional to its cubic diameter, the larger air voids occupy a large volume but usually represent only a small percentage of the total number of voids, and thus contribute little to the protection against freezing. A sphere with a diameter of 300 μm occupies the same volume as 1000 spheres of 30 μm! This means that if a few large air voids are added to a system of small voids, the air content is significantly increased but the spacing is little affected. Thus, the objective should always be to produce a large number of small entrained air voids (about 25–50 μm in diameter) while avoiding as much as possible the large voids (larger than about 300 μm) which are naturally entrapped during the mixing process. The production of small entrained air voids can be easily obtained by the use of an adequate dosage of an air-entraining admixture. **The real challenge consists of avoiding, as much as possible, the presence of entrapped air voids which increase the air content without offering any significant protection against freezing and thawing cycles.** Unfortunately, there is no simple way to achieve this objective in all circumstances and each mixture represents a different problem. However, it is generally possible to reduce the number of entrapped air voids, for instance by modifying the mix characteristics, or even sometimes the mixing process.

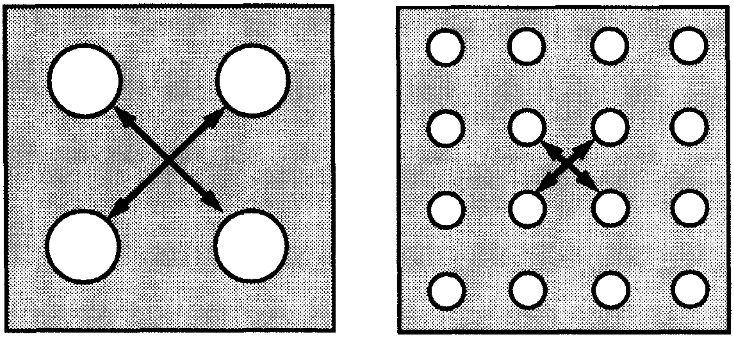

Figure 9.1 Illustration of the influence of the size of air voids on the value of the spacing factor.

The production of an adequate air-void system at the time of mixing is not sufficient. It is also important to maintain this system until the final setting of concrete, since it has been demonstrated that transportation, for instance, or placing techniques can have a detrimental effect on the characteristics of the air-void system. The stability of the air-void system (i.e. the modification of its characteristics with time) is a fundamental concept too often neglected when durable concrete is to be produced. This stability is influenced by many different parameters such as the type of cement, or the presence of admixtures (Chapter 6). All commercial air-entraining admixtures have the ability to produce an adequate air-void system, but this does not mean that these products will never be associated with problems of air-void instability. Acceptance tests cannot take into account the stability aspect, since stability is generally not simply related to the air-entraining admixture alone, but to a large number of parameters (material characteristics, mix composition, type of mixer and compatibility between the various admixtures and cement). An insufficient dosage of the air-entraining admixture can be a source of instability, and **the dosage should never be smaller than the minimum value recommended by the manufacturer**. To avoid problems it is recommended, as mentioned in Chapter 6, to test all combinations of admixtures and cements with which the air-entraining agent is likely to be used in the course of concrete production, and to verify that the air-void system in the hardened concrete is adequate even if the specimens are cast one hour after the initial contact between water and cement.

When stability problems are considered, it is fundamental to make a clear distinction between the stability of the air content and the stability of the spacing factor. As explained in Chapter 6, large variations of the air content can occur without any significant variations of the spacing factor (it happens when large air voids escape to the surface). Conversely, large variations of the spacing factor are possible without any significant variation of the air content (it happens when small air voids coalesce together). A good illustration of this phenomenon is given in Figure 9.2 which shows the variation of the air content versus the variation of the spacing factor for a series of laboratory and field concretes made with different cements and different admixtures used at different dosages. **The variation of the air content gives no clear indication of the variation of the spacing factor.** From a practical point of view, this means that, unfortunately, the difference between the air content measured at the plant and at the job site cannot be used to assess the stability of the spacing factor. As mentioned in the preceding paragraph, the only way to verify the stability of the spacing factor is to cast concrete specimens at different time intervals after mixing (for instance at the plant and later at the job site) and to measure the characteristics of their air-void system by means of microscopic examination according to the ASTM C 457 Standard.

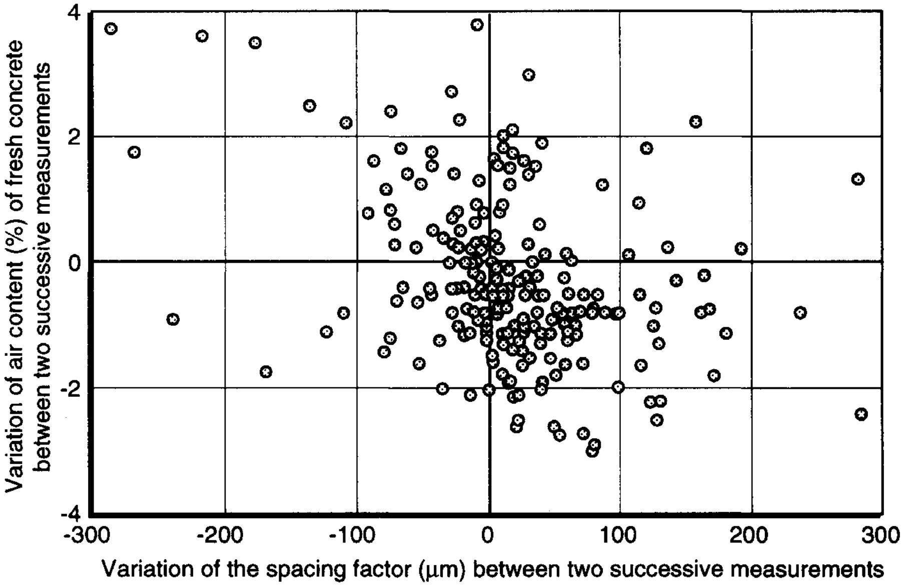

Figure 9.2 Variation of the air content versus variation of the spacing factor for different concrets. Each result was obtained from two samplings of the same concrete made at different time intervals after initial mixing (after Saucier *et al.,* 1991).

Retempering (i.e. the addition of water at the job site to maintain slump) is not usually recommended (for obvious reasons!), but nevertheless is a quite common practice. Care should be exercised when concrete is retempered, since it has been shown that this can increase the air content without any significant effect on the spacing factor (Pigeon *et al.,* 1990).

The addition of more air-entraining agent in ready-mix concrete at the job site is also used, sometimes, to correct an insufficient air content. Although this effectively increases the air content, the spacing factor is generally little affected unless very large dosages of the air-entraining agent are added. This procedure should also be avoided as much as possible.

The vibration of concrete during the casting operations may reduce the total air content, because it facilitates the escape of large air voids to the surface. Most of the time, however, the spacing factor of a correctly air-entrained concrete will not be significantly affected by normal vibration.

9.3 MIXTURE CHARACTERISTICS

Frost resistance, like almost all properties of concrete, is closely related to the water/cement ratio. The use of low water/cement ratios enhances the mechanical resistance of concrete and, most of all, reduces the amount of freezable water inside the cement paste, both of which contribute to a better frost resistance. It also reduces, however, the permeability of the cement paste, which can be detrimental to frost resistance (because a decrease in permeability increases the internal stresses caused by the forced movement of water during freezing) but beneficial to the scaling resistance. The overall effect of the water/cement ratio is thus a function of the relative importance of the amount of freezable water and of the permeability of the cement paste (as illustrated in Table 3.1). Nevertheless, the reduction of the water/cement ratio most generally has a positive effect on the frost and de-icer salt scaling resistance of concretes, particularly those with water/cement ratios higher than 0.40.

The amount of cement in a mixture (and thus, for a given water/cement ratio, the quantity of cement paste) should have no influence as such on the resistance to freezing and thawing cycles. This, however, has never been experimentally verified. Minimum amounts of cement are often recommended, if only to ensure that the water/cement ratio will not exceed certain limits.

9.4 MIXING PROCEDURES

Apart from the influence that they have on the homogeneity of concrete, mixing procedures *per se* have no influence on the frost durability of concrete. They are, however, very important as regards air entrainment. As explained in Chapter 6, it is the action of mixing which entrains the air bubbles in the mixture, the role of the air-entraining agent being to facilitate air entrainment and, mostly, to stabilize these bubbles. According to the concept of surface energy, a given amount of energy is required to form air bubbles, this amount being inversely proportional to the size of the bubbles. The energy provided by the mixer thus has a direct influence on air entrainment, this energy being a function of many parameters including the type of mixer, the mixing time, the speed of rotation of the drum (or pan) and the volume of the batch. The number and shape of the blades also have a very significant influence. Mixers that have not been cleaned properly and have lumps of cement paste or mortar on the blades tend to lose efficiency, particularly as regards air entrainment.

Pan-type mixers are generally more efficient than drum-type mixers, and laboratory mixers are therefore often more efficient than ready-mix trucks. A given concrete mixture having a good air-void system when made in a pan-type laboratory mixer may thus have only a marginal spacing factor when made in a ready-mix truck. This is particularly important considering the fact that two concretes having the same air content can have different spacing factors depending on the mean size of the air voids (which is related to the energy developed by the mixer).

9.5 TRANSPORTATION AND PLACING TECHNIQUES

The characteristics of the air-void system of concrete can be altered during transportation in ready-mix trucks (in which concrete is continually agitated). It is quite common to observe a decrease in air content from the time when concrete is mixed at the plant to the time when it is placed in the formwork at the job site. In properly air-entrained concretes however, the decrease in air content is mainly due to the loss of large air bubbles, and it seems that the value of the spacing factor is little affected because it is mainly related to the presence of the smaller air voids (Pigeon *et al.,* 1987; Gjorv *et al.,* 1978; Pleau *et al.,* 1990). The characteristics of the air-void system of concrete can also be affected by pumping or conveying over long distances at the job site, although very little data is available on this subject. When pumping or conveying is required, it is highly recommended to carry out field tests to verify that the spacing factor of the air voids will not be adversely affected.

Placing operations can influence the frost durability of concrete in two different ways. First, the use of vibration for placing concrete in the formwork may cause air losses. Fortunately, most of the time, the spacing factor of correctly air-entrained concrete is little affected by vibration because, as previously mentioned, the air loss is primarily due to the loss of a relatively few large air bubbles. Nevertheless, it has been observed that the use of vibrators operating at a high frequency (which is a very uncommon practice) can be detrimental to the stability of the spacing factor (Stark, 1986).

The second problem associated with the placing of concrete is related to the resistance to surface scaling. This resistance is strongly dependent on the quality of the surface layer of concrete (i.e. the first few millimetres) and all phenomena which can be detrimental to the overall quality of this zone, such as excessive bleeding or plastic shrinkage, can be detrimental to the scaling resistance, and must therefore be avoided as much as possible. Finishing operations are also particularly important. Care should be taken to avoid overworking the surface, since overworking can remove some of the entrained air voids (Cordon, 1966) and also attract water from the body of the concrete to the surface layer (which is then weakened). It was found that the use of wooden trowels is preferable to steel trowels since it reduces the risks related to overworking.

9.6 CURING

Good curing (to ensure proper cement hydration) is important to obtain frost-resistant concrete, and particularly de-icer salt scaling-resistant concrete, since curing mostly affects that part of the concrete which is close to the surface. The influence of different curing procedures on the resistance of concrete to surface scaling was analysed by Beaupré (1987). The results obtained are summarized in Figure 9.3 which shows the mass of the scaledoff particles versus the number of daily freezing and thawing cycles in the presence of de-icer salts (according to ASTM Standard C 672). Each curve on the figure represents the mean value obtained from six concretes (with or without silica fume as partial Portland cement replacement). Five different curing procedures were tested: moist curing for 2 and 14 days, respectively, 7-day curing with two different curing compounds, and accelerated heat curing (6 h after mixing, the specimens were stored at 65°C for approximately 18 h).

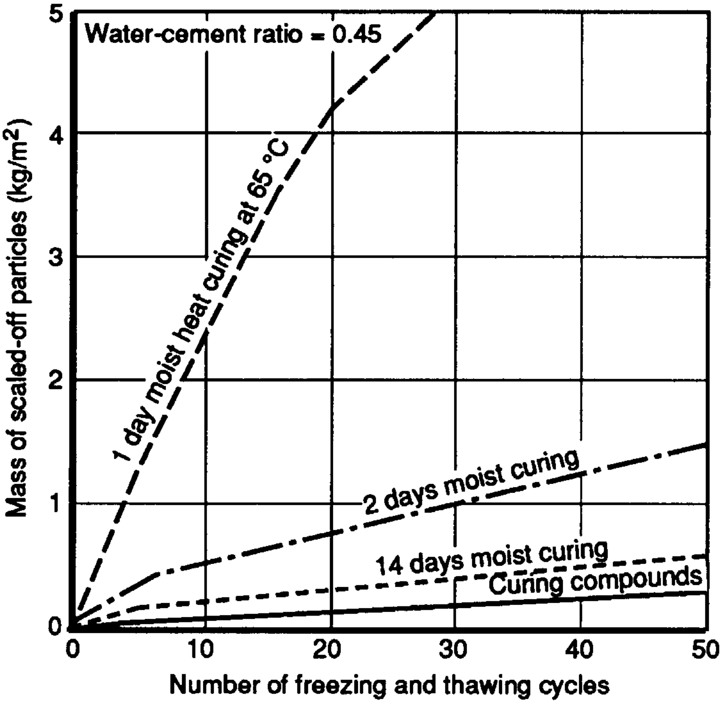

Figure 9.3 Average mass of scaled-off particles (for three concretes) versus number of freezing and thawing cycles in the presence of a de-icer salt solution for four different curing methods (after Beaupré, 1987).

The data in Figure 9.3 indicate that increasing the moist curing period from 2 to 14 days significantly reduces the extent of surface scaling. It also indicates that the use of curing compounds is beneficial since a 7-day curing period with each of the two different curing compounds gave better results than a 14-day moist curing period. This positive influence of curing compounds (also observed by other investigators (Marchand *et al.,* 1991; Bilodeau *et al.,* 1991)) cannot be attributed to a lower chloride ion penetration during the tests because microprobe analyses have shown that the concentration of chloride ions was about the same in the specimens cured for 14 days and those cured with a curing compound. It is also not just related to better cement hydration, since a loss of mass (due to evaporation) was recorded during the curing period with the curing compounds. The exact role of curing compounds is not perfectly understood yet, but one of their main advantages could simply be to slow down the drying process and thus reduce the surface damage due to drying. As explained in Chapter 3, the moisture history of concrete is very important as regards its frost behaviour and any product that can influence the way in which concrete dries (and reabsorbs water) can exert an influence on its frost behaviour.

It has been clearly established, again as mentioned in Chapter 3, that, although the mechanisms involved are not fully understood, drying can significantly increase the amount of freezable water, probably because the drying process leads to an ‘opening’ of the pore structure leading to a coarser pore-size distribution and a better interconnection between these pores, both of which promote ice formation (Bager and Sellevold, 1986). Research is needed to investigate the phenomena related to the influence of drying on the microstructure of cement paste and concrete. Nevertheless, it is commonly agreed that a sufficiently long curing period (using an adequate technique such as, for example, the use of a curing compound) before concrete dries is a very good practice, especially in the summer period when drying can be particularly severe. High drying temperatures have definitely been shown to be detrimental to the scaling resistance of many concretes (Sorensen, 1983), and preliminary observations from a study carried out recently in the province of Québec (Canada) tend to suggest that, contrary to common belief, sidewalks cast during the summer could be more susceptible to de-icer salt scaling than sidewalks cast in the fall.

The curing temperature is another important parameter, and recent experimental data tend to show that a high curing temperature is detrimental to the surface scaling resistance of normal concrete. As can be seen in Figure 9.3, the deterioration due to surface scaling is much higher for the specimens cured at 65 °C than for all the others (after only five cycles, the mass of scaled-off particles is already larger than the commonly accepted limit of 1 kg/m^2). This could explain the poor service record of certain pre-fabricated steam-cured concrete elements exposed to de-icer salts.

9.7 PROTECTIVE COATINGS AND SEALERS

Since deterioration due to frost action will generally only occur in elements that are close to full saturation, protective coatings are sometimes used to prevent the ingress of moisture into concrete. The use of such products, however, is often detrimental. Most concrete elements have access to moisture, and, as pointed out by Litvan (1980),

> *while* (these products) *do not prevent the accumulation through condensation of moisture in the pores, they hinder egress of water*.

Certain products, such as silane- or siloxane-based sealers, prevent the ingress of chloride ions and water. These sealers have been shown to be very effective in reducing the corrosion of steel reinforcement. Unfortunately, even if they do not act as water vapour barriers, they can nevertheless increase in certain cases the deterioration due to de-icer salt scaling (Figure 9.4).

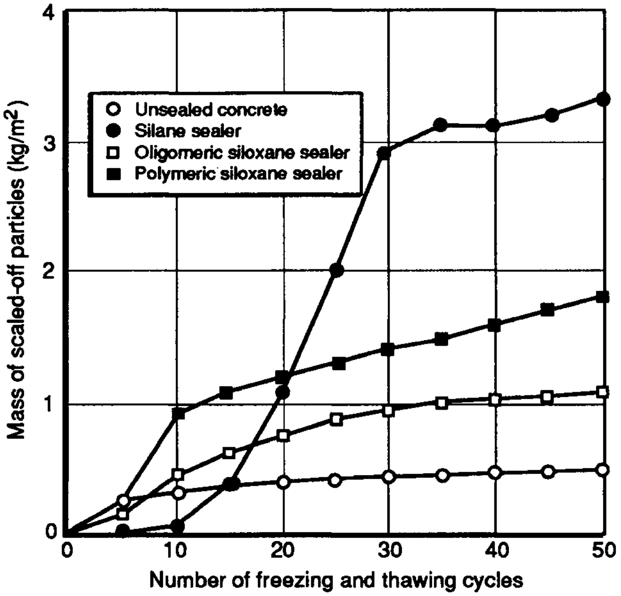

Figure 9.4 Mass of scaled-off particles versus number of freezing and thawing cycles in the presence of a de-icer salt solution for an ordinary air-entrained Portland cement concrete protected with various penetrating sealers after having been subjected to salt applications (after Sedran *et al.,* 1993).

9.8 DESIGN AND MAINTENANCE OF CONCRETE STRUCTURES

The careful design of structures can be very helpful in preventing deterioration due to freezing and thawing. Frost action is highly dependent on the degree of saturation of concrete and damage usually only occurs when concrete is fully saturated with water (or nearly so). All possible ways to protect concrete from moisture are then useful to enhance frost durability. Even non-air-entrained concretes can be frost resistant when the degree of saturation is sufficiently low.

In such circumstances, architectural design should be concerned with providing a good drainage of water on horizontal surfaces. This can be achieved by choosing a good drainage system and a geometric arrangement which avoids ponding of water and eases the flow of water to the drain locations. Great care should also be taken to prevent the infiltration of water inside joints; this phenomenon often represents the way deterioration is initiated and is a common source of severe damage in practice. Of course, the use of a waterproof membrane at the surface of the concrete may be useful to prevent the infiltration of water, but this practice must be used with great care. If concrete is saturated when the membrane is applied, water will be trapped inside the concrete and this can decrease frost resistance. Similarly, if the membrane is weakened by the presence of cracks, water may slowly penetrate inside the concrete. Since the membrane will reduce evaporation of water during the drying periods, deterioration will be more likely to occur.

On horizontal surfaces, such as roads or sidewalks, the accumulation of snow must be avoided as much as possible since, during thawing, it will provide a high moisture level for a relatively long period of time.

In certain circumstances, particularly to reduce rebar corrosion due to frequent applications of de-icing salts on structures such as bridge decks which are exposed to severe climatic conditions and for which the formation of ice on the surface is a problem, it is preferable to use sand or other abrasives instead of de-icing chemicals.

Urea is often used as a de-icer on airport runways. It does not induce or accelerate metal corrosion and is perhaps somewhat less harmful to concrete.

9.9 COLD WEATHER CONCRETING

Certain construction procedures must be followed in order to ensure that concrete placed in cold weather will be strong and durable and will satisfy all its service requirements. According to the ACI 306 *Guide for Cold Weather Concreting,* cold weather may be defined as ‘a period when, for more than three successive days, the mean daily temperature drops below 5 °C’. When temperatures above 10°C occur during more than half of any 24 hour period, the climatic conditions should no longer be considered as cold weather.

Two particular types of deterioration are possible when concrete is placed in cold weather. These deteriorations are completely different from that due to repeated cycles of freezing and thawing. First, the fresh concrete may freeze before the final setting of the cement paste. When this occurs, part of the mixing water is transformed into ice and the setting and hardening process is delayed, simply because no water is available for hydration. The cement paste is not significantly disrupted because only a small number of hydration products have been formed, but the overall volume of concrete is increased due to the 9% increase in volume associated with ice formation. When thawing takes place, however, concrete sets and hardens in its expanded state which results in a larger porosity and, consequently, a lower strength. It has also been shown that the formation of small ice lenses tends to leave flaws which will not become filled with hydration products and which will reduce strength significantly (Lacroix and Houde, 1991)

The second type of problem arises when freezing occurs after the setting of concrete, but before it has developed significant strength. In this case, ice lenses are formed in large capillary pores and their growth produces internal disruptive pressures which damage the microstructure of cement paste and cause a permanent loss of strength. Sometimes, the damage is so severe that the concrete structure must be, at least partially, reconstructed.

To avoid early freezing of concrete, all unformed surfaces should be protected against freezing for at least the first 24 h. Concrete should also be placed and maintained above a minimum temperature for a sufficiently long period of time. This precaution will prevent concrete from early freezing and ensure that, after the protection period, concrete will have developed sufficient strength to resist satisfactorily freezing and thawing cycles. Table 9.1 indicates that this minimum temperature is a function of the size of the section of the concrete element because the heat loss is higher for smaller sections. This minimum temperature ranges from 5 °C (for sections larger than 180 cm) to 13 °C (for sections smaller than 30 cm). At the job site, this temperature is usually provided by temporary heated enclosures placed over the formwork. Care must be taken, however, to ensure that the heating units do not contribute to rapid drying of the concrete and do not exhaust a high level of carbon dioxide (CO_2) in the heated enclosures which would cause carbonation of concrete.

Considering that the heat of hydration of hardening cement is mainly developed during the first three days, heat from outside sources is not always necessary if the heat liberated by hydration can be suitably conserved. This can be achieved by placing insulating blankets on unformed surfaces and by using insulated forms. Polystyrene foam, urethane foam, foamed vinyl, mineral wool and cellulose fibres are materials commonly used in the making of insulating blankets. Straw is still popular although it is not as effective as blankets.

Table 9.1 Minimum concrete temperatures recommended during cold weather construction (°C) (after ACI 306R-78).

Air temperature	Section size, minimum dimension (cm)			
	<30	30–90	90–180	>180
Minimum concrete temperature as placed and maintained				
–	13	10	7	5
Minimum concrete temperature as mixed for indicated weather*				
above−1	16	13	10	7
−18 to −1	18	16	13	10
below−18	21	18	16	13
Maximum allowable gradual temperature drop in first 24 hours after end of protection				
–	28	22	17	11

*For colder weather a greater margin in temperature is provided between concrete as mixed, and required minimum temperature of fresh concrete in place.

Table 9.2 indicates the period of time for which air-entrained concrete should be maintained at the minimum temperature given in Table 9.1. This period has been established to avoid early freezing, and also to ensure that concrete will have developed sufficient strength and will be able to resist satisfactorily the freezing and thawing cycles which may occur afterwards. As indicated in Table 9.2, this period of protection is a function of the exposure conditions and can be shortened if the heat of hydration is increased by the use of an ASTM type III Portland cement, an accelerating admixture, or even an extra quantity of type I Portland cement. However, the period should be prolonged if concrete is expected to develop a load-carrying capacity after the removal of the heating system.

Table 9.3 shows, for concrete exposed to cold weather and which will be loaded as soon as the formwork is removed, the recommended length of time during which it should be maintained at 10 °C or 21 °C. This period of protection may range from 3 to 35 days, depending on the type of cement used (ASTM type I, II or III) and the percentage of the design strength which is required by the structural engineer after the removal of the formwork.

Table 9.2 Minimum periods of protection (from heat loss) recommended during cold weather construction (after ACI 306R-78).

Service category	Protection recommended at temperature indicated in first line of Table 9.1 (days)			
	From frost damage by freezing		For safe strength	
	Type I or II cement	Type III cement, accelerator, or 60 kg/m^3 extra cement	Type I or II cement	Type III cement, accelerator, or 60 kg/m^3 extra cement
No load, no exposure	2	1	2	1
No load, exposed	3	2	3	2
Partial load, exposed	3	2	6	4
Full load	3	2	–	–

Table 9.3 Minimum periods of protection (days) from heat loss recommended during cold weather construction as a function of the required percentage of the design strength required when forms and shores are removed (after ACI 306R-78).

	Type of cement					
	At 10°C			At 21°C		
Percentage of design strength required	I	II	III	I	II	III
50	6	9	3	4	6	3
65	11	14	5	8	10	4
85	21	28	16	16	18	12
95	29	35	26	23	24	20

The periods of protection given in Tables 9.2 and 9.3 have been established for normal weight aggregates. Experience indicates, however, that lightweight aggregates often have a higher heat retention and, for concretes made with such aggregates, the period of protection could be shortened accordingly.

Table 9.1 indicates the minimum concrete temperature ‘as placed and maintained’, but the concrete must be mixed at a higher temperature to compensate for the loss of heat during transportation as well as during the placement operations on the job site. This table therefore also gives the minimum concrete temperature as mixed, this temperature ranging from 7 °C to 21 °C depending on the air temperature and the minimum dimension of the concrete element. The ingredients may be heated to produce freshly mixed concrete at the desired minimum temperature. When the aggregates are free of frozen water, it is usually easier to heat only the mixing water but, when the air temperature is consistently below 0 °C, it is usually necessary also to heat the aggregates. Care should be exercised when water at a temperature over 60 °C is used, because, when hot water comes into contact with cement, small clumps of cement can form and, in some cases, flash setting can occur. It is not advisable either to exceed significantly the minimum concrete temperature given in Table 9.1 to shorten the period of protection, simply due to the fact that heat loss is more rapid with greater temperature differentials. Moreover, higher temperatures require more mixing water, increase the slump loss and the thermal shrinkage, and can be detrimental to the long term resistance of concrete. Higher temperatures also facilitate moisture loss at the surface of the concrete which can result in plastic shrinkage. The temperature of concrete should therefore be kept as close as possible to the minimum value given in Table 9.1.

If the weight and temperature of all constituents and their moisture content are known, the final temperature of the freshly mixed concrete can be computed as

$$T = \frac{[0.22(T_s W_s + T_a W_a + T_c W_c) + T_w W_w + T_s W_{ws} + T_a W_{wa}]}{[0.22(W_s + W_a + W_c) + W_w + W_{wa} + W_{ws}]} \tag{9.1}$$

where T is the final temperature of the concrete mixture, T_c is the temperature of the cement, T_s is the temperature of the fine aggregate, T_a is the temperature of the coarse aggregate, T_w is the temperature of the mixing water, W_c is the weight of the cement, W_s is the weight of the fine aggregate, W_a is the weight of the coarse aggregate, W_w is the weight of the mixing water, W_{ws} is the weight of the free water in the fine aggregate, and W_{wa} is the weight of the free water in the coarse aggregate (all temperatures in °C and weights in kg).

If the temperature of the aggregate is below 0 °C, it contains frozen water and (9.1) must be corrected to take into account the heat required to melt the ice as well as the fact that the specific heat of ice is approximately equal to half of that of water. As an approximation, $T_s W_{ws}$ and $T_a W_{wa}$ should then be replaced by (0.5 T_s—80) W_{ws} and (0.5 T_a—80) W_{wa}, respectively, where 80 is the number required to take into account the heat of fusion necessary to melt the ice.

The ACI 306 *Recommended Practice* also limits the maximum allowable gradual temperature drop (in the ambient air) during the first 24 h after the end of the protection period to prevent any risk of thermal cracking. As indicated in Table 9.1, the allowable temperature drop is a function of the minimum dimension of the concrete element since, for larger sections, the temperature differential between the surface and the core of the element is higher and the allowable temperature drop must be correspondingly reduced. The maximum allowable value ranges from 11 °C (for sections larger than 800 mm) to 28 °C (for sections smaller than 300 mm).

The minimum protection described in Tables 9.1 to 9.3 is defined for air-entrained concretes which are designed to resist freezing and thawing cycles. It frequently occurs, however, that concretes which will not be exposed to freezing and thawing cycles during their service life, and for which air entrainment is not provided, are placed during cold weather. In this particular case, the requirements in Tables 9.1 to 9.3 are not sufficient and concrete must be protected against freezing during the entire construction process, or must be air entrained.

9.10 CODES OF PRACTICE

In most countries where cold winters are common, codes of practice prescribe certain requirements for concretes exposed to freezing and thawing cycles. The most important requirements are obviously related to air entrainment. Table 9.4 shows, for instance, the air contents recommended by the ACI 201 *Guide to Durable Concrete* (assuming that a reasonable tolerance for air content in field construction is ±1.5%). These air contents range from 3% to 7.5% depending on the exposure conditions and the maximum nominal size of the coarse aggregates (for coarser aggregates, the total air content can be reduced simply because the paste content is normally smaller and the air voids are all contained in the paste fraction). It is assumed that such air contents will provide a system of well distributed and closely spaced air voids which will satisfactorily protect concrete against frost action.

The requirements of the Canadian CSA A23.1 M90 Standard are summarized in Tables 9.5 and 9.6. The recommended air contents are also a function of the exposure conditions and of the maximum nominal size of the coarse aggregates, but they are generally a little higher than those prescribed in the ACI *Guide to Durable Concrete*. The Canadian standard also provides requirements for the maximum water/cement ratio of the concrete mixtures (these are quite similar to those of the ACI). This maximum water/cement ratio varies from 0.55 (for concretes subjected to freezing and thawing in an unsaturated condition and not exposed to de-icing salts) to 0.40 (for concretes exposed to de-icing chemicals and for which protection against corrosion of the reinforcement is deemed critical). For concretes exposed to de-icing chemicals, the standard also requires a minimum specified 28-day compressive strength of 32 MPa or even 35 MPa (when the protection against corrosion is deemed critical). These requirements reflect the fact that the frost resistance of concrete is

Table 9.4 Air contents recommended for frost-resistant concrete (after ACI 306R-78).

Nominal maximum	Average air content (%)	
	Severe exposure*	Moderate exposure**
9.5	7.5	6.0
12.5	7.0	5.5
19.0	6.0	5.0
38.0	5.5	4.5
75.0	4.5	3.5
150.0	4.0	3.0

*Outdoor exposure in a cold climate where the concrete may be in almost continuous contact with moisture prior to freezing, or where de-icing salts are used. Examples are pavements, bridge decks, sidewalks and water tanks.

**Outdoor exposure in a cold climate where the concrete will be only occasionally in contact with moisture prior to freezing, and where no de-icing salts will be used. Examples are certain exterior walls, beams, girders and slabs not in direct contact with soil.

not only related to the characteristics of the air-void system, but also to the overall quality of the cement paste. The quality of the cement paste is particularly important for concretes exposed to very severe conditions.

The requirements concerning the air content are very useful since the air content can be easily measured at the job site and can thus serve as an acceptance criterion (concrete can be rejected if it fails to meet the specifications). But since, as previously mentioned, a high air content does not necessarily guarantee an adequate spacing factor, the 1990 version of the CSA A23.1 Standard has introduced a new requirement concerning the air-void spacing factor for concretes subjected to severe exposure conditions (i.e. the conditions corresponding to classes F-1, C-1, and C-2 in Table 9.5). According to the standard, to be considered as satisfactory, the spacing factor shall be such that the average value obtained

Table 9.5 Requirements for concrete subjected to freezing and thawing and for concrete exposed to de-icing chemicals or sea water (after CAN/CSA-A23.1-M90).

Exposure classification	Exposure condition	Minimum specified 28-day compressive strength (MPa)	Maximum water/cementing materials ratio	Air content category (see Table 9.6)
Requirements for concrete subjected to freezing and thawing				
F-1	Concrete subjected to freezing and thawing in a saturated condition	30	0.50	1
F-2	Concrete subjected to freezing and thawing in an unsaturated condition	25	0.55	2
Requirements for concrete exposed to de-icing chemicals or sea water				
C-1	Concrete for which protection against corrosion of reinforcement is deemed critical	35	0.40	1
C-2	Concrete not falling under C-1 but subjected to cycles of freezing and thawing	32	0.45	1
C-3	Concrete in a saturated condition, not falling under C-1 and not subjected to cycles of freezing and thawing	30	0.50	2
C-4	Concrete in a relatively dry condition, not falling under C-1 and not subjected to cycles of freezing and thawing	25	0.55	2

from all tests will not exceed 230 μm with no single value over 260 μm. Because the spacing factor can usually only be obtained after the end of the placement operations (since, like strength, it is measured on the hardened concrete), the composition of the concrete mixtures must be carefully designed to ensure that, in all circumstances, the concrete delivered at the job site will have an adequate air-void spacing factor. This means, of course, that the stability of the air-void system must be considered, and that tests to verify that the spacing factor obtained is adequate must be carried out if any change in the materials that are used (cement, sand, admixtures etc.), or in the composition of the concrete mixtures, occurs.

Table 9.6 Air contents recommended for frost-resistant concrete (after CAN/CSA-A23.1-M90).

Air content category	Range in air content for concretes with indicated nominal maximum sizes of coarse aggregates (%)		
	10 mm	20 mm	40 mm
1	7–10	5–8	4–7
2	5–8	4–7	3–6

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