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Durable Concrete—Guide

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Durable Concrete—Guide

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This guide describes specific types of concrete deterioration. Each chapter contains a discussion of the mechanisms involved and the recommended requirements for individual components of concrete, quality considerations for concrete mixtures, construction procedures, and influences of the exposure environment, which are all important considerations to ensure concrete durability.

This guide was developed for conventional concrete but is generally applicable to specialty concretes; however, specialty concretes, such as roller-compacted or pervious concrete, may have unique durability-related issues that deserve further attention that are not addressed herein.

Keywords: abrasion resistance; alkali-aggregate reaction; chemical attack; curing; deterioration; durability; freezing and thawing; physical salt attack; sulfate attack.

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

Concrete is the most widely used construction material in the world. The design, detailing, and execution of concrete to resist weathering action, chemical attack, abrasion, and other processes of deterioration over its intended service life will determine its durability. Durable concrete will retain its original form, quality, and serviceability when exposed to its environment. Properly designed, proportioned, transported, placed, finished, and cured concrete can provide decades of service with little or no maintenance, yet certain conditions or environments exist that can lead to concrete deterioration. Deterioration mechanisms are either chemical or physical in nature and may originate from within the concrete, or may be the result of the external environmental exposure. Chemical and physical attacking mechanisms often work synergistically. Depending on the nature of the attack, distress may be concentrated in the paste, aggregate, or reinforcing components of the concrete, or a combination thereof.

The various factors influencing durability and a particular mechanism of deterioration should be considered in the context of the environmental exposure of the concrete. In addition, consideration should be given to the microclimate to which the specific structural element is to be exposed. The type and severity of deterioration of a given structure may be affected by its proximity to sources of deleterious agents or agents that facilitate distress, exposure to wind, precipitation, or temperature. For instance, exterior girders in a bridge structure may be exposed to a more aggressive environment than interior girders.

The concept of service life is increasingly used for the design of new structures. To produce concrete suitable for a particular application, required service life, design requirements, and expected exposure environments, both macro and micro, should be determined before defining the necessary materials and mixture proportions.

The use of good materials and proper mixture proportioning will not, by itself, ensure durable concrete. Appropriate placement practices and workmanship are essential to the production of durable concrete. Fresh concrete can be consolidated and molded to the shape desired to serve its intended purpose. During this stage, numerous properties significantly influencing the durability of the hardened concrete are established. Pore structure development, air-void system formation, material uniformity, and potential for cracking are established at early ages and are important to the ultimate durability of concrete. As such, durable concrete requires the application of good quality control during construction. Inspection and testing by trained personnel

personnel can help ensure the use of durable mixtures and proper practices.

1.2—Scope

This guide discusses the important mechanisms of concrete deterioration and gives recommendations on how to mitigate or minimize such damage. This guide also addresses durability by first discussing the importance of mass transport and then addressing specific modes of attack in separate chapters. These include freezing and thawing, alkali-aggregate reaction (AAR), sulfate attack, aggressive chemical attack, physical salt attack, corrosion of metals and other embedded materials, abrasion, or a combination of these. Fire resistance of concrete and cracking are not addressed directly. Fire resistance is covered in [ACI 216.1](#) and cracking is covered in [ACI 224R](#) and [ACI 224.1R](#). While cracking does impact the durability of concrete in severe exposures, the different causes of cracking and their specific impacts are not discussed. Cracking is only mentioned in general terms regarding its impact on fluid ingress.

CHAPTER 2—DEFINITIONS

2.1—Definitions

Please refer to the latest version of ACI Concrete Terminology for a comprehensive list of definitions. Definitions provided herein complement that resource.

advective transport—transfer of heat or matter via the bulk motion of a fluid.

alkali loading (or content)—total amount of equivalent alkalis (Na_2O_e) in a concrete mixture expressed as mass per volume.

calcium sulfoaluminate cement—product obtained by pulverizing clinker containing mainly ye'elimite [$\text{Ca}_4(\text{AlO}_2)_6\text{SO}_4$] that is often used in expansive cements and ultra-high-early-strength cements.

diffusion—movement of species, such as ions, gas, or vapor, from an area of higher concentration to an area of lower concentration, independent of the bulk motion of a fluid.

electrical migration—transport of electrons or ions due to an electric potential gradient.

ice lens—layer of ice, generally parallel to the exposed surface of the concrete, that can produce internal damage and also lead to scaling or delamination.

leaching—dissolution and removal of soluble components such as calcium hydroxide from concrete.

permeability—the ability of a given concrete to permit liquids or gases to pass through.

permeation—flow of a liquid, gas, or vapor within a solid under the action of a pressure gradient.

physical salt attack—mechanism in which concrete or mortar is damaged as a result of salt crystallization pressure.

reactive silica—form of silica, often amorphous or crypto-crystalline, that dissolves when in contact with concrete pore solution having a sufficiently high concentration of hydroxyl ions.

salt weathering—form of deterioration most commonly observed in arid climates where exposure to soluble salts and cyclic variations in temperature and relative humidity can lead to salt crystallization.

thaumasite—silicate mineral, colorless to white prismatic hexagonal crystals typically as acicular radiating groups, with the chemical formula $\{[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12(\text{H}_2\text{O})](\text{SO}_4)(\text{CO}_3)\}$.

CHAPTER 3—MASS TRANSPORT

3.1—Introduction

Concrete is a multiphase porous medium consisting of a multiscale porous cement paste matrix with aggregate inclusions. Liquid and gas may be present in any pores and micro-cracks. As such, it is susceptible to the ingress and movement of substances (fluids or ions) from its environment within and through its pore system. This chapter discusses the transport of gases, liquids, and ions in solution through concrete ([Lichtner et al. 1996](#); [Baer 1988](#); [Hearn et al. 2006](#); [Hall and Hoff 2012](#)). Methods for improving the durability of concrete and some of the common test methods used to measure the transport properties, along with their advantages and limitations with regard to assessing concrete durability, are also discussed. It is recognized that the rate of ingress of fluids and ions will increase by the presence of cracks. However, the specific influences of different types of cracks and crack widths are not discussed herein.

The ingress of gases, liquids, or ions in solution through concrete may initiate chemical processes, physical processes, or both, that affect the durability of the concrete under a given set of service conditions. Water itself may be harmful because of its ability to leach calcium hydroxide (CH) from the hardened cement paste and because of osmotic pressures generated as water flows to sites of higher alkalinity ([Powers et al. 1954](#); [Powers 1975](#); [Helmuth 1960b,c](#)). In addition, water may also be acidic or carry harmful dissolved chemicals, such as chlorides or sulfates, into the concrete. The ingress of gases such as oxygen and carbon dioxide through the concrete pores can contribute to the corrosion of steel reinforcement.

Different substances may interact with components of the concrete in different ways; therefore, transport of a substance through concrete is unique to that substance. For example, water can hydrate previously unhydrated cement particles or leach calcium. Chloride ions may be bound by the hydration products of cement or supplementary cementitious materials (SCMs). The size of the molecules or ions that are transported through the concrete, viscosity of the fluid, valence of the ions, and other ionic species present also affect the transport properties. Thus, permeability and diffusivity must be expressed in terms of the substance that is migrating through the concrete. In general, concrete with transport properties that limit the rate of ingress of external agents is not immune to chemical deterioration, but the effects are mainly near the exposed surfaces, so the concrete tends to be more durable.

3.2—Transport processes in nonreactive porous media

This section provides a brief overview of the transport processes of fluids (gases and liquids) and ions in solution within a nonreactive porous medium. This is a simplifying assumption because concrete changes chemically and physically with time in response to its environment. Physical changes, chemical changes, or both, in the internal structure of the porous medium resulting from interactions with the migrating fluids or ions are not discussed herein. The transport pathways described here include:

- (a) Transport by permeation
- (b) Advective transport
- (c) Hydrodynamic dispersion
- (d) Diffusion within the pores
- (e) Transport due to electrostatic interactions or electrical migration

Martín-Pérez et al. (2001) modeled transport related to corrosion of reinforcement in concrete based on chloride transport, moisture diffusion, heat transfer, and oxygen transport using a two-dimensional (2-D) finite element model. They used a modified version of Fick's second law.

Johannesson (2003) developed a theoretical model for diffusion of different types of ions in concrete pore solution. The model incorporates diffusion caused by concentration gradients of ions (for example, due to drying), internal electrical potential, convection, effects of changes in moisture content, and mass exchange of ions between solution and solid hydration phases.

Chung and Consolazio (2005) developed a finite difference model to simulate heat and mass transport in rapid heating conditions, such as fires in reinforced concrete structures. The model accounts for the interference between liquid and gas phases, slip-flow effects in steam flow, and the interference of steel reinforcement in moisture movement in concrete.

3.2.1 Transport by permeation—Permeation is the flow of a fluid under the action of a pressure gradient. Permeability is the property that characterizes the ease with which fluid passes through a porous material under a pressure gradient. For a steady laminar flow through a saturated porous medium, the fluid flow is related to the hydraulic pressure gradient according to Darcy's law.

$$dq/dt = K_1 A \Delta h / l \quad (3.2.1)$$

where dq/dt is the flow (expressed as a rate); K_1 is the permeability coefficient; A is the cross-sectional area; Δh is the hydraulic head; and l is the thickness of the specimen. The permeability coefficient K_1 is the rate of discharge of water under laminar flow conditions through a unit cross-sectional area of a porous medium under a unit hydraulic gradient and standard temperature conditions. Darcy's law indicates that for a given cross-sectional area and permeability coefficient, the flow is proportional to the hydraulic gradient $\Delta h/l$. Under service conditions, flow is three-dimensional, and the concrete may not be saturated. In concrete, the permeability coefficient may change with increased hydration, cracking,

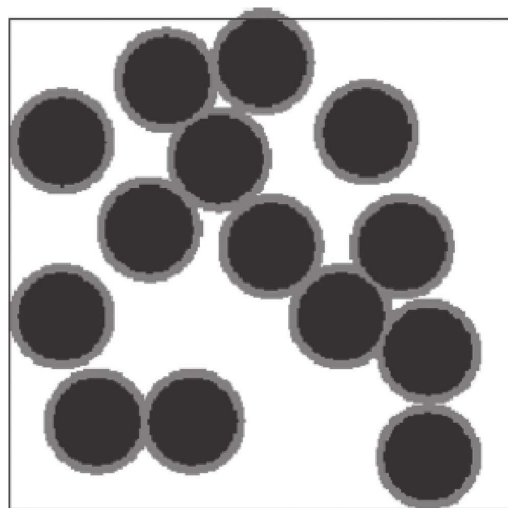


Fig. 3.2.1—Graphical representation of a simple percolation theory model used to model the permeability of concrete.

or changes in the pore structure due to various physical and chemical processes.

Permeability coefficients of plastic portland cement pastes of 0.5 water-cement ratio (w/c), calculated from measurements of bleeding, ranged from 5 to 8×10^{-7} m/s for four cements with different chemical composition but the same specific surface ($180 \text{ m}^2/\text{kg}$ by the Wagner turbidimeter). The permeability coefficient of mature paste (for example, at greater than 28 days of age) is between 1 millionth and one 10 millionth of that of fresh paste. It ranges from 1×10^{-15} to 1.2×10^{-12} m/s for w/c ranging from 0.3 to 0.7 (**Powers et al. 1954**).

To understand the effects of microstructure on the permeability of concrete, **Bentz et al. (1999)** at the National Institute of Standards and Technology (NIST) used percolation theory. One useful application of percolation theory is the examination of the time needed for a material to progress through a complex maze (**Stauffer and Aharony 1992**). This maze consists of areas that can allow free movement, as well as areas that impede the transport of a fluid to different degrees. These models can be made in two and three dimensions and can include the effects of cracks. **Lu et al. (2012)** were able to use a three-dimensional version of the NIST model to predict chloride ingress into cracked concrete.

Work has also been done by NIST that models changes in the properties of these systems with time. This allows the change in the microstructure of the concrete to be examined with time and observe the effects on the ability of a fluid to move through the system.

A graphical representation of a simple percolation theory model has been used by **Bentz (2000)** to model the transport of a fluid through concrete in two dimensions, as shown in Fig. 3.2.1. Very dense areas are used for aggregates. Moderately dense material is used for the cement paste and low-density material is used to model the interfacial transition zone (3.3.4).

3.2.2 Advective transport—Advective transport is the movement of molecules and ions with the bulk solution

flow. This transport process is related directly to the velocity of fluid flow and concentration of ions in solution. Depending on exposure condition and degree of saturation, the velocity of fluid flow depends on the sorptivity or permeability of concrete, viscosity of the fluid phase, and pressure head of the permeating fluid or rate of evaporation from the exposed surface in the case of wick action (Buenfeld et al. 1995).

3.2.3 Hydrodynamic dispersion—Dispersion is the spreading of the ion concentration during advective transport due to variations in the pore fluid velocity. These variations can be a result of the tortuosity of the pore structure, the connectivity of the pore network, or variation in the fluid properties.

3.2.4 Diffusion within pores—Diffusion refers to the transport mechanism whereby ions or gases migrate from areas of higher concentration to areas of lower concentration. For the idealized one-dimensional case, Fick's second law describes the non-steady-state diffusion of ions within the pores

$$dc/dt = D_e \cdot d^2c/dx^2 \quad (3.2.4)$$

where c is the concentration of the ion at distance x from the surface after time t , and D_e is the effective diffusion coefficient or effective diffusivity. The effective diffusivity is a function of the porosity and tortuosity of the porous medium and the molecular diffusivity of the ion of concern. Many factors affect diffusion of ions in concrete. Based on measurements obtained under controlled conditions in the laboratory, diffusion coefficients increase with temperature and water-to-cementitious materials ratio (w/cm) and decrease with increasing degree of hydration. Because concrete pore solutions have high ionic strength, electrical charge effects can be significant. Diffusion coefficients can also vary with the species of other ions present in solution. For these and other reasons discussed in 3.4.1.2, the values obtained experimentally using Fick's second law are generally termed "apparent diffusion coefficients". Diffusion coefficients for Na^+ in concrete are on the order of 10^{-11} to 10^{-13} m^2/s , and for Cl^- , on the order of 10^{-11} to 10^{-12} m^2/s (Taylor 1997).

3.2.5 Transport due to electrostatic interactions or electrical migration—Migration refers to the transport mechanism due to the charged nature of ions and is the result of the potential difference across the specimen. The electrical coupling between ions in concentrated solutions was demonstrated by Snyder (2001) and Snyder and Marchand (2001). Electrical migration occurs when an external electric field such as in ASTM C1202 (or AASHTO T 277) is applied to the medium (Buenfeld et al. 1998). The migration flux J_i of ion i is given by

$$J_i = -D_i C_i \frac{z_i F}{RT} \frac{\partial \phi}{\partial x} \quad (3.2.5)$$

where $\partial \phi / \partial x$ is the potential difference; Z_i is the charge of the ion; F is the Faraday constant; T is the temperature; D_i is the ion diffusivity; R is the gas constant; and C_i is the concentration of the ion in solution.

Further information on ionic transport in concrete can be found in McGrath and Hooton (1996) and for the more complex case of multi-species transport in Truc et al. (2000) and Samson et al. (1999).

3.3—Factors affecting mass transport in concrete

3.3.1 Porosity and pore size distribution—Porosity is defined as the volume of voids as a fraction that is usually expressed as a percent of the total volume

$$\text{porosity (\%)} = (\text{volume of voids} / \text{total volume}) \times 100\% \quad (3.3.1)$$

Figure 3.3.1a shows the size ranges for the various types of pores in concrete. Pores in concrete range in size from nanometers to millimeters. The capillary pores, also ranging in size from tens of nanometers to millimeters, have the most significant effect on the transport properties. Transport properties, however, depend more on the connectivity of the pores than on either the porosity or size of the pores. Figure 3.3.1b shows two hypothetical porous materials with

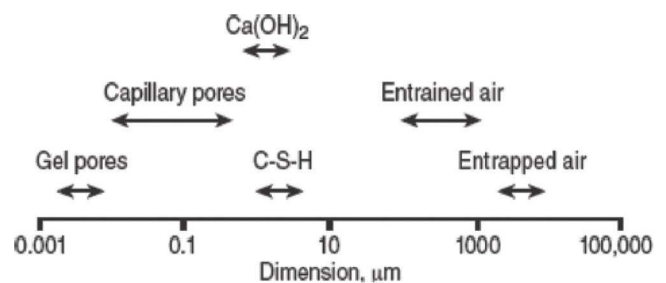


Fig. 3.3.1a—Relative sizes of different types of pores and other microstructural features (adapted from Mehta [1986]).

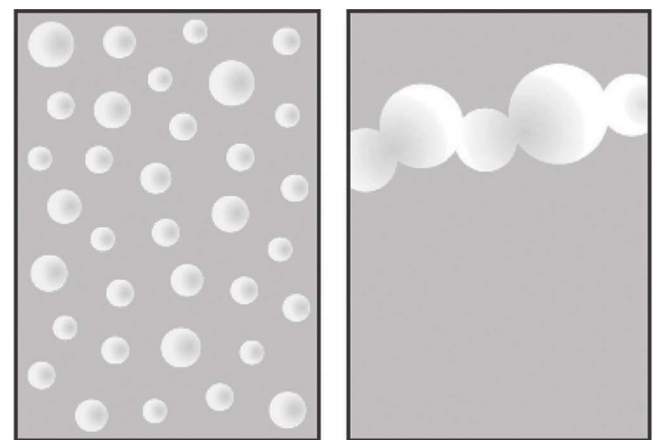


Fig. 3.3.1b—Porosity and permeability are related but distinct. The two hypothetical materials shown have approximately the same porosity (total volume of pores), but different permeabilities. Discrete pores, such as those resulting from air entrainment, have almost no effect on permeability, but interconnected pores increase permeability.

approximately the same porosity. In one material, the pores are discontinuous, as would be the case with entrained air bubbles, whereas in the other the pores are continuous. The latter material would allow for more rapid rates of transport than the former.

3.3.2 Water-cement ratio (w/c)—The initial porosity of a cement paste is determined by the w/c . As cement hydrates, hydration products fill some of the void space formerly occupied by water. With time, this process results in a continued

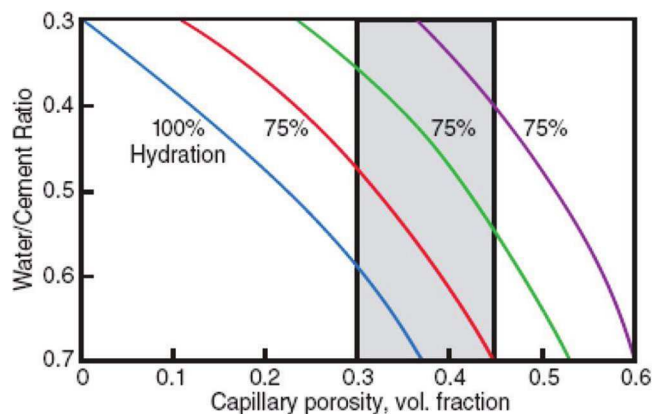


Fig. 3.3.2a—Water-cement ratio versus capillary porosity for cement paste at different degrees of hydration (Mehta 1986) based on equations developed by Powers and Brown-yard (1948).

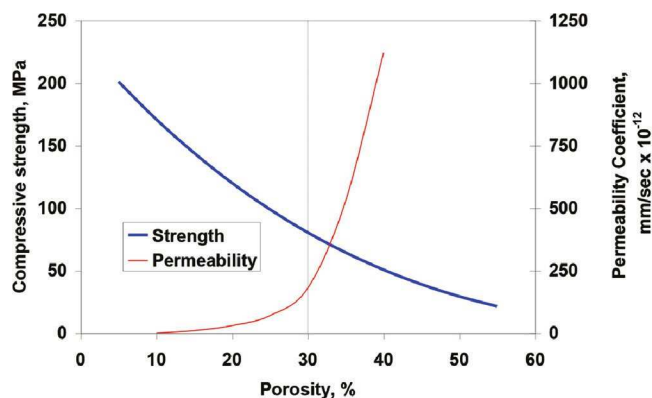


Fig. 3.3.2b—Both compressive strength and permeability are related to the capillary porosity of the cement paste (adapted from Powers [1958]).

Table 3.3.2—Approximate age required to produce maturity at which capillaries become discontinuous for concrete continuously moist-cured (Powers et al. 1959)

w/c by mass	Time required
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
Over 0.70	Impossible

decrease in the porosity of the cement paste. Figure 3.3.2a (Mehta 1986) illustrates the relationship among w/c , degree of hydration, and capillary porosity. For a w/c of 0.45, the degree of hydration must reach approximately 70% to bring the porosity down to 30%. For a w/c of 0.60, the degree of hydration must reach approximately 100% to reach the same porosity. The degree of hydration that could be expected for good curing conditions—for example, moist curing for 5 to 7 days—would range between 70 and 80%, depending on cement chemistry and fineness, and on hydration temperatures; a 100% degree of hydration is not a practical possibility. Figure 3.3.2b shows the relationship between porosity and permeability. Above a porosity of approximately 30%, the coefficient of permeability increases sharply.

Powers (1962b) calculated that for cement paste with a w/c of 0.38, all of the capillary pore space was just filled by maximum density gel when all of the cement was hydrated. Sealed, fully hydrated cement pastes made at w/c above 0.38 have remaining capillary pore space equal to the excess above 0.38. Partially hydrated mixtures have proportionately less gel and more capillary space. Powers et al. (1959) calculated the time required for capillary pores to become discontinuous with increasing hydration of the cement, as shown in Table 3.3.2. It is notable that mixtures with a w/c greater than 0.7 will always have continuous pores. Even for w/c of 0.40 to 0.45, extended moist curing or other favorable curing conditions are necessary to achieve the desired low permeability.

3.3.3 Curing temperature

3.3.3.1 At normal temperatures—Soon after mixing cement with water, a gel layer forms on the surfaces of the cement grains (Taylor 1997). Between 3 and 24 hours after mixing cement with water, approximately 30% of the cement reacts. Rapid formation of calcium silicate hydrate (C-S-H) and CH is accompanied by significant evolution of heat. The CH forms massive crystals in the originally water-filled space. The C-S-H forms a thickening layer around the cement grains. As the shells grow outward, they begin to coalesce at about 12 hours, a time coinciding with the maximum rate of heat evolution (Fig. 3.3.3.1) and corre-

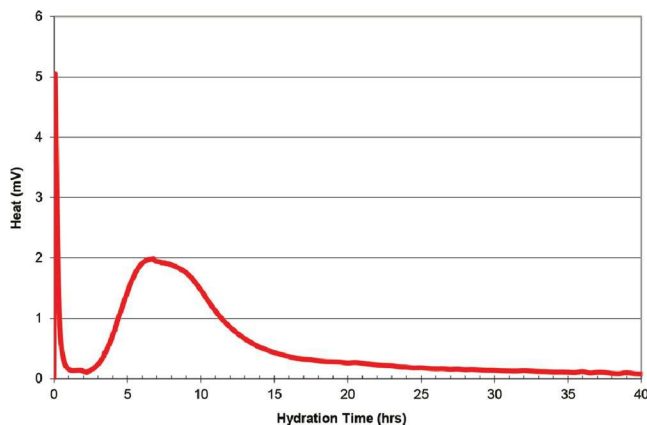


Fig. 3.3.3.1—Heat evolution of Type I/II portland cement paste as measured by conduction calorimetry. (Image courtesy of E. Shkolnik.)

sponding approximately to completion of setting (Taylor 1997). In Fig. 3.3.3.1, the first heat peak is associated with the initial hydrolysis of the C_3S and the hydration of the C_3A . The acceleration period begins with the renewed evolution of heat at the beginning of the second peak as the initial hydration products of the C_3S begin to form. Initial set coincides with the beginning of the acceleration period. Final set takes place just before the maximum point of the second peak. The shoulder of the second peak is associated with the renewed formation of ettringite (Taylor 1997). Further hydration of the cement continues at a much slower rate, asymptotically approaching 100% (Mindess and Young 1981). After the spaces between the hydration shells and the cement grains fill with hydration products, further hydration is slow (Taylor 1997). Capillary pores remaining in mature cement paste increase in size with w/c and have diameters of 10 nm and higher (Mindess and Young 1981).

3.3.3.2 At high or low temperatures—Like most chemical reactions, cement hydration is faster with increasing temperature. Verbeck and Helmuth (1969) postulated that at elevated temperatures, cement hydration products would not have time to diffuse any significant distance from the cement grain, thus forming relatively dense hydration shells around the cement grains. A consequence of the uneven distribution of the solid phases is a coarser pore structure. Goto and Roy (1981) found that the total porosities of pastes hydrated at 140°F (60°C) were greater than those of pastes hydrated at 81°F (27°C). For cement pastes hydrated at low temperatures, on the order of 50°F (10°C), the hydration products are more evenly distributed and the pores fine and discontinuous. For cement pastes hydrated at elevated temperatures, pores are coarser and more interconnected (Kjellsen et al. 1991). Cement pastes containing fly ash, slag cement, or both, are less sensitive to the effects of elevated temperatures, as discussed in 3.3.5.

3.3.4 Aggregates—Aggregates generally have fundamentally different transport properties from those of cement paste. For example, the permeability of granite is typically two to three orders of magnitude lower than that of cement paste. The presence of the aggregate in a cement-paste matrix creates an inhomogeneity in the structure of hardened concrete known as the interfacial transition zone between the cement paste and aggregate. Mehta (1986) reported that, compared to the bulk cement paste, the interfacial transition zone has a higher void content, higher contents of CH and ettringite, reduced content of C-S-H, and larger crystals of CH strongly oriented parallel to the aggregate surface (Fig. 3.3.4). Factors contributing to the anomalous nature of the interfacial transition zone include bleeding, which creates pockets of water-filled space beneath aggregate particles; less efficient packing of particles of cementitious materials in the vicinity of a surface, which is called the wall effect; and the one-sided growth effect of dissolved cementitious materials and hydration products diffusing in from the bulk cement paste, but not from the aggregate (Bentz et al. 1995). As the cementitious materials hydrate, the interfacial transition zone fills preferentially with CH and ettringite. Because of the relatively open space, the crystals can grow large.

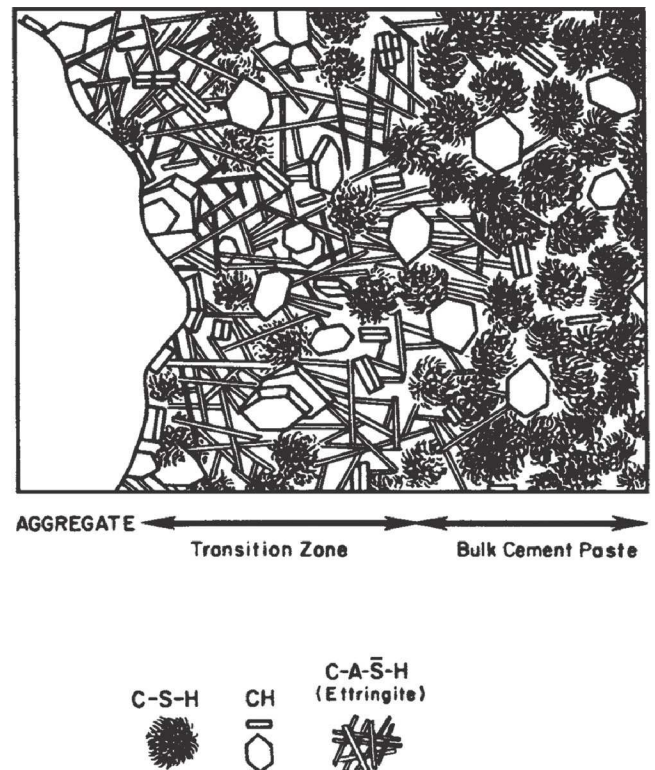


Fig. 3.3.4—Representation of transition zone at paste/aggregate interface in concrete, showing more coarsely crystalline and porous microstructure than in interzonal mass (Mehta 1986).

Thus, in most concrete, the interfacial transition zone is the weakest link in terms of mechanical behavior and transport properties. For the latter, the interfacial transition zone can serve as a relatively open channel for fluids and ions, and the CH is vulnerable to leaching and acid attack. For a given w/c and degree of hydration, water permeability of concrete made with low-permeability aggregates is approximately one to two orders of magnitude lower than that of cement paste due to the interfacial transition zone between aggregate and cement paste (Mehta 1986). It was found that the diffusivity of chloride in the interfacial transition zone is 10 times greater than that in bulk cement paste (Delagrave et al. 1997). The connectivity of pores in the interfacial transition zone may be high, leading to significantly greater rates of transport for some concretes than might be predicted from their mixture proportions. For mixtures with high coarse aggregate contents, such as paving concretes, flow through the interfacial transition zone can completely dominate moisture movement in the concrete over a wide range of w/c (Janssen and Snyder 1994).

3.3.5 Supplementary cementitious materials—The use of SCMs can significantly reduce the permeability and diffusivity of concrete. These materials may not reduce the total porosity to any great extent, but instead act to refine and subdivide the pores so that they become less continuous. Some benefits are obtained by the improvements in workability, particularly the reduction in bleeding, afforded by these materials. The use of fly ash can also reduce the water demand of some concrete mixtures, allowing for a more

in water-cementitious materials ratio (w/cm) while maintaining equivalent workability. The lower specific gravity of SCMs relative to cement results in an increased volume of solids for a given w/cm with increasing dosage. The greatest benefits from the standpoint of durability, however, derive from the pozzolanic reaction associated with many SCMs. In this reaction, CH from the hydration of the cement reacts with noncrystalline silica in SCMs and water to form C-S-H. Because C-S-H has a greater volume than the CH and pozzolan from which it forms, the pozzolanic reaction results in a finer system of capillary pores.

Slag cement and alumina-bearing pozzolans have an additional benefit, as the hydration products are highly effective in binding chloride ions, preventing further penetration into the concrete (Thomas et al. 2012). This effect is particularly important in applications such as parking garages, bridge decks, and marine construction, where the reinforcing steel is vulnerable to chloride-induced corrosion.

The indiscriminate use of SCMs is not necessarily beneficial. Their pozzolanic and hydraulic reactions take time, partly because the cement must hydrate sufficiently to produce CH to participate in the reaction, and partly because SCMs may vary significantly in terms of kinetics or rate of reactivity. The engineer must consider the properties of the concrete at early ages. Because the pozzolanic reactions typically proceed more slowly than the hydration of cement, extended moist curing is necessary to achieve the best results.

Supplementary cementitious materials can often mitigate the deleterious effects of elevated-temperature curing. Cao and Detwiler (1995) found that both silica fume and slag were effective in refining the pore structure. Campbell and Detwiler (1993) tested a series of steam-cured concretes in which the proportions of the various cementitious materials were varied. They found that the total charge passed in 6 hours using AASHTO T 277 varied by two orders of magnitude, with CSA Type 10 (now designated Type GU) portland cement alone performing the worst, and optimized blends of cement, slag, and silica fume performing the best. They did not use fly ash in their study.

Bentz et al. (1995) showed that silica fume particles both reduce the initial thickness of the interfacial transition zone and react to convert CH to C-S-H. Fly ash has a similar, but less-pronounced, effect due to its larger particle size and lower pozzolanic activity.

3.4—Measurement of transport properties

Measurement of the transport properties of concrete is complicated by the interactions between the concrete and the substance that is moving through it; the changing properties of concrete with time; and the sensitivity of transport properties to variations in moisture, temperature, and other conditions. Because many tests accelerate the transport mechanism of the fluid or ion in question, they may induce different or additional mechanisms of transport than what would occur in service. They often make it impossible to achieve the steady-state conditions that form the basis of the various equations used to describe mass transport and

may invalidate the assumption of laminar flow used in many calculations (Eq. (3.2.1)). Furthermore, laboratory tests are often conducted under highly controlled conditions that may not accurately reflect actual service conditions. When used judiciously, however, the tests described in the following may be helpful in comparing the suitability of different concrete mixtures for a given exposure condition, or for quality assurance/quality control purposes during construction (Puerto Rico DOT SP934). The following sections discuss available ASTM tests used to characterize transport properties, along with commonly used variations.

3.4.1 Ions

3.4.1.1 Coulomb test (ASTM C1202/AASHTO T 277)—Standard tests of ion transport focus on the penetration of chloride ions into concrete. The most common test used for this purpose is ASTM C1202 (or AASHTO T 277), in which a cylindrical specimen with a nominal diameter of 4 in. (100 mm) and a length of 2 in. (50 mm) is vacuum saturated with water before being placed in a test cell. The cell contains a 3% solution of sodium chloride on one side and a 0.3 N solution of sodium hydroxide on the other side. An electrical potential of 60 V DC is applied for 6 hours. The total charge passed during the test period is an indirect indication of the chloride ion penetrability of the concrete.

Essentially, ASTM C1202 (or AASHTO T 277) uses the electrical conductivity of the concrete as a rapid index test or surrogate for diffusivity. The main objections to the use of this test method stem from the indirect nature of the measurement. While ion diffusion depends primarily on the microstructure and chemical binding capacity of the matrix, electrical conductivity depends on both microstructure and pore solution chemistry (Buenfeld and Newman 1987). Different proportions of SCMs can profoundly affect the pore solution chemistry. For example, Page and Vennesland (1983) found that 10% silica fume, by substitution, reduced the concentrations of Na^+ , K^+ , and Ca^{2+} by approximately 50% and that of OH^- by approximately 75% in the pore solution. Detwiler and Fapohunda (1993) compared the results of AASHTO T 277 to those of a direct measure of chloride ion migration for portland-cement concretes with and without slag cement, and found that AASHTO T 277 unduly favored the concretes containing SCMs. They attributed the differences between the two sets of test results to differences in electrical conductivity due to differences in pore solution chemistry.

Corrosion inhibitors such as calcium nitrite add ions to the pore solution that increase the pore fluid conductivity and the charge passed. There is some evidence that calcium nitrite increases the penetrability of the concrete matrix. That is, increased coulomb values may be due to microstructural effects as well as changes in the pore solution chemistry (Ann et al. 2006; Reou and Ann 2008). If ASTM C1202 (or AASHTO T 277) is used in qualifying concrete mixtures for use in construction, typically the concrete will be tested without the corrosion inhibitor to qualify it, and then with the corrosion inhibitor to provide a baseline value for quality-control purposes. The latter measurement will be considerably higher.

The relationship between electrical conductivity and diffusion may also vary with the mechanism and type of diffusion. Diffusion through voids and cracks differs from bulk diffusion; thus, the presence of flaws in the concrete can significantly affect the results of the test. In addition, the measurement is taken before steady-state conditions are reached (Zhang and Gjrv 1991).

Low-quality concrete is difficult to evaluate properly because the temperature of the specimens rises when current is applied, increasing the rate of diffusion. McGrath and Hooton (1999) proposed a modification to reduce the test period to 30 minutes to eliminate this problem. High-quality concretes may be difficult to distinguish from one another because the total charge passed is so low, and because the test results are variable (Hooton 1989).

ASTM C1202 (or AASHTO T 277) has been criticized for many of the previously cited interferences (Andrade 1993; Feldman et al. 1994; Streicher and Alexander 1994; Shi 2004).

Despite its limitations, ASTM C1202 (or AASHTO T 277) is rapid, convenient, and according to Hooton (1989), whatever property it is measuring probably is coincident with permeability. If properly interpreted, it can be used effectively for quality control in construction (Bognacki et al. 2010), although it should not be used to make fine distinctions among concretes and cannot be used to compare concretes made with different materials or mixture proportions, or both (Shi 2004).

3.4.1.2 Ponding (ASTM C1543; AASHTO T 259) and bulk diffusion (ASTM C1556)—Another standard test that is sometimes used is ASTM C1543 (or AASHTO T 259), which involves ponding three concrete slabs at least 3 in. (75 mm) thick and a surface area of 46 in.² (0.030 m²) with a 3% sodium chloride solution for 90 days. The sides of the slab are sealed, and the bottom exposed to a drying environment at 50% relative humidity. If desired, the exposure period can be extended to 6 months or 1 year. At the end of the exposure period, the excess solution and salt buildup are removed. Half-inch (12 mm) thick samples of the concrete can be taken at two or three depths and analyzed for chloride ion content, which is compared to a baseline value determined on a companion concrete specimen not exposed to external chlorides. Alternatively, the concrete slab can be sampled and tested according to ASTM C1556, in which a core from the slab is milled or sliced to obtain samples at eight depths for the purpose of determining the apparent chloride diffusion coefficient using Fick's second law. This test can also be conducted using a different salt in the ponding solution. Note that the type of cation(s) present affects the rate of ingress of chloride ions because charge balance must be maintained, and the associated cation(s) diffusing at a slower velocity will impede the movement of chloride ions.

One of the most common objections to the use of ASTM C1543 is its duration. As the specimens must be cured for 14 days and then dried for 28 days before the beginning of the ponding, the 90-day version of the test takes 118 days, or longer in the case of extended curing, to conduct, after which the samples must be analyzed. Most test programs for

high-performance concretes would use a ponding period of at least 180 days.

Although the ponding test does provide a crude one-dimensional (1-D) profile of chloride ion ingress, the profile is not a reflection of chloride diffusion alone. The initial mode of ingress of the ions is by sorption into the dried concrete. The exposure of the bottom face to a 50% relative humidity environment during the test induces vapor transmission from the wet front on the top surface to the dry bottom surface, and chloride ions penetrate by wick action (Buenfeld et al. 1995). Diffusion of the chlorides also takes place. McGrath and Hooton (1999) observed that, while all three of these mechanisms do occur in bridge decks, the test exaggerates the importance of the sorption component.

The 28-day drying period before the ponding begins significantly increases the apparent diffusion coefficient, especially for concretes containing SCMs (Ngala and Page 1997). For high-quality concretes, it may be difficult to develop a chloride profile based on a 90-day ponding period because so little chloride penetrates the concrete. Extending the ponding period to 180 days and increasing the number of samples taken help to resolve this problem (Berke and Hicks 1992; Andrade and Whiting 1996; Sherman et al. 1996; McGrath and Hooton 1999).

Precision of the sampling can make a significant difference in the conclusions drawn from the results. In analyzing their data from AASHTO T 259 (a predecessor of ASTM C1543), McGrath and Hooton (1999) showed that imprecise sampling makes it difficult to distinguish between a high-quality concrete in which there is a high concentration of chlorides near the surface, and a low-quality concrete in which the chlorides penetrate much farther. Precision of the sampling specified in ASTM C1556 avoids this problem.

ASTM C1556 avoids some of the problems associated with ASTM C1543, as the concrete specimen is sealed on all sides except the finished surface, and is saturated with a CH solution before exposure to the sodium chloride solution. Thus, the chlorides penetrate into the specimen only by diffusion, not by sorption. The specimen is then placed in a concentrated (165 g/L) sodium chloride solution for at least 35 days. Longer exposure times are recommended for mature concretes, concretes with low *w/cm*, or high-performance concretes containing SCMs. In practice, the exposure time could be extended to 90 days or longer.

The sampling is more precise than for ASTM C1543, as indicated previously. A nominal 4 in. (100 mm) diameter core from the slab is mounted in a mill or lathe and a series of thin layers ground off. The dust from each layer is collected separately and analyzed for acid-soluble chloride content. The apparent diffusion coefficient is determined using nonlinear regression analysis to fit the data to Fick's second law.

The use of Fick's second law to reduce the data is a convenient but questionable practice. Pettersson (1994) noted that the applicability of Fick's second law, which is a simplification of a more general equation describing ion transport, depends on the validity of three assumptions:

- (a) The material in which diffusion takes place is permeable and homogeneous.
- (b) The diffusion properties of the material do not change with time or with the concentration of the diffusant.
- (c) No chemical reaction or physical binding of the diffusant occurs.

Pettersson (1994) further noted that all three of these assumptions are violated in the diffusion of chloride ions through concrete—that is, concrete is heterogeneous, its diffusion properties change with time and with the concentration of the diffusant, and both chemical reactions and physical binding can occur. ASTM C1556 uses the term “apparent chloride diffusion coefficient” to make clear that the result obtained is not a true diffusion coefficient. Although ASTM C1556 in some cases may be conducted in less time than ASTM C1543, it is still a lengthy test.

3.4.2 Fluids—One test for the absorption of water by hardened concrete is ASTM C642, in which a piece of concrete at least 350 mL in volume is oven dried to constant mass and then immersed in water until it again reaches constant mass. The specimen is then boiled for 5 hours, allowed to cool, and the mass determined again. The absorption after immersion and the absorption after immersion and boiling are determined. This test is a measure of the absorption of the bulk concrete. Note that oven drying may induce cracking in the specimen, thus increasing the measured absorption.

ASTM C1585 measures the water sorptivity, which is the rate of absorption of a concrete surface, which is often of greater interest than the bulk concrete. A cylinder or core 4 in. (100 mm) in diameter and 2 in. (50 mm) in length is conditioned to an internal relative humidity of 50 to 70% and then sealed on all but one surface. The mass of the specimen is determined initially and after being placed in contact with water. The mass is determined at close intervals initially and at longer intervals up to an exposure time of 7 days, after which one additional measurement is taken. The initial slope of the absorption-versus-time curve is taken as the rate of absorption.

Abbas et al. (1999) measured the permeability of concrete to oxygen, which is easier than measuring its permeability to water. Their calculations were based on Darcy’s Law, which assumes laminar flow. This simplifying assumption is not strictly true because in very small pores the flow is partly molecular in nature. Gas permeability varies with the degree of saturation of the concrete; the coefficient of permeability varied over two orders of magnitude as a function of the degree of saturation. Acceptable limits on the permeability for durability vary depending on the exposure conditions and performance requirements.

3.5—Obtaining durable concrete

Obtaining durable concrete for given conditions of exposure requires suitable mass transport properties for the fluids and ions of interest. Proper attention to all aspects of good concrete practice is important. The most significant factors, however, are an appropriately low w/cm ; judicious use of SCMs; and good workmanship, including mixing, placement, compaction, and curing. Elevated curing temperatures

can be deleterious to the transport properties of concrete, although the use of an appropriate combination of cementitious materials can largely mitigate this effect. Optimization of the concrete mixture proportions should be done using the curing regime anticipated on the job and a test method that bears some relation to the anticipated exposure conditions. In particular, compressive strength is not a surrogate for durability.

Proper attention to control of cracks is also important; there is little to be gained from concrete of low permeability between the cracks. Good aggregate grading to minimize the paste content, control of temperature and moisture conditions, and appropriate structural design and detailing can minimize the width of cracks. Further guidance is available from the Transportation Research Board (2006) and Detwiler and Taylor (2003).

CHAPTER 4—FREEZING AND THAWING OF CONCRETE

4.1—Introduction

Deterioration of concrete exposed to freezing can occur when there is sufficient internal moisture that can freeze at the given exposure conditions. The source of moisture can be either internal or external. Internal is water that is already in the pores of concrete that is redistributed by thermodynamic conditions to provide a sufficient degree of saturation at the point of freezing to cause damage. External is when the water enters the concrete from an external source, such as rainfall. Dry concrete (generally below approximately 75 to 80% internal relative humidity) is normally immune to damage from freezing.

Young concrete can be damaged by a single freeze (4.2.2). Mature concrete may be able to withstand repeated cycles of freezing and thawing without damage. Thus, concrete that is properly cured and reaches sufficient maturity before being exposed to freezing, such as concrete for columns or floor slabs, may tolerate freezing from exposure to a single winter season before it is protected from the elements. Similar concrete that is not properly cured and is exposed to freezing conditions at an early age, such as sidewalks and exposed foundation walls, may show deterioration after a few years of exposure to repeated cycles of freezing and thawing.

The severity of exposure should be quantified by a combination of freezing, which is the number of annual cycles of freezing plus average low temperature reached during each cycle, and moisture condition before each cycle of freezing (4.2.6.4).

4.1.1 Concrete made with durable aggregate—Concrete made with aggregate that is resistant to freezing and thawing is primarily protected from damage through the use of entrained air in the concrete mixture, with secondary protection from steps taken to limit the fractional volume of freezable water in the concrete. A description of damage due to freezing and thawing of concrete made with durable aggregates, along with protection methods, is given in 4.2.

4.1.2 Concrete made with frost-susceptible aggregates—A properly proportioned concrete mixture that has received

adequate curing can suffer damage from freezing and thawing if it contains an aggregate (generally the coarse aggregate) that is susceptible to damage from freezing and thawing. A description of damage in concrete made with aggregates susceptible to freezing and thawing, along with a description of aggregate identification procedures, is given in 4.3.

4.2—Frost attack of concrete made with durable aggregates

4.2.1 *Description of frost damage*

4.2.1.1 Damage at early ages—Concrete in the early stages of hydration ordinarily contains a considerable amount of freezable water and has little or no tensile strength to resist pressures due to freezing. Concrete that is allowed to freeze under these conditions will develop ice lenses approximately parallel to the surface exposed to freezing. Additional ice lenses can develop under coarse aggregates. When the concrete thaws and hydration resumes, the space previously occupied by the ice lenses will form weak planes that are susceptible to delamination or surface scaling.

4.2.1.2 *Damage in cured concrete*

4.2.1.2.1 Surface scaling—The most common form of damage from freezing and thawing in hardened concrete is surface scaling—that is, the loss of paste and mortar from the surface of the concrete. Generally, layers less than 0.04 in. (1 mm) thick are lost, but repeated cycles of freezing and thawing can lead to removal of additional material. Scaling is considerably accelerated by deicing salts. Vehicle traffic or other surface contact can also accelerate scaling by aiding in the removal of loosened material. Consequences of scaling include change in appearance; change in surface smoothness; and, in severe cases, loss of concrete cover over reinforcing steel.

4.2.1.2.2 Internal deterioration—Though less common, internal deterioration can have more severe consequences than surface scaling due to the loss of structural integrity of the concrete. Internal deterioration manifests itself as a loss of strength in the paste of the concrete. Modern concrete practice has practically eliminated this form of damage from freezing and thawing by requiring a proper air-void system and adequate curing before the first exposure to freezing temperatures.

4.2.2 *Preventing frost damage in new concrete*

4.2.2.1 Protection from early freezing—Young concrete should be protected from freezing by following the procedures and maintaining the minimum temperatures recommended in ACI 306R. After consolidation and finishing, the concrete should be protected from cooling too rapidly by using insulated forms, curing blankets, and other procedures described in ACI 306R. Allowing the concrete to cool too rapidly could result not only in early freezing, but also in thermal cracking of the concrete (ACI 306R; ACI 308R).

4.2.2.2 Minimum curing before freezing—Adequate curing, including preventing excessive drying and maintaining adequate temperature, will ensure that the concrete has hydrated sufficiently to substantially reduce the amount of freezable water. A recommended minimum strength that should be attained before the concrete temperature is allowed

to drop below freezing is 500 psi (3.5 MPa) (Powers 1962a). Once this strength has been achieved, a single freeze will generally not permanently damage the concrete (ACI 308R). If repeated cycles of freezing and thawing are anticipated, the concrete should be kept warm long enough to allow it to develop a compressive strength of at least 3500 psi (25 MPa) if it will not be exposed to deicing salts, and 4500 psi (32 MPa) if it will be exposed to deicing salts. The strengths of 3500 and 4500 psi are average in-place strengths needed before the concrete is exposed to repeated cycles of freezing and thawing. Table 19.3.2.1 in ACI 318-14 refers to the specified design strength. The two strengths are not the same, as concrete could be exposed to repeated cycles of freezing and thawing at an age significantly earlier than the age associated with the specified design strength.

4.2.3 Preventing frost damage by proper design—Much concrete now in service has withstood repeated cycles of freezing and thawing for many years. While some of this concrete has remained undamaged because it was never allowed to contain enough freezable water to cause damage, most of it has remained durable because proper precautions were taken to avoid such damage (Mather 1990). The three most important precautions to provide resistance to freezing and thawing are discussed in 4.2.3.1 through 4.2.3.3.

4.2.3.1 Reducing freezable water—The likelihood of damage from freezing and thawing is reduced by decreasing the amount of freezable water in concrete. For conventional mixtures, this has generally been accomplished by lowering the w/cm , which is a maximum of 0.50 for moderate exposure and 0.45 for severe and very severe exposure (Table 4.2.3.1a), combined with adequate curing to ensure a minimum compressive strength of approximately 3500 psi (25 MPa) before exposure to repeated cycles of freezing and thawing (4500 psi [32 MPa] if deicing salts are present). Note that for instances in which corrosion is a concern, a lower w/cm may be required if deicing salts are present (ACI 318-14).

Limiting the w/cm to a specified maximum has the effect of reducing the amount of freezable water in the cured concrete initially. Requiring a minimum strength before freezing helps ensure that the tensile strength of the paste is sufficient and the fractional volume that could be occupied by freezable water in saturated concrete has been adequately reduced by the formation of hydration products.

Modern concrete mixtures may contain admixtures, additives, and supplementary cementitious materials (SCMs) that permit reduction of the amount of freezable water in concrete. Slag cement or pozzolans can refine the pore structure at a given w/cm , resulting in a smaller fraction of the porosity containing freezable water. The use of slag cement or pozzolans has the added beneficial effect of reducing the rate that water can penetrate through the concrete. This means that water removed by evaporation or hydration will be replaced more slowly when the concrete is exposed to water. Numerous field observations have indicated when surfaces are finished by hand, as opposed to machine-finished or cast against formwork, and exposed to deicing salts (Mather 1990). Class F3a in Table 4.2.3.1b, limits on the SCMs may be

Table 4.2.3.1a—Freezing-and-thawing exposure classes

Exposure Class	Severity	Condition
F0	Not applicable	Concrete not exposed to freezing conditions
F1	Moderate	Concrete exposed to freezing-and-thawing conditions, but very low probability of concrete being near saturation at time of exposure*
F2	Severe	Concrete exposed to freezing-and-thawing conditions, with a high probability of concrete being near saturation at time of exposure, but no deicing chemical exposure†
F3	Very severe	Concrete exposed to freezing-and-thawing conditions as well as deicing chemicals‡

*Examples are vertical surfaces above the level of snow accumulation or horizontal elevated floors in areas protected from direct exposure to moisture.

†Examples are: vertical surfaces below the level of snow accumulation; vertical surfaces with sufficient moisture exposure to allow the concrete to be near saturation prior to freezing; retaining walls or other vertical elements with one side exposed to moisture; and slab-on-ground that is not protected from freezing.

‡Examples are: vertical surfaces that may have deicing-chemical-contaminated snow piled against them; sidewalks or pavements that receive deicing chemicals; and concrete that received frequent exposure to seawater as well as freezing-and-thawing conditions.

Table 4.2.3.1b—Requirements by freezing-and-thawing exposure class

Exposure Class	Minimum $\bar{f}_c$, * MPa (psi)	Maximum w/cm †	Air content	Limits on cementitious materials
F0	No restriction	No restriction	No restriction	No restriction
F1	25 (3500)	0.50	Table 4.2.3.2.4	No restriction‡
F2	25 (3500)	0.45	Table 4.2.3.2.4	No restriction‡
F3a§	32 (4500)	0.45**	Table 4.2.3.2.4	Table 4.2.3.1c‡
F3b#	32 (4500)	0.45**	Table 4.2.3.2.4	No restriction‡

*The minimum average compressive strength that should be achieved before initial exposure to freezing and thawing.

†The maximum w/cm for the in-place concrete to provide adequate restriction of freezable water in the properly cured concrete.

‡High cementitious material replacement for portland cement frequently results in lower rates of strength gain. Care should be taken to ensure that adequate curing (moisture, temperature, and time) is provided so that the minimum $\bar{f}_c$ is achieved before initial exposure to freezing and thawing.

§Hand-finished surfaces.

#Formed and machine-finished surfaces.

**A lower w/cm may be needed when corrosion is of concern (ACI 318-14).

Table 4.2.3.1c—Cementitious materials limitations for Exposure Class F3b

Cementitious materials	Maximum percent of total cementitious materials by mass*
Fly ash or other pozzolans conforming to ASTM C618	25
Slag conforming to ASTM C989/C989M	50
Silica fume conforming to ASTM C1240	10
Total of fly ash or other pozzolans, slag, and silica fume	50†
Total of fly ash or other pozzolans and silica fume	35†

*The total cementitious materials also include ASTM C150/C150M, ASTM C595/C595M, ASTM C845/C845M, and ASTM C1157/C1157M cements. The maximum percentage should include: (a) fly ash or other pozzolans in Type IP blended cement, ASTM C595/C595M or ASTM C1157/C1157M; (b) slag used in the manufacture of an IS blended cement, ASTM C595/C595M or ASTM C1157/C1157M; and (c) silica fume, ASTM C1240, present in a blended cement.

†Fly ash or other pozzolans and silica fume shall constitute no more than 25 and 10%, respectively, of total mass of the cementitious materials.

required due to a variety of factors that appear to include modification of the entrained air-void system (4.2.3.2) as well as superficial changes to the w/cm . Table 4.2.3.1c gives recommended cementitious materials limitations for Exposure Class F3a (Thomas 1997).

Some researchers have hypothesized that it may be possible to produce concrete with so little freezable water that the concrete would not be damaged on freezing. Hooton (1993) and Pigeon (1994) found that the cost and difficulty in placing and finishing such low w/cm concrete would make it impractical.

4.2.3.2 Entrained air-void system—Resistance to freezing and thawing of a concrete mixture is substantially improved by incorporating entrained air voids into the concrete. To achieve maximum effectiveness, these air voids should

be evenly distributed throughout the paste portion of the concrete. Their spacing should be close enough to prevent the development of sufficient pressures from freezing to fracture the concrete.

Because voids reduce the strength and stiffness of most concrete mixtures, there is a natural tendency to limit entrained air in concrete. An adequate air-void system, however, is necessary for resistance to freezing and thawing. The specific parameters normally used to evaluate an air-void system along with the generally accepted minimum (or maximum) values are described (4.2.3.2.1 through 4.2.3.2.4).

4.2.3.2.1 Spacing factor $\bar{L}$ —Spacing factor $\bar{L}$ is an approximation of the average distance from anywhere in the cement paste to an air void. The following assumptions are

made for this parameter: the voids are spherical, of equal size, and evenly distributed in a simple cubic lattice throughout the paste (Powers 1949). The method for determining this parameter is described in ASTM C457/C457M. The range of spacing factors is generally from 0.004 in. (0.1 mm) or less to approaching 0.04 in. (1 mm) for mixtures that do not contain entrained air. The generally accepted maximum spacing factor value for concrete with good resistance to freezing and thawing is approximately 0.008 in. (0.20 mm) (Powers 1954; Backstrom et al. 1954, 1958b). Other researchers (Dubovoy et al. 2002; Attiogbe et al. 1992) have shown that concrete with spacing factors greater than 0.008 in. (0.20 mm) may exhibit satisfactory freezing-and-thawing resistance under specific conditions in laboratory tests. CSA A23.1-14/CSA A23.2 requires an average spacing factor of less than 0.009 in. (0.23 mm) with no single value to exceed 0.010 in. (0.26 mm). This is relaxed to an average value of 0.0098 in. (0.25 mm) for concrete with specified strength greater than 10,000 psi (70 MPa).

4.2.3.2.2 Specific surface α —Specific surface α is a measure of the surface area per unit volume of voids. The method for determining this parameter is described in ASTM C457/C457M. A basic assumption of specific surface is that all voids are spherical, which makes it a function of average chord length alone (Powers 1949). Specific surface is, therefore, a good indicator of average void size. As average void size goes up, specific surface goes down. Smaller voids provide compliance with the $\bar{L}$ requirement at lower air contents. The generally accepted value of specific surface for resistance to freezing and thawing is a minimum of 600 in.²/in.³ (25 mm²/mm³) (Powers 1949), though other researchers have shown that concrete with a specific surface area less than 600 in.²/in.³ (25 mm²/mm³) may exhibit satisfactory freezing-and-thawing resistance in laboratory tests (Dubovoy et al. 2002; Attiogbe et al. 1992).

4.2.3.2.3 Philleo factor F' —Philleo (1955) developed an air-void parameter as a means to eliminate the assumptions made for the spacing factor—namely, that all voids are of equal size and spacing. His equation is based on the assumption that voids are randomly sized and distributed and establishes a relationship between the air-void distribution and the percentage of paste that is within a given distance of an air void. Philleo used the work of Willis and Lord (1951) to establish a relationship between air-void chord lengths and voids per unit volume. The equation is used to either determine the percentage of paste that is protected because it is within a specified distance of an air-void, or alternately, to determine the distance from an air-void resulting in a specified percentage of the paste. This distance, called the Philleo factor, is often compared with the spacing factor. In actuality, however, the Philleo factor is more sensitive to the true air-void distribution than the air content, paste content, and number of voids that influence the spacing factor.

This parameter has not been widely accepted as a measure of resistance of concrete to freezing and thawing, primarily due to the difficulty in acquiring the data necessary for calculation. These data consist of a record of all chord lengths measured in a linear traverse (ASTM C457/C457M).

Most petrographers, however, use the alternate modified point count method (ASTM C457/C457M), which does not collect the necessary data. While no specific criterion for the maximum F' , which is the distance for a given percentage of paste protected, has been determined, an examination of a considerable amount of linear traverse (ASTM C457/C457M) data for a number of concrete specimens having spacing factors of approximately 0.008 in. (0.20 mm) and specific surface values of approximately 600 in.²/in.³ (25 mm²/mm³) suggests that a maximum acceptable distance between an air void and 90% of the paste, P_{90}' , should be approximately 0.002 in. (0.04 mm) (Janssen and Snyder 1993, 1994).

4.2.3.2.4 Air content—The abovementioned air-void parameters, while excellent indicators of the protection from freezing and thawing provided by the air-void system, are difficult to measure in the field. Total air content is therefore generally specified and measured. Total air content includes both the entrained air voids and the larger air voids that are not removed by consolidation.

The use of an air-entraining admixture complying with ASTM C260/C260M can provide a proper system of entrained air voids when a specified total air content of the concrete mixture is achieved. The actual air content necessary to ensure the production of the necessary air-void system is affected by mixing action, workability of the mixture, cement composition, types and amounts of other admixtures, and others (Whiting and Stark 1983). In addition, concrete handling during transport, placing, and finishing can affect the entrained air-void system (4.2.4). Recommended air contents for fresh concrete are given in Table 4.2.3.2.4. These recommendations consider the higher air requirements of concrete mixtures with higher paste contents, which would be smaller nominal maximum aggregate sizes, as determined by Klieger (1952, 1956) and the severity of exposure; higher exposure severity increases the probability of damage from freezing and thawing and, therefore, demands greater protection. The values shown are

Table 4.2.3.2.4—Recommended air contents

Nominal maximum aggregate size, in. (mm)	Air content, %*	
	Exposure Class F1	Exposure Class F2 and F3
3/8 (9.5)	7	7.5
1/2 (12.5)	7	7
3/4 (19)	6.5	7
1 (25)	6.5	6.5
1-1/2 (37.5)	6	6.5
2 (50)	6	6
3 (75)	5	5.5

*Field tolerance on air content is recommended as $\pm 1-1/2\%$. Air content recommendations are based on 18% air in the paste portion of the concrete with a Vinsol resin air-entraining agent (from an analysis of work by Klieger [1952]). Mixture proportions based on guidance in ACI 211.1 for angular coarse aggregates along with the maximum w/cm values from Table 4.2.3.1b were used to determine the minimum recommendations. Mixtures using rounded aggregates will require approximately 1% less air due to the lower paste contents associated with rounded aggregates.

general recommendations; local conditions and experience with specific mixtures, admixtures, and construction procedures could warrant other values.

Achieving the total air content specified in Table 4.2.3.2.4 does not always ensure frost protection of the paste. Rather, a mixture should achieve the minimum and maximum values for the air-void parameters discussed previously. In most cases, the minimum air contents from Table 4.2.3.2.4 will achieve the necessary air-void parameters.

4.2.3.3 Design details—Physical details that allow for the repeated wetting or restricted drying of concrete surfaces should be avoided. Examples of these include roof drip-lines on sidewalks, and structural members directly below unsealed joints of bridge slabs. Be careful to always provide positive drainage of runoff from flat areas by methods such as sloping surfaces, which is typically 2%. Special precautions should be taken when runoff is likely to contain deicing salts or other aggressive chemicals to avoid increasing the risk of damage to concrete surfaces.

Consideration should also be given to structures that allow water contact with the side away from freezing, such as water tanks. In many cases, the evaporation rate on the outside of the tank will exceed the rate that water can migrate through the tank wall to replenish the evaporation. In these instances, the amount of freezable water in the portions of the concrete that freeze will be below critical degree of saturation. In some cases, however, water migration to the freezing surface can exceed the evaporation rate, leading to potential damage from freezing and thawing. In very cold climates, freezing can extend through the concrete wall, resulting in severe damage. Low rates of moisture movement and consideration of the depth of freezing are necessary in the design of these types of structures (ACI 350).

4.2.4 Preventing frost damage by proper practice—A properly proportioned concrete mixture can still suffer damage from freezing and thawing if either the air-void system or the amounts of freezable water are adversely affected during construction. The effects of construction practices on maintaining the quality of the concrete mixture are described in 4.2.4.1 through 4.2.4.4.

4.2.4.1 Transporting and placing—The air voids that provide protection against freezing-and-thawing damage are produced during mixing (Whiting and Stark 1983). Air-entraining admixtures stabilize the bubbles that are produced during mixing, but do not generate them. Therefore, mixing is critical in forming and distributing the bubbles throughout the mixture. Upon delivery and discharge of the concrete, the number, volume, and size distribution of the bubbles depend on the mixing action and the degree to which the particular combination of ingredients has worked to generate, stabilize, and retain the bubbles.

The system of air bubbles in the fresh concrete at placement will be sensitive to many factors, including the type and effectiveness of the mixer, duration of mixing, mixing speed (rpm), haul time, batch size, and general condition of the mixing equipment. These factors affect the time required for the air-entraining admixture to stabilize the bubbles. Fast-acting air-entraining admixtures may perform well even with

short mixing periods or brief haul times, whereas more slowly acting admixtures can perform better with a longer mixing or haul time. The degree that air is incorporated in the fresh concrete during mixing depends on the shearing, tumbling, or wave-breaking action of the concrete in the mixer itself. This action will depend on the slump of concrete and cleanliness and efficiency of the mixing blades. Air incorporated in concrete is subdivided into smaller bubbles by continued mixing and stabilized by the air-entraining admixture, thus minimizing air loss. Immediately before being discharged, the freshly mixed concrete contains air bubbles of a wide distribution of sizes and with varying effectiveness in terms of providing frost resistance, which all have their origin in the engulfment or entrapment of air during mixing (Mielenz et al. 1958a,b; Backstrom et al. 1958a,b).

Concrete is often placed by pumping from the delivery truck to the formwork. Advances in pumping technology have resulted in increased distances, lift heights, and delivery rates. These advances have been accompanied by increases in the pressure capacity of the pumps, with pressures in the range of 300 to 500 psi (2 to 3.5 MPa) being fairly common (Cooke 1990). Unfortunately, concerns have developed when the air content measured after pumping was not the same as the air content before pumping. In most cases, the air content had decreased after pumping, but in some instances, it increased (Cooke 1990; Dyer 1991; Whiting and Nagi 1998). The possible loss of entrained air can be a major concern for concrete exposed to severe freezing-and-thawing environments.

Pumping concrete includes numerous activities that could contribute to a change in the air content of the concrete. During pumping, the concrete falls through a grating in the pump hopper, is forced under pressure through a relatively small-diameter pipe, moves through a series of bends, experiences changes in both elevation and pipe material, which is generally steel to rubber, is then released from pressure as it exits the pipe, and often falls some distance into the formwork. Pumping may also be continuous or interrupted at various times. This sequence of events makes it difficult to isolate the mechanism(s) that induce(s) the loss or gain of air.

Numerous mechanisms have been proposed to explain the change in air content that sometimes occurs when concrete is pumped. During pumping, a vacuum could form in the line, especially at low pumping rates with a long portion of the pumping being downhill, which would enlarge and remove air voids. Air voids could also be lost when the concrete falls through the grating in the pump hopper or when it falls into the formwork after exiting the pump line (Yingling et al. 1992; Janssen et al. 1995). While changes in the air-void system have been documented in multiple cases (Whiting and Nagi 1998; Janssen et al. 1995; Pleau et al. 1995), evidence of reduced resistance to freezing and thawing has not been identified (Elkey et al. 1993; Whiting and Nagi 1998).

4.2.4.2 Consolidating—On discharge of fresh concrete, air voids could be entrapped in the concrete. When in the forms, it is virtually impossible to avoid the inclusion of air

pockets. When such large air pockets form during mixing, continued mixing breaks them down to smaller sizes and distributes them into the mixture. No such opportunity exists once the concrete is cast. For this reason, it is necessary to reduce the number and size of these pockets trapped in the mixture by vibration.

Vibration accomplishes two purposes with regard to the removal of air pockets in fresh concrete. First, vibration can liquefy the concrete in the same manner as earthquakes liquefy certain types of soils. Many of the large, buoyant air pockets that were trapped in the semifluid mixture can rise to the surface through the temporarily fluid mixture. Second, vibration imposes a cyclic compression in the concrete that locally increases, then decreases, the water pressure surrounding the air bubbles. This causes the bubbles themselves to compress and decompress at the frequency of the vibrator (Young 1989). Air bubbles break when forced to compress and decompress at a critical frequency that varies with their size—the larger the bubble, the lower the frequency. Conversely, the higher the vibration frequency, the smaller the bubble that can be broken. Simon et al. (1992) showed that vibration at approximately 6000 vibrations per minute begins to break bubbles in the size range of the so-called entrained air. Evidence also indicates that some portion of the air from broken bubbles escapes, while the rest is incorporated into other air bubbles in the mixture.

It takes time for the energy imparted by the vibrator to liquefy the surrounding concrete and for the water pressure to build up so as to compress the air bubbles. It also takes time for the bubbles to rise to the surface, break, or both. For these reasons, short intermittent vibration may have little effect on the concrete in general or on the air bubble system. Refer to ACI 309R for guidelines for appropriate vibration procedures.

In summary, vibration of fresh concrete refines the air-void system by encouraging the loss of larger air voids while retaining the smaller ones. The exact distinction between the size of bubbles removed and those left in place depends on the concrete mixture and on the frequency, duration, and intensity of vibration.

4.2.4.3 Finishing—After concrete is placed and consolidated, it is still possible to modify the air bubbles at the surface of the fresh concrete, and therefore the air voids in the hardened concrete, during finishing. Repeated passes of a finishing tool can force bubbles together, resulting in fewer, larger bubbles. The air content of the concrete at the surface can be reduced by over-finishing—that is, over-manipulation of the surface can reduce resistance to freezing and thawing. This is particularly the case if the surface is finished while it is still covered with bleed water or if water has been applied to make it easier to finish. Finishing with free water on the surface not only weakens that surface by increasing the w/cm locally, but also increases porosity. When coupled with a localized reduction in air content, resistance to freezing and thawing is likely to be significantly reduced. Thomas (1997) found that this was especially true for hand-finished concrete having a high dosage of SCMs (50% Class F fly

ash). Machine-placed and finished areas of the same concrete did not show scaling damage.

For concrete slabs, it has been found that hard-troweling of air-entrained concrete has the potential to blister or delaminate at the surface (ACI 301; ACI 302.1R; Tarr and Farny 2008). Hence, as per ACI 301, concrete for slabs to receive a hard trowel finish should not contain an air-entraining agent or have a total air content greater than 3%.

4.2.4.4 Curing—Curing is defined as the maintenance of a satisfactory moisture content and temperature in concrete during its early stages so that the desired properties may develop (ACI 308R). Overall, resistance to freezing and thawing increases as continued curing develops microstructure and reduces the porosity and hydraulic conductivity of the concrete. The result is a concrete that is less likely to become critically saturated. Curing further increases the compressive and tensile strength of the concrete, which increases the resistance to pressure from freezing. These attributes combine to produce a concrete that is less susceptible to freezing-and-thawing damage. The issue is made more complicated, however, when concrete is cast in weather where there is risk of freezing. In this situation, attempts to cure the concrete to improve its overall durability can conflict with the fact that curing can increase the risk of saturating concrete during exposure to early freezing. It is generally accepted that properly air-entrained concrete can sustain one freeze cycle when it has attained a compressive strength of 500 psi (3.5 MPa), and repeated freezing-and-thawing cycles when saturated at a compressive strength (in-place) of 3500 psi (25 MPa). This means that curing procedures need to be carried out to maintain moisture content to improve the quality of the concrete, as well as measures to prevent early freezing (ACI 306R; ACI 308R).

4.2.5 Preventing frost damage in existing concrete that lacks adequate air-void system—Concrete that lacks an adequate air-void system to protect it from the anticipated exposure conditions is sometimes encountered. Protecting the concrete from damage caused by freezing and thawing then requires keeping it dry. Powers and Brownyard (1947) presented the thermodynamic calculations to show that concrete dried to 85% relative humidity at room temperature would contain no freezable water at -0.4°F (-18°C). Therefore, concrete dried to an internal relative humidity below approximately 75 to 80% would rarely, if ever, contain freezable water.

4.2.5.1 Sealers—Concrete that can be adequately dried can sometimes be kept dry by sealing the surface of the concrete with some sort of protective barrier system to prevent the reintroduction of moisture. Slab-on-ground and similar construction would also require a vapor retarder beneath the concrete to reduce the movement of water in either liquid or vapor form from entering the concrete from underneath. Details of various protective barrier systems can be found in ACI 515.2R. Vapor retarders for use under slabs are discussed in ACI 302.1R.

In many cases, not all sides of a concrete member are accessible for sealer treatments. Care must be taken so that the sealed surface does not prevent the evaporation of

moisture that may have entered from unsealed surfaces. An example would be the sealing of the top surface of a slab-on-ground. The sealer could restrict evaporation of moisture entering the slab from the bottom. The concrete could end up wetter than if it had never been sealed. Vapor-permeable sealers, which limit the intrusion of liquid water and permit evaporation of moisture from the sealed surface, should be evaluated for application-specific conditions.

4.2.5.2 Drainage and other methods—The moisture in concrete can often be sufficiently limited to reduce the possibility of damage due to freezing and thawing if attention is given to the removal of water from the area of the concrete. While methods of moisture reduction are generally application-specific, the examples in 4.2.5.2.1 through 4.2.5.2.3 are presented.

4.2.5.2.1 Drainage—Water allowed to pond on a concrete surface can contribute significantly to the moisture in the concrete. By providing adequate drainage to prevent ponding, the water absorbed in the concrete can be minimized.

4.2.5.2.2 Maintenance—Designs that provide for rapid drainage from concrete surfaces can be defeated by poor maintenance. An example is the ponding of water on a concrete slab being caused by leaves blocking a drain. Proper design should be supported by adequate maintenance. Other times, improper maintenance or other activities could result in the unnecessary accumulation of water. Snow pushed off a sidewalk and against a concrete wall could result in the accumulation of moisture in the wall. As the snow against the wall melts, the remaining snow could serve as a dam, holding the water against the wall. Normally a surface with little moisture absorption, this vertical wall section could absorb enough melted snow to lead to damage from subsequent freezing.

4.2.5.2.3 Redirection of water flow—Downspouts emptying water across a concrete slab can be redirected so that runoff does not flow across the concrete. This can reduce the moisture exposure of the surface enough to reduce damage from freezing and thawing.

4.2.6 Theories for frost damage—Damage in concrete from freezing and thawing occurs as internal damage or surface deterioration (Cordon 1966). Historically, the capillary-void system of the cement paste has been the focus of most investigations. There is no consensus regarding the mechanisms responsible for damage in cement paste. The damage has been attributed to hydraulic pressure buildup as water is forced away from the freezing front, to osmotic pressure gradients driving water toward the freezing centers, to vapor pressure potentials, and to combinations of these processes (Powers 1945, 1954, 1955, 1975; Powers and Helmuth 1956; Helmuth 1960a; Litvan 1972; Penttala 1998; Setzer 1999, 2002; Scherer and Valenza 2005; Coussy and Monteiro 2008, 2009). These are described in more detail in the following sections.

4.2.6.1 Moisture expulsion—Powers proposed that ice nucleated and grew in capillary pores, forcing them to dilate or expel excess water from freezing sites. Elevated hydraulic stresses would arise as water was expelled due to the relatively low permeability of cement paste. Distance from

the void boundary, the degree of saturation, and the rate of freezing would influence the magnitude of hydraulic-stress buildup (Cordon 1966; Powers 1945, 1954, 1955).

4.2.6.2 Osmotic pressure—The hydraulic-pressure concept was later modified when experiments showed significant evidence that moisture was moving toward, rather than away from, freezing sites (Powers and Helmuth 1956; Helmuth 1960a; Powers 1975). Marchand et al. (1995) and Penttala (1998) proposed that not all the water in the capillary pores is freezable due its surface tension and the small diameter of the pores containing it. Water in the largest voids would freeze before the water in the smaller voids. When the water in the larger voids freezes, the concentration of the dissolved salts increases locally, causing a concentration gradient in the pore solution. Water is thought to move from the smaller voids to the larger ones to reduce this gradient. The resulting flow is thought to cause damage. Litvan (1972) proposed a similar theory, also founded on thermodynamic arguments, but cast in terms of vapor-pressure gradients between super-cooled water and ice instead of salt concentration gradients.

Penttala (1998), Scherer and Valenza (2005), Setzer (1999, 2002), and Coussy and Monteiro (2008, 2009) have combined the moisture expulsion and osmotic pressure theories to account for the rate of freezing, degree of saturation, dispersion of air voids, and the paste microstructure. These theories agree that forces are exerted on the paste from the movement of water from the small to the large voids. Scherer and Valenza (2005) add that when the larger voids fill with ice, local pressure from ice crystallization would be expected. These pressures will increase with the shape and curvature of the pores. A combination of these factors lead to initial damage.

4.2.6.3 Ice lens growth—Whereas the previous mechanisms may describe the deterioration in small, saturated samples frozen rapidly and cyclically in the laboratory, progressive ice accretion in cracks during periods of sustained temperatures slightly below 32°F (0°C) may generally dominate the further degradation of previously damaged or microcracked concrete (Litvan 1978). A theoretical model was developed and proven successful for predicting freezing-and-thawing damage in rock (Walder and Hallet 1985; Hallet et al. 1991). In this model, freezing attack in homogeneous porous solids is viewed as occurring in an open system where microcracks are internally pressurized by ice accretion fueled by migration moisture from either liquid or vapor; the latter is in turn induced by thermally driven free-energy gradients. This ice accretion model, also known as the segregation ice model, is consistent with Gilpin's (1980) study of freezing effects in porous media as applied to soils.

4.2.6.4 Implications of freezing-and-thawing damage mechanisms—Uncertainty and opposing views of fundamental processes governing freezing in concrete undermine efforts to develop tests of the resistance to freezing and thawing of concrete. Several testing strategies have been used that involved relatively rapid cycling of freezing and thawing in saturated and dry environments. In North America, a freezing-and-thawing cycling test, ASTM C666M, is used to determine the resistance of concrete

mixtures to internal damage. [ASTM C672/C672M](#) evaluates scaling resistance. The latter relies on visual classifications, sometimes supplemented with mass loss measurements. These tests, like some of their predecessors, are criticized for not adequately representing typical environmental conditions. The tests cycle between extreme temperatures too rapidly. The CDF test ([RILEM TC 117-FDC 1996](#)) provides greater reproducibility and is more quantitative with respect to scaling measurements. [Hallet et al. \(1991\)](#) proposed that conventional tests give only limited guidance for understanding the processes governing freezing at field sites where the thermal or hydraulic regimes are very different from those in the laboratory. Extrapolation from diurnal or more frequent freezing-and-thawing experiments to field conditions should be viewed with extra caution because distinct physical processes may govern each. This situation calls for consideration of diagnostic freezing-and-thawing tests in which both processes can be distinguished and probed systematically. This also suggests that considerably more caution is needed when attempting to relate standard laboratory test results to spacing factors and to other design criteria for effective resistance to freezing and thawing in service. Some concrete mixtures pass accepted laboratory tests and do not perform well in the field, while others fail the tests and perform quite satisfactorily in the field. This is probably because the tests for internal damage and scaling due to freezing and thawing do not address all the significant variables. [Stark \(1989a\)](#) indicated that the potential role of several key factors in freezing-and-thawing damage has not been appreciated; these include the magnitude and duration of exposure to sustained temperature and moisture gradients, and the cumulative time of exposure to specified temperature ranges.

4.3—Frost attack of concrete made with nondurable aggregates

Deterioration due to freezing and thawing of properly proportioned, air-entrained concrete made with aggregate susceptible to freezing-and-thawing damage is often referred to as D-cracking. Many types of coarse aggregate have been identified as susceptible to D-cracking, while other sources of the same kind of rock have not been found susceptible. The pore structure of the coarse aggregate is thought to be the primary contributing factor to susceptibility to D-cracking. Descriptions of the appearance and development of D-cracking are presented in 4.3.1, while the prevention of D-cracking in new construction is covered in 4.3.2. Mitigation of D-cracking in existing construction is given in 4.3.3. Theories and mechanisms of D-cracking are covered in detail in 4.3.4.

4.3.1 Description of D-cracking

4.3.1.1 General description—D-cracking is characterized by cracks through the coarse aggregate and mortar of the concrete. Away from the cracks, both mortar and coarse aggregate are strong and show no signs of deterioration.

The development of D-cracking requires considerable moisture and repeated cycles of freezing and thawing. As a result, D-cracking usually appears close to joints, cracks,

edges, and corners where moisture enters from more than one surface. D-cracking generally appears as a series of cracks approximately parallel to the primary moisture source.

4.3.1.2 Flatwork—The most common appearance of D-cracking is in at-grade flatwork such as highway pavements, parking lots, and sidewalks. These are areas that frequently have readily available moisture from precipitation runoff, from multiple directions at joints and cracks, and on the bottom of the slab unless there is an effective vapor retarder beneath it. Often, the earliest appearance of D-cracking will be at the intersection of transverse and longitudinal joints in a pavement. At these locations, moisture is often available at the tops and the bottoms of the vertical joint faces.

In climates cold enough to freeze through the thickness of the concrete slab, D-cracking usually starts at the bottom and progresses to the surface ([Schwartz 1987](#)). This is probably due to the greater availability of moisture at the bottoms of slabs. By the time telltale cracks appear on the surface, deterioration can extend 1.5 ft (0.5 m) or more away from the joint.

The appearance of D-cracking in milder climates is somewhat different because the concrete never freezes all the way through. D-cracking in these cases often appears as shallow spalling at joints; closer examination reveals the characteristic cracks parallel to the joint.

4.3.1.3 Vertical construction—Though much less common, D-cracking can also appear on vertical construction. Construction details, maintenance practices, or both, that allow the accumulation of moisture against the corners of walls or columns can contribute to D-cracking if susceptible aggregates were used in the construction. An example of such maintenance practices at a building would be the shoveling of snow off a sidewalk and depositing it against a concrete foundation wall.

4.3.2 Prevention of D-cracking

4.3.2.1 Role of mixture proportioning—The primary factor in a concrete mixture that contributes to the development of D-cracking is the susceptibility of the coarse aggregate, whereas the air-void system and the w/cm have little or no effect ([Schwartz 1987](#); [Missouri Highway and Transportation Department 1990](#)). Most coarse aggregates identified as susceptible to D-cracking are sedimentary rocks, although many sedimentary rocks have not been found to be susceptible to D-cracking. Igneous rocks are generally not considered to be susceptible to D-cracking unless the rocks are weathered. Weathered rocks would probably be undesirable for concrete production anyway due to their low strength and likelihood to break down from handling. Most metamorphic rocks have not shown D-cracking susceptibility; however, some partially metamorphosed sedimentary rocks have been identified as susceptible ([Stark 1976](#)).

The maximum aggregate size is also important in the development of D-cracking. Numerous studies ([Stark and Klieger 1973](#); [Klieger et al. 1974](#); [Stark 1976](#); [Missouri Highway and Transportation Department 1990](#); [Almond and Janssen 1991](#)) have shown that reducing the maximum size of the aggregate reduces its susceptibility.

Unfortunately, reducing the nominal maximum aggregate size can have less-desirable side effects, including increased paste demand to maintain workability at a given strength level, increased drying shrinkage potential, and reduced joint load transfer in pavements.

4.3.2.2 Importance of aggregate identification—D-cracking can require numerous years to fully develop, during which time much susceptible concrete could be placed before a problem is identified. This, combined with natural variability of aggregate sources, leads to the need for identification of D-cracking-susceptible aggregates before they are used in concrete exposed to moisture and cycles of freezing and thawing.

D-cracking has been known since the 1930s (Stark and Klieger 1973); wide ranges of tests have been developed to try to identify susceptible aggregates. The most common procedure for identifying susceptible aggregates is ASTM C666/C666M. Concrete specimens made with the aggregate in question are subjected to repeated cycles of freezing and thawing in the laboratory and are evaluated in terms of either increase in length or decrease in dynamic modulus of elasticity.

4.3.2.3 Aggregate beneficiation—A variety of techniques have been proposed to improve the performance of susceptible aggregates. Limiting the nominal maximum size was discussed in 4.3.2.1. Schwartz (1987) summarized other methods, including coating the aggregates to prevent their absorption of water, heavy media separation, and blending durable aggregate with a nondurable aggregate to reduce its D-cracking susceptibility. He reported that aggregate size reduction was the most effective method of reducing D-cracking susceptibility.

4.3.3 Mitigation of existing D-cracking—A considerable amount of concrete containing D-cracking-susceptible aggregates has been placed where it is exposed to both moisture and cycles of freezing and thawing. This is especially true of concrete pavements. Joint deterioration associated with D-cracking can significantly reduce the service life of such pavements. The concrete as little as 1.5 ft (0.5 m) away from the joints often shows no deterioration or loss of strength.

A typical concrete pavement can have transverse joints 12 ft (4 m) or more apart. With less than 1.5 ft (0.5 m) of D-cracked concrete at each end of a slab, most of the concrete is in good condition. While replacement of the deteriorated concrete near the joints with a full-depth patch would seem to be a cost-effective method of extending the life, D-cracking often appears at the newly created joints adjacent to the patches in as little as 5 years. Thus, the D-cracking continues as before, but at twice as many joints (Janssen and Snyder 1994).

4.3.3.1 General—Three conditions are necessary for the development of D-cracking: concrete made with susceptible aggregate, moisture, and cycles of freezing and thawing. As the aggregates already in the concrete would be difficult or impossible to render nonsusceptible, D-cracking mitigation should attempt to either prevent freezing and thawing or remove the source of moisture.

4.3.3.2 Preventing freezing—Portland-cement concrete pavements often receive asphalt concrete overlays to improve the condition of the pavement and extend its life. In climates that do not get too cold in winter, freezing in a concrete pavement that contains D-cracking-susceptible aggregates could be prevented by covering it with a sufficient thickness of asphaltic concrete. Janssen et al. (1986) found that the freezing should be almost completely prevented in the concrete to stop the progression of D-cracking; merely decreasing the number of cycles of freezing and thawing with an overlay could actually accelerate the rate of D-cracking due to the increased potential for moisture migration during slower freezing rates. More than 6 in. (150 mm) of asphalt concrete overlay would be required to prevent freezing at the surface of the concrete pavement for central latitudes of the United States. Using asphalt concrete overlay to prevent freezing in concrete made with D-cracking-susceptible aggregates is probably not an effective D-cracking mitigation method for these conditions (Janssen et al. 1986; Janssen and Snyder 1994).

4.3.3.3 Reducing moisture—The use of sealers on the cut ends of the existing concrete pavement sections (4.3.3) before placing the patches could reduce the lateral movement of moisture into the concrete. This could increase the time before D-cracking appeared in the patched concrete. This method was attempted in a D-cracked concrete pavement section in Ohio in 1992 (Janssen and Snyder 1994). Although initial laboratory testing indicated that sealer treatment delayed the resumption of D-cracking, field monitoring showed that the D-cracking reappeared after 6 years (Janssen 2001).

4.3.4 Theories and mechanisms of D-cracking—Theories of damage to concrete from freezing and thawing have already been discussed in 4.2.5. With the exception of the role of air voids in protecting concrete from damage, these same theories generally apply to D-cracking. This section, therefore, will concentrate on the characteristics of specific aggregates that make them susceptible, while other aggregates of the same type are not susceptible.

4.3.4.1 Pore size and size distribution—Kaneuji et al. (1980) observed qualitative correlations between concrete durability and pore size distributions of aggregates. At a constant total pore volume, aggregates with smaller pores result in a lower resistance to freezing and thawing. For aggregates with similar predominating pore sizes, a greater pore volume results in less resistance to freezing and thawing. By correlating aggregate service records with mercury porosimetry studies, Marks and Dubberke (1982) found that with one exception, the D-cracking-susceptible aggregates analyzed exhibited a predominance of pore sizes of 1.5×10^{-6} to 8×10^{-6} in. (0.04 to 0.2 μ m) whereas aggregates with good to excellent service records had a majority of pores that were larger than this.

4.3.4.2 Deicing salt effect—Dubberke and Marks (1985) noted a reduced resistance to D-cracking for some aggregates when pavements containing susceptible aggregates were exposed to deicing salt. Other aggregates that they examined showed no effect. A possible explanation is a

change in pore structure due to etching of the pore walls by the salt. Such action has been identified for aggregates containing calcite (Gillott 1978). This possible deicing salt effect should be noted when using field performance records to evaluate the D-cracking potential of an aggregate. Satisfactory performance in a pavement that never received deicing salt may not ensure the same performances where deicing salts are used.

CHAPTER 5—AGGREGATE REACTIONS

This chapter presents guidelines for minimizing the risk of damage in concrete construction caused by alkali-aggregate reaction (AAR), including both alkali-carbonate and alkali-silica reactive aggregates, and iron sulfide mineral oxidation. Procedures are discussed for evaluating aggregates and selecting appropriate measures for controlling expansion. ACI 221.1R provides more detailed information on types of reaction, reaction mechanisms, reactive rock types, methods of testing aggregates, and preventive measures.

5.1—Alkali-aggregate reaction

The first case of alkali-carbonate reaction (ACR) was observed in Ontario, Canada, in the late 1950s (Swenson 1957). ACR occurs between alkali hydroxides and certain argillaceous dolomitic limestones. This reaction is characterized by rapid expansion and extensive cracking of the affected concrete. Structures suffering from ACR generally exhibit deleterious effects within 5 years of initial construction. The only way to avoid ACR is through selective quarrying to avoid construction with potentially alkali-carbonate reactive aggregates. This type of reaction is limited to select geographical regions.

Alkali-silica reaction (ASR) was first detected in the late 1930s and first reported in 1940 by Thomas Stanton of the California Highway Department (Stanton 1940a,b). Since its initial detection, ASR has been identified as a major cause of premature concrete deterioration throughout the world. Since Stanton's first investigations, a wide range of testing procedures for assessing aggregate reactivity has been developed. Most recently, efforts have focused on developing accurate testing methods to determine the effectiveness of mitigation measures. Much focus has been placed on the incorporation of supplementary cementitious materials (SCMs) as well as chemical admixtures (namely, lithium salts such as LiNO_3). The reliability of these techniques varies and depends, to some extent, on the nature of the aggregate being tested, specimen size, and the testing environment.

Criteria for interpreting test results vary among different national standards. They also differ among and within states or provinces, with different limits being adopted by various local agencies and state, federal, or provincial authorities. Methods for addressing expansion due to AAR also vary regionally. Many specifications do not permit the use of reactive aggregates. When alkali-silica-reactive aggregates are used in concrete, recommended preventive measures include limiting the alkali content of the concrete; using SCMs such as fly ash, slag cement, silica fume, or natural pozzolans; using lithium nitrate; or combining these methods.

As referenced in 5.1.5.1, a history of satisfactory field performance may be the most effective method for evaluating the potential for an aggregate to cause AAR. Where such satisfactory field performance can be demonstrated, aggregates may be accepted for use in concrete without AAR testing, provided that similar materials are incorporated in the batching process (for example, concrete with an alkali content less than or equal to that of the satisfactory concrete in-service). In the absence of such field performance data, however, aggregates should be subjected to suitable laboratory testing procedures to establish their degree of reactivity. If the results of such laboratory testing do not indicate a potential for AAR, aggregates may be used without any precautionary measures. Aggregates that demonstrate the potential for ASR may be used in concrete, provided that suitable measures are implemented to control the risk of expansion. However, aggregates susceptible to ACR are generally avoided because there are no known mitigation measures to effectively control expansion in concrete with those aggregates.

5.1.1 Types of reactions—Two types of AAR have been recognized: 1) ACR; and 2) ASR. ACR is associated with the use of certain argillaceous dolomitic limestones. Confirmed cases of ACR have been restricted to a few locations in North America—mainly in Virginia, Kentucky, Indiana, Iowa, Illinois, and in the Canadian province of Ontario. ACR involves a reaction between an alkali source and certain argillaceous dolomitic limestones. ASR is distinctly different, and results from a reaction between alkali hydroxides in the pore solution and certain forms of reactive silica present in some types of siliceous or carbonate aggregates, including limestone aggregates that contain siliceous components as well. Table 5.1.1 presents a list of several common reactive rock types and mineral forms that are susceptible to ASR.

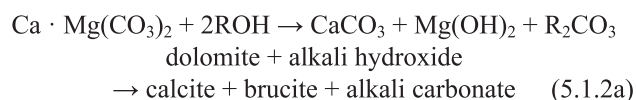
Table 5.1.1—Examples of rock types and minerals susceptible to ASR

Reactive rocks	Reactive minerals
Shale	Opal
Sandstone	Tridymite
Silicified carbonate rock	Cristobalite
Chert	Volcanic glass
Flint	Cryptocrystalline (or microcrystalline) quartz
Quartzite	Strained quartz
Quartz-arenite	
Gneiss	
Argillite	
Granite	
Greywacke	
Siltstone	
Arenite	
Arkose	
Hornfels	



ASR is far more widespread than ACR and is further subdivided into two categories: 1) reactions involving poorly crystalline or metastable silica materials; and 2) reactions involving certain varieties of quartz. From an engineering perspective, the main distinctions between these two categories of ASR involve the time to the onset of expansion and cracking, and the perceived duration of the reaction in the field. Reactions involving poor crystalline and metastable silica materials, which are sometimes referred to as classical ASR, are characterized by a relatively short time to the onset of cracking (cracking usually occurs within 5 to 10 years), whereas the manifestation of reactions involving quartz minerals usually takes much longer, although the reaction may continue for many decades.

5.1.2 ACR background—The alkali-carbonate reaction occurs between alkali hydroxides and certain argillaceous dolomitic limestones characterized by a matrix of fine calcite and clay minerals with scattered dolomite rhombohedra. The reaction is manifested in the rapid expansion and extensive cracking of concrete, and structures affected by ACR usually show cracking within 5 years. Although there is a lack of consensus regarding the precise mechanisms involved, it is generally agreed that the reaction is accompanied by dedolomitization



where R represents K or Na. However, because this reaction results in a reduction in solid volume, the expansion must be attributed to an alternative mechanism. Several theories have been proposed to explain the expansion mechanism (Swenson and Gillott 1964; Tang et al. 1987; Fournier and Bérubé 2000), including:

- Hydraulic pressures caused by the migration of water molecules and alkali ions into the restricted spaces of the calcite/clay matrix around the dolomite rhombs
- Adsorption of alkali ions and water molecules on the surfaces of the active clay minerals scattered around the dolomite grains
- Growth and rearrangement of the products of dedolomitization (that is, brucite and calcite)

The alkali carbonate produced in the dedolomitization reaction may react with calcium hydroxide in the cement paste as follows



thereby “regenerating” alkalis for further reaction. Thus, provided there is sufficient alkali available to initiate the reaction, the process may continue independently of the amount of alkalis available in the concrete. This could explain why low-alkali cements are not effective in controlling damaging reaction (Thomas and Folliard 2007).

5.1.3 ASR background—ASR has been a known cause of concrete deterioration for more than 70 years. Since its discovery in the late 1930s (Stanton 1940a,b), ASR has

been observed as a cause of premature concrete deterioration throughout the world. Although the factors that lead to deleterious ASR are commonly agreed on, the mechanism by which the alkali-silica gel causes expansion and subsequent cracking in concrete is not yet entirely understood.

ASR results from a chemical reaction in which the hydroxyl ions attack siliceous species in certain aggregates. The attack liberates silica, which then combines with alkalis (Na^+ and K^+) and with lesser amounts of calcium (Ca^{++}) that are present in the concrete pore solution to maintain charge balance. The resulting alkali-silica gel then absorbs water and expands, which may result in cracking of the aggregates, the cement paste, and, ultimately, the concrete matrix. It is widely accepted that for the ASR to cause damage in concrete, three components are necessary: sufficient alkali, reactive silica, and adequate moisture.

5.1.3.1 Alkalis—The alkalis (Na^+ and K^+) are typically supplied by the portland cement. However, supplementary cementitious materials (SCMs); chemical admixtures; and external sources such as seawater, deicing salts, and anti-icing chemicals can also contribute to the alkalinity of the pore solution. Certain aggregate species, particularly those containing feldspars, may also release alkalis to the pore solution (Bérubé et al. 2002). The amount of alkali in cement is usually expressed as the sodium oxide equivalency, written: $\text{Na}_2\text{O}_{\text{eq}}$.

The following equation is used to determine the sodium oxide equivalency in the portland cement

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658\text{K}_2\text{O} \quad (5.1.3.1)$$

where $\text{Na}_2\text{O}_{\text{eq}}$ is the total sodium oxide equivalent, in percent by mass; Na_2O is the sodium oxide content, in percent by mass; and K_2O is the potassium oxide content, in percent by mass.

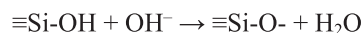
The concentration of alkalis in portland cement generally ranges from 0.2 to 1.3% $\text{Na}_2\text{O}_{\text{eq}}$, which is relatively low in comparison to other compounds and oxides. Initial research on ASR proposed that expansion due to ASR was unlikely to occur when the percentages of alkalis in the cement fell below 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ (Stanton 1940b). This approach has since been used as a mitigation option to limit ASR in new concrete. However, it has been determined that reducing the percent contribution of alkalis from portland cement does not effectively mitigate ASR for all reactive aggregate types because it does not limit the total alkali content of the concrete (or alkali loading). This is the case because, within the pore solution of concrete, the alkalis dissociate in solution, leaving K^+ and Na^+ , which must then be balanced by an equivalent concentration of hydroxyl ions (OH^-) to maintain charge equilibrium. The increased concentration of dissociated alkalis in the concrete pore solution effectively increases the concentration of hydroxyl ions, which in turn increases the pH in the pore solution. As referenced in 5.1.3.4, this OH^- -induced increase in pH, if high enough, leads to the initial breakdown of the reactive silica in the aggregate, resulting in the formation of alkali-silica gel. Diamond (1983a) reports that the OH^- ion threshold concen-

tration for ASR is unlikely to be less than 0.25M, and [Kollek et al. \(1986\)](#) suggest a threshold of 0.20M; this equates to a pH threshold of 13.2 to 13.3 for ASR to occur. The alkali threshold may vary depending on the nature of a particular aggregate source ([Liu and Mukhopadhyay 2014](#)).

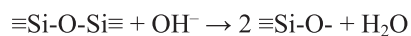
5.1.3.2 Reactive silica—The degree of reactivity of aggregates depends on numerous factors, including the mineralogy of the aggregate, and the crystallinity and solubility of the silica. Reactive silica is amorphous or disordered silica found in certain aggregates. This poorly crystalline silica dissolves more readily in the high pH of the pore solution of concrete than do well-crystallized or dense forms of silica. Because of its increased solubility, amorphous silica is more susceptible to ASR. Common reactive minerals susceptible to ASR include microcrystalline, cryptocrystalline, and strained quartz; cristobalite; tridymite; opal; chert; and volcanic glass (for example, obsidian).

5.1.3.3 Adequate moisture—The third and final component necessary for ASR to occur is adequate moisture, which is one of the key components in the expansion of the gel. Water is found within the pore solution of concrete and is also introduced from external sources. A minimum internal concrete relative humidity of 80% is required to provide enough moisture to drive the expansion of the alkali-silica gel and sustain the reaction ([Pedneault 1996](#)).

5.1.3.4 Mechanism of gel formation—The term “alkali-silica reaction” is somewhat misleading, as the initial reaction occurs between the reactive siliceous aggregate and the hydroxyl (OH^-) ions (not the alkalis) of the pore solution. The high concentration of the hydroxyl ions in the pore solution is equal to that of the alkali cations to maintain charge equilibrium. It is this high OH^- concentration that results in a high pH, which, in turn, leads to the initial breakdown of the reactive silica in the aggregate. When poorly crystalline hydrous silica is exposed to a strong alkaline solution, there is an acid-base reaction between the hydroxyl ions in solution and the acidic silanol (Si-OH) groups ([Dent Glasser and Kataoka 1981](#)) as follows



As further hydroxyl ions penetrate the structure, some of the siloxane linkages (Si-O-Si) are also attacked as follows ([Dent Glasser and Kataoka 1981](#))



The negative charges on the terminal oxygen atoms are balanced by alkali cations (Na^+ and K^+) that simultaneously diffuse into the structure. The disruption of siloxane bridges weakens the structure and, provided sufficient reserves of alkali hydroxide are available, the process continues to produce an alkaline silicate solution. The extent or rate of dissolution is controlled by the alkalinity of the solution and the structure of the silica.

5.1.3.5 Role of calcium—Research ([Bleszynski and Thomas 1998](#); [Thomas 2006a](#)) has concluded that significant expansion only occurs when an adequate supply of calcium

is available as calcium hydroxide. In systems with abundant alkali hydroxides and reactive silica but no calcium hydroxide, silica dissolved and remained in solution. Although the precise role calcium plays in gel expansion remains unclear, a series of mechanisms has been proposed, as listed:

- Calcium may replace alkalis in the reaction product, regenerating alkalis for further reaction (alkali recycling) ([Thomas 2006b](#); [Hansen 1944](#)).
- CH may act as a buffer, maintaining a high level of OH^- in solution ([Wang and Gillott 1991](#)).
- High calcium concentrations in the pore solution prevent the diffusion of silica away from reacting aggregate particles ([Bleszynski and Thomas 1998](#); [Chatterji 1979](#); [Chatterji and Clausson-Kass 1984](#)).
- If calcium is not available, reactive silica may merely dissolve in alkali hydroxide solution without causing damage ([Thomas 2006a](#); [Diamond 1989](#)).
- The formation of calcium-rich gels is necessary to cause expansion either directly or through the formation of a semi-permeable membrane around reactive aggregate particles ([Thomas 2006a](#); [Thomas et al. 1991](#); [Bleszynski and Thomas 1998](#)).

These hypotheses suggest that promoting the formation of C-S-H at the expense of calcium hydroxide (for example, through the use of pozzolans) may result in successful mitigation of expansion due to ASR.

5.1.4 Mechanism of gel expansion—Although the mechanisms behind the formation of the gel are well understood, the actual mechanism for expansion of the gel remains uncertain. Four main theories have emerged over the past 70 years to explain the mechanism of gel expansion, all of which maintain that water is the main component driving the process. The four theories of expansion include the osmotic pressure; CSH-shell; calcium/alkali exchange; and double-layer.

The osmotic pressure theory speculates that the cement paste surrounding the reactive aggregates acts as a semi-permeable membrane, preventing the presence of large silicate ions while allowing the water and alkali hydroxides to diffuse through to the aggregate surface. Under these conditions, the alkali silicate formed on the surface of the aggregate particle draws solution through the cement paste, resulting in continued formation of the alkali-silica gel. As the gel continues to swell, an osmotic pressure cell is formed and increasing hydrostatic pressure is applied to the cement paste, eventually resulting in cracking ([Hansen 1944](#)).

The C-S-H shell theory considers the effect of calcium on the durability of concrete. This theory hypothesizes that in the presence of calcium hydroxide, alkali ions from alkali salts and hydroxyl ions from $\text{Ca}(\text{OH})_2$ enter the reactive silica aggregate grains, leaving calcium and anions in the pore solution. The penetration of the solvated hydroxyl and alkali ions causes the Si-O-Si bonds of the reactive aggregate to break apart, opening the grains for further penetration of ions, and permitting the release of some SiO_2 into the pore solution. As the solvated hydroxyl and alkali ions infiltrate the aggregate grains, calcium hydroxide and water

molecules also migrate into the reactive siliceous material. When high concentrations of $\text{Ca}(\text{OH})_2$ and alkali salts are present in the pore solution, only a limited amount of SiO_2 can diffuse out, while additional materials penetrate into the aggregate structure. This imbalance results in an expansive force within the aggregate grain. If, however, the $\text{Ca}(\text{OH})_2$ and alkali salt concentrations are low, the rate of penetration of the hydroxyl and alkali ions is also low, while the migration of SiO_2 is increased, thus resulting in a lower expansive force (Chatterji et al. 1987).

The calcium/alkali exchange theory also considers calcium to be an essential component in the expansion of alkali-silica gel. This theory hypothesizes that the gel absorbs Ca^{2+} ions and, in turn, exchanges them for alkali ions, which then react with the pore solution to create additional alkali-silica gel. As additional gel forms, it fills more space and eventually causes cracking. The ion and water uptake is governed by the temperature and moisture conditions of the material and thus is coupled to physical transport (Rotter 1995). Some work has indicated that the gel's viscosity may change as calcium content increases in the gel, increasing its ability to impart damage to the surrounding system as it swells but decreasing its swelling capacity (Urhan 1987; Rajabipour et al. 2015).

The double-layer theory suggests that the expansion of the gel is caused by swelling due to electrical double-layer repulsive forces. When a liquid and a solid come into contact, the surface of the solid carries excess charge, which electrifies the interface. This excess charge alters the properties of both the solid and liquid materials. ASR involves the interaction of the highly charged silica aggregate surface with the alkaline pore solution of the concrete. This is the reaction that leads to the breakdown of the silica and the formation of the alkali-silica gel. Within the gel, negatively charged solid silica particles attract positively charged cations that thus bind to form a rigid layer around the solid particle. Surrounding this rigid layer, a diffuse layer is formed that comprises more cations and anions found within the gel. Thus, the electrical double layer is composed of sodium, potassium, and calcium ions, which surround the negatively charged silica surface. Once this double layer has been established, it imbibes water and swells. As water is introduced into the layer, electrostatic forces predominate, and particles are pushed apart as the gel expands (Prezzi et al. 1997).

While it is commonly understood that water is the primary driving force for expansion of alkali-silica gel, no single theory about the mechanism of gel expansion is widely agreed upon, and none appears to have completely and accurately explained the mechanism. For example, none of the four main theories discussed previously considers the potentially crucial role that short-range forces (such as atomic substitution of Ca^{2+}) might play in expansion. Neither the osmotic pressure theory nor the double-layer theory considers the potential effect of calcium on expansion. Additionally, work is still needed to understand how the gel viscosity may change based on temperature, relative curing conditions, and gel structure, and how gel viscosity may impact its ability to exert pressure and cause damage to the surrounding system.

Although at this time it remains unknown exactly how alkali-silica gel expands in concrete, portions of the theories described previously may together explain the mechanism or lead to a more complete explanation.

5.1.5 Evaluating aggregates for potential alkali-aggregate reactivity

5.1.5.1 Field performance—A history of satisfactory field performance is possibly the best method for evaluating the potential for an aggregate to cause AAR. Numerous factors must be considered when analyzing field performance data. These include:

- The cement content of the concrete and the alkali content of the cement should be the same, or higher, in the field concrete as proposed in the new structure.
- The concrete examined should be at least 15 years old.
- The exposure conditions of the field concrete should be at least as severe as those in the proposed structure.
- In the absence of documentation conclusively demonstrating that the aggregate to be used in the proposed structure is sufficiently similar to the aggregate in the field structure under investigation, a petrographic examination should be conducted to make that determination.
- The possibility that SCMs, lithium-based admixtures, or both, were used in the field structure should be considered.

Provided that satisfactory field performance can be demonstrated, the aggregate can be used in concrete (following the above guidance) with no further testing for AAR.

5.1.5.2 Petrographic examination (ASTM C295/C295M)

A petrographic examination should be the first step in assessing the suitability of a particular aggregate source for use in concrete construction. Petrography is a powerful tool that yields a wide range of information regarding the physical, chemical, and mineralogical characteristics of an aggregate, including the presence of rocks or mineral phases that are known to cause deleterious reaction in concrete.

In some cases, a petrographic examination may produce sufficient evidence to reject an aggregate on the basis of potential alkali reactivity or require that suitable preventive measures be explored and implemented. Generally, the examination cannot predict whether the type and distribution of reactive minerals present will cause damaging expansion in concrete, and further laboratory testing is usually required. Results of petrographic examination may form the basis for directing the laboratory test program in terms of selecting the type and sequence of tests and any relevant evaluation criteria.

The reliability of petrographic examination for screening aggregates for potential reactivity is strongly dependent on the skill and experience of the individual petrographer. There have been cases where aggregates that were accepted for use on the basis of results of petrographic examination have been later implicated in AAR. This is not necessarily the result of incorrect material classification, but more likely is due to a failure to recognize certain mineral assemblages as reactive (Rogers and Hooton 1991). Furthermore, the reac-

tive constituents of some rocks may not be readily identified by optical microscopy.

5.1.5.3 Laboratory tests to identify reactive alkali-carbonate rock aggregates

5.1.5.3.1 Rock cylinder method (ASTM C586)—In this method, cylinders (or prisms) cut from the rock are immersed in a solution of 1 N NaOH at room temperature (after having attained dimensional stability in distilled water) and the expansion is monitored for at least 1 month. Expansions in excess of 0.10% at 1 month are generally taken to indicate potentially deleterious chemical reaction between the alkalis and the rock. This test does not provide an indication of the potential for expansion in concrete, and further testing of the aggregate in concrete (ASTM C1105) is recommended if the rock cylinder expansion exceeds 0.10%.

5.1.5.3.2 Chemical composition (CSA A23.2-26A)—The determination of potential alkali-carbonate reactivity by chemical composition (CSA A23.2-26A) involves analysis for CaO, MgO, and Al₂O₃. Relatively pure limestones or dolomites are readily identified by composition and tend not to be alkali-carbonate-reactive. These aggregates may require further testing for alkali-silica reactivity. Interpretation of the results of this method are provided by ASTM C1778, which notes that aggregates that are determined to be potentially expansive per the chemical composition test require further testing using ASTM C1105. This test has helped to remove some of the difficulty in identifying reactive dolomitic limestones by petrographic examination.

5.1.5.3.3 Concrete prism test (ASTM C1105)—This test is similar to ASTM C1293 used to assess ASR, except for differences in storage temperature and the alkali content of the concrete. ASTM C1105 requires the testing to be carried out using a specific concrete mixture, with specimens stored at 73°F (23°C). Potentially deleterious reactivity is indicated if the expansion exceeds 0.015% at 3 months, 0.025% at 6 months, or 0.030% at 1 year.

Users of this test should recognize that the test yields information about the specific cement-aggregate combination tested, and that the absence of significant expansion in this test does not necessarily indicate that the aggregate is nonreactive. For instance, deleterious expansion may occur if the aggregate is used in concrete with a higher alkali content. The Canadian Standards Association (CSA A23.2-14A) requires potentially alkali-carbonate reactive rocks to be tested in concrete prisms under the same conditions as those used for ASR (that is, with 8.85 lb/yd³ [5.25 kg/m³] Na₂O_{eq} and stored at 100°F [38°C]). Furthermore, the same expansion criteria are applied; aggregates are deemed to be reactive if the expansion exceeds 0.040% at 12 months, with no criteria for earlier test results. The Canadian test is aimed at establishing the reactivity of the rock and not assessing the performance of a particular cement-aggregate combination.

5.1.5.3.4 Concrete microbar test (AAR-5)—The concrete microbar test (formerly known as the Chinese accelerated concrete microbar test) was introduced by Xu et al. (1998, 2000) to capture reactivity of alkali-carbonate rocks. In 2005, this test method was introduced as a draft test method by RILEM, identified as AAR-5 (Sommer et al. 2005) and

was subsequently published as a RILEM recommended test method (AAR-5) in 2016 (RILEM Technical Committee 219-ACS 2016). Work by Lu et al. (2008) has shown the ability of this test to detect alkali-carbonate reactive aggregates across a range of aggregate gradations (1/4 to 1/2 in. [5.0 to 10.0 mm] particles and 1/8 to 1/4 in. [2.5 to 5.0 mm] particles). The advantage to using a 1/8 to 1/4 in. (2.5 to 5.0 mm) particle size is that the test can be used on a single aggregate sample for both alkali-silica reactivity as well as alkali-carbonate reactivity. Further investigation (for example, petrographic examination) would be required to distinguish the type of reaction present so that appropriate mitigation measures could be followed. This test shows promise for detecting alkali-carbonate-reactive aggregates in a relatively short time (4 weeks) while providing more reliable results than the accelerated concrete microbar test. This test is an attractive alternative to the longer-duration ASTM C1105 test for detecting alkali-carbonate reactivity; however, RILEM recommendations for using the test state that should results between the concrete prism test and AAR-5 conflict, the concrete prism test results should take precedence (RILEM Technical Committee 219-ACS 2016).

5.1.5.4 Laboratory tests to identify alkali-silica reactive aggregates—Many test methods have been developed for identifying alkali-silica-reactive aggregates, and these methods vary in terms of testing environment, duration of test, and reliability of results. A comprehensive review is provided by Thomas et al. (2006); generally, the tests of longer duration such as the concrete prism test produce more reliable results than shorter-duration, highly aggressive tests such as the accelerated mortar bar test. In this section, a brief description is provided of test methods to detect alkali-silica reactivity in aggregates.

5.1.5.4.1 Accelerated mortar bar test (ASTM C1260)—This test is essentially the same as that developed at the National Building Research Institute (NBRI) by Oberholster and Davies (1986). In this method, the length change of mortar bars (measuring nominally 1 x 1 x 11.25 in. [25 x 25 x 285 mm]) stored in 1 N NaOH solution at 176°F (80°C) is monitored for 14 days (Oberholster and Davies 1986; Hooton and Rogers 1989). Some agencies specify that length change be measured over 28 days in 1 N NaOH; however, ASTM C1260 recommends determining reactivity based on expansions at 14 days after immersion in 1 N NaOH. The test has been successfully used to identify alkali-silica-reactive aggregates from across Canada (Grattan-Bellew 1989; Hooton and Rogers 1989, 1992; Bérubé and Fournier 1992b; Durand et al. 1990; Hooton 1991) and the United States (Stark et al. 1993; Folliard et al. 2006a) but is not considered suitable for evaluating reactive alkali-carbonate rocks.

Interpretation of results is not simple, and various expansion criteria have been suggested (Thomas et al. 2007). Bérubé and Fournier (1992b) proposed a limit of 0.10% expansion after 14 days in 1 N NaOH for quarried silicate and siliceous carbonate aggregates, and a limit of 0.20% for natural sands and gravels. Many aggregates with satisfactory field performance, however, produce expansions in excess of 0.25% in this test (Bérubé and Fournier 1992b). Conse-

quently, aggregates should not be rejected on the basis of this test unless petrographic examination confirms that the material is similar to known deleteriously reactive aggregates.

Research has shown that certain aggregate types may pass this test having expansions less than 0.10% at 14 days, yet cause deleterious expansion in [ASTM C1293](#) and in the field ([Folliard et al. 2006b](#); [Ideker et al. 2012b](#)). In summary, this test should be used with caution, owing to the many potential discrepancies between the performance of aggregates in this test and in the field ([Thomas et al. 2007](#)). [ASTM C1778](#) and [AASHTO R 80](#) (discussed in 5.1.8) provide further guidance on the interpretation of ASTM C1260 results.

5.1.5.4.2 Concrete prism test (ASTM C1293)—This test is considered the most reliable for correctly identifying ASR-susceptible aggregates ([Thomas et al. 2006](#)). A concrete mixture is proportioned with a cement content of $708 \pm 17 \text{ lb/yd}^3$ ($420 \pm 10 \text{ kg/m}^3$) using a portland cement with an equivalent alkali content ($\text{Na}_2\text{O}_{\text{eq}}$) of $0.90 \pm 0.10\%$. Sodium hydroxide is then added to the mixing water to provide a total alkali loading of the concrete of 8.85 lb/yd^3 (5.25 kg/m^3). This high alkali loading is necessary to induce expansion of slowly reactive rocks such as greywacke and argillites ([Magni et al. 1987](#)). Prisms are stored above water at 100°F (38°C), and the expansion is monitored for at least 1 year.

An expansion limit of 0.004% at 1 year is currently specified in Canada ([CSA A23.2-27A](#)) and an expansion limit of 0.04% is recommended in [ASTM C1778](#). This expansion correlates approximately to the point where cracking and signs of distress are first observed on the prisms. It also relates well to field performance. The Canadian Standard ([CSA A23.2-27A](#) and [A23.2-28A](#)) carries a caveat stating that lower expansion limits may be appropriate for assessing aggregates for use in critical structures, such as nuclear containment or dimensionally sensitive structures such as hydraulic dams, where small expansions may result in relatively large movements.

This test method has distinct advantages over the accelerated mortar bar test ([ASTM C1260](#)), as coarse aggregates can be tested without crushing to sand sizes. Furthermore, the larger test specimen reduces the effect of alkali leaching. The 12-month duration is necessary unless the temperature is raised or other changes are made to accelerate expansion; however, further acceleration of the test may have undesirable side effects ([Ideker et al. 2012b](#)).

5.1.5.4.3 Miniature concrete prism test (AASHTO T 380)—AASHTO T 380, or the miniature concrete prism test, was developed by [Latifee and Rangaraju \(2015\)](#) to overcome some of the limitations of ASTM C1260, [ASTM C1567](#), and ASTM C1293. Similar to ASTM C1293, this test requires a cementitious content of 708 lb/yd^3 (420 kg/m^3) and an equivalent alkali content ($\text{Na}_2\text{O}_{\text{eq}}$) of the cement of $0.90 \pm 0.10\%$. Sodium hydroxide is added to the mixing water to increase the alkali content ($\text{Na}_2\text{O}_{\text{eq}}$) of the mixture to 1.25% by mass of cement and a water-cementitious materials ratio (w/cm) of 0.45 by mass is used. Coarse aggregate grading requirements for this test are 57.5% of rock retained on a 3/8 in. (9.5 mm) sieve (passed through 1/2 in. [12.5 mm])

and 42.5% of rock retained on a No. 4 (4.75 mm) sieve (passed through 3/8 in. [9.5 mm]). Prisms are stored in 1 N NaOH solution at 140°F (60°C) for 56 to 84 days.

For evaluating the reactivity of aggregates, the aggregate is considered potentially alkali-reactive if 56-day expansion is greater than 0.040%. In case of low or slow reacting aggregates, an additional 28 days of testing may be required. The aggregate is considered nonreactive if 56-day expansion is lower than or equal to 0.030%. This test method has been found to have a similar reliability to that of ASTM C1293 in terms of determining aggregate reactivity, except with a shorter test duration (56/84 days compared to 1 year for ASTM C1293), particularly for assessing coarse aggregate reactivity ([Rangaraju et al. 2016](#)). Despite indications that this test method is reliable, it is important that this test method be further benchmarked against the other field exposure blocks to determine its reliability for assessing the effectiveness of ASR prevention measures, especially for concretes with moderate and low reactive aggregates.

5.1.5.4.4 Accelerated concrete prism test (RILEM AAR-4)—Due to the duration of the concrete prism test, there has been a push since the early 1990s to accelerate the test by increasing the temperature from the standard 100°F to 140°F (38°C to 60°C) ([Ranc and Debray 1992](#); [Murdock and Blanchette 1994](#); [DeGrosbois and Fontaine 2000](#); [Touma et al. 2001](#)). The accelerated concrete prism test is run for 3 months, compared to the standard concrete prism test, which is run for 1 year.

Unfortunately, simply raising the temperature and identifying expansion limits was not enough to produce a consistent and reliable test method. [Fournier et al. \(2004\)](#) identified factors leading to the variability in the accelerated test, including increased leaching of alkalis, reduced pore solution pH, increased mass loss, and a potential concern related to selection of the nonreactive fine aggregate; they also proposed expansion limits. Further work by [Ideker et al. \(2010\)](#) made clear the profound effect of the selection of the nonreactive fine aggregate on expansions in the accelerated test: expansions were reduced by as much as 50% compared to the 1-year expansions obtained with the Spratt coarse aggregate, depending on the source of nonreactive fine aggregate used in the test.

The accelerated version of the concrete prism test results in a reduction in expansion at 3 months as compared to the 1-year expansion obtained in ASTM C1293 ([Ideker et al. 2010](#)), which shows that the accelerated concrete prism test does not accurately measure the alkali-silica reactivity of an aggregate in the 3-month testing window mandated by the test method. Thus, the accelerated concrete prism test is not recommended for assessing aggregate reactivity or for determining the efficacy of mitigation measures.

5.1.5.4.5 The concrete microbar test (RILEM AAR-5)—A test method, now commonly referred to as the Concrete Microbar Test (formerly known as the Chinese Accelerated Mortar Bar Method), was introduced by [Xu et al. \(1998, 2000\)](#) to capture reactivity of alkali-carbonate reactive rocks and has been published as AAR-5: Rapid Preliminary Screening Test for Carbonate Aggregates ([Fournier et al. 2005](#)). The

concrete microbar test uses similar storage conditions as the accelerated mortar-bar test, but uses a larger aggregate size 0.16 to 0.32 in. (4 to 8 mm) and shorter, thicker bars 1.6 x 1.6 x 6.3 in. (40 x 40 x 160 mm).

Since the method was introduced, promising results have also been obtained for the detection of alkali-silica reactivity across a wider range of rock types (Lu et al. 2008; East 2007) and it has been included as part of the RILEM (2016) report on “Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures” as a test method for determining alkali-silica reactivity when used alongside the RILEM version of the Accelerated Mortar-Bar Test Method (AAR-2). In particular, the ability of this test to detect deleterious ASR in coarse aggregates is advantageous where reactive phases are removed due to crushing and processing in other accelerated methods (ASTM C1260). ASTM C1260 requires coarse aggregates to be crushed to a fine fraction, which can result in the loss of reactive phases within the aggregates and result in false negatives. This method may serve as a complementary test method, especially when ASTM C1260 produces a false negative. Lu et al. (2008) have recommended it as a universal accelerated test for alkali-aggregate reactivity.

5.1.5.5 Field exposure tests—Several ASR exposure sites have been built in different locations in North America and around the world (Hooton et al. 2013; Fournier et al. 2018b). The field exposure sites developed around the world have been an important tool for the development and understanding of accelerated testing methods for ASR and long-term performance of ASR mitigation techniques. Data obtained from field exposure sites have been used to aid in the development of specifications, standards, and guidance documents on ASR. Accelerated laboratory tests have benchmarked the performance of outdoor exposure blocks at these sites, leading to recommended minimum SCM replacement dosages and maximum alkali loadings for different aggregate reactivities for concrete mixtures. Studies have shown the correlation of accelerated laboratory testing and field exposure blocks; these are suggested for review of the applicability of the aforementioned test methods (Folliard et al. 2006b; Ideker et al. 2012a,b, 2016; Drimalas et al. 2012; Lute et al. 2016; Fournier et al. 2018b). The EU PARTNER project included 24 partners located in 14 different countries that examined a wide variety of aggregates (22 types). This work found that laboratory tests, such as the accelerated mortar bar test, are reliable for use with aggregates that react within 5 to 20 years in the field but are less reliable with slower-reacting aggregates (Lindgård et al. 2010; Fournier et al. 2018b).

5.1.6 Preventive measures—There are numerous preventive measures that can be used to minimize the risk of damage due to ASR; these include:

- (a) Using nonreactive aggregates
- (b) Limiting the alkali content of the concrete
- (c) Incorporating SCMs
- (d) Using chemical admixtures—namely, lithium compounds

These approaches are discussed in the following section. For alkali-carbonate reactive aggregates, avoidance or reduction in proportion to the reactive phases is the only recommended practice. The other methods listed, though proven effective with alkali-silica-reactive aggregates, are typically not a remedy for alkali-carbonate reaction (Rogers and Hooton 1992).

5.1.6.1 Use of nonreactive aggregate—This approach is perhaps the most obvious and certain way of avoiding damaging reaction in concrete structures. Nonreactive aggregates are not available in many locations, and importing nonreactive material may not be economically viable. Furthermore, AAR has occurred in numerous cases where prior testing of the aggregates indicated they were not deleteriously reactive. Methods of testing aggregates for reactivity have increased in severity, and acceptance criteria have become more stringent to reflect the increasing number of aggregates implicated in field cases of AAR. Adoption of existing testing practices, however, does not guarantee that aggregates will give satisfactory performance in every situation. Consequently, even if aggregates are found not to be deleteriously reactive, further precautions are frequently taken as circumstances demand. Such circumstances may include prestigious (or critical) structures, aggressive environments (external source of alkalis such as seawater or deicing salts), high cement contents, or extended service life.

5.1.6.2 Limiting alkali content of concrete—Stanton's (1940a,b) work on AAR indicated that expansive reaction is unlikely to occur when the alkali content of the cement is below 0.60% $\text{Na}_2\text{O}_{\text{eq}}$. This criterion, however, takes no account of the cement content of the concrete, which, together with the cement alkali content, governs the total alkali content of concrete and is considered a more accurate index of potential reactivity. The total alkali content of concrete has been taken into account and adopted into standards as “alkali loading,” which is defined as the amount of alkalis contributed by the portland cement in a concrete mixture, expressed in lb/yd^3 (kg/m^3). It is calculated by multiplying the portland cement content (or portland cement portion of a blended cement) by the equivalent alkali content of the portland cement, divided by 100. Alkali loading does not consider the alkali contribution from SCMs and is abbreviated as KGA (LBA) when SCMs are used. Alkali loading limits (maximum alkali content in the concrete) were incorporated and reported to range from 4.2 to 7.6 lb/yd^3 (2.5 to 4.5 kg/m^3) $\text{Na}_2\text{O}_{\text{eq}}$ (Nixon and Sims 1992). In many standards and specifications, the limit may vary depending on the reactivity of the aggregate (Oberholster 1994). In ACI 301, alkali loading in concrete, excluding that from SCMs, shall not exceed 4 lb/yd^3 (2.4 kg/m^3) for aggregate with ASTM C1293 expansions greater than or equal to 0.04% and less than 0.12%, or not exceed 3 lb/yd^3 (1.8 kg/m^3) for aggregate with ASTM C1293 expansion greater than or equal to 0.12% and less than 0.24% at 1 year. These limits shall not be used with natural pozzolan or fly ash that has a CaO content greater than 18%, or for aggregate with an ASTM C1293 expansion greater than 0.24% at 1 year. Canadian (CSA A23.2-27) limits range between 3.0 to

5.1 lb/yd³ (1.8 and 3.0 kg/m³) Na₂O_{eq}. A similar range has been adopted in FHWA guidelines (Thomas et al. 2008a), ASTM C1778, and AASHTO R 80.

The use of low-alkali cement and limitation of the alkali loading is not a sufficient safeguard in all cases, and the amount of alkalis needed to initiate ASR can vary depending on concrete mixture and conditions. Stark (1980) reported damaging AAR in highway structures constructed using cements with alkalis in the range of 0.45 to 0.57% Na₂O_{eq}; the reactivity of certain aggregates with low-alkali cements was confirmed in laboratory mortar bar expansion tests. Thomas (1996) reported evidence of ASR in numerous hydraulic structures with alkali contents below 4.0 lb/yd³ (2.4 kg/m³) Na₂O_{eq}.

Aggregates that are not normally reactive when used in concrete with low-alkali cement may be deleteriously reactive in concrete of higher alkali content. This may occur through alkali concentration caused by drying gradients, alkali release from aggregates, or the ingress of alkalis from external sources (deicing salts or seawater). Stark (1978) reported increases in soluble alkali from 1.85 to 6.07 lb/yd³ (1.1 to 3.6 kg/m³) Na₂O_{eq} close to the surface of some highway structures. Migration of alkalis due to moisture, temperature, and electrical gradients has also been demonstrated in laboratory studies (Nixon et al. 1979; Xu and Hooton 1993).

Research has demonstrated that many aggregates contain alkalis that may be leached out into the concrete pore solution, thereby increasing the risk of AAR (Stark 1980; Stark and Bhatti 1986; Way and Cole 1982; Van Aardt and Visser 1977; Thomas et al. 1991; Bérubé et al. 2002). Stark and Bhatti (1986) reported that, in extreme circumstances, some aggregates release alkalis equivalent to 10% of the portland cement content, and others reported that up to 1.7 lb/yd³ (1 kg/m³) of alkalis can be contributed by aggregates (Bérubé et al. 2002; Grattan Bellew 1995).

Alkalis may penetrate concrete from external sources such as brackish water, sulfate-bearing groundwater, seawater, or anti-icing/deicing salts. Nixon et al. (1987) showed that seawater (or NaCl solutions) present in the mixing water elevates the hydroxyl-ion concentration and increases the amount of expansion of concrete. Oberholster (1992) showed that the expansion of large concrete blocks exposed to saltwater spray may be doubled compared with the same blocks exposed to tap water spray. In addition, studies in Denmark (Chatterji et al. 1987) have shown that exposure to NaCl solution (and other alkali salts) can cause considerable expansion and cracking in concrete.

5.1.6.3 Use of supplementary cementitious materials—Stanton (1940b) reported that expansion due to the reaction could be reduced by the use of pozzolanic cement containing finely ground shale or by replacement of 25% of high-alkali portland cement with pumicite. Subsequent tests by Stanton (1950) confirmed the beneficial effect of a wide range of natural pozzolans and demonstrated that partially replacing portland cement with a sufficient quantity of pozzolan (pumicite or calcined shale) eliminated deleterious expansion, whereas replacement with similar

quantities of ground quartz (Ottawa) sand did not, indicating that the beneficial action of the pozzolan extended beyond merely diluting the cement alkalis. The first major use of a natural pozzolan to control ASR dates back to the 1940s, when calcined siliceous shale (Puente shale) was used in the Davis Dam, together with low-alkali cement (Gilliland and Moran 1949). In the 1950s, various studies (Cox et al. 1950; Barona 1951; Pepper and Mather 1959) showed that other SCMs (namely, fly ash and slag cement) were also effective in reducing expansion. Later research showed that silica fume was highly effective in controlling ASR, with levels of 10% or less being sufficient to suppress damaging expansion in mortar bars with reactive aggregate from Iceland (Asgeirsson and Gudmundsson 1979) and South Africa (Oberholster and Westra 1981).

All SCMs contain alkalis and some—for example, fly ash—may contain substantially more than the portland cement they replace. This has led to considerable controversy in the past regarding whether the alkalis in SCMs are potentially available for reaction and how they should be treated when calculating the alkali loading of the concrete. However, it is now generally accepted that the main mechanism by which SCMs reduce the potential for damaging reaction is by reducing the availability of alkali in the concrete pore solution. Alkalis released by portland cement and SCM may be available in one of three forms: dissolved in the pore solution, bound by the products of hydration, or fixed by the products of alkali-silica gel. In systems free of reactive aggregate, the partition of the alkalis between the pore solution and the hydrates is largely a function of the composition of the binder (Thomas 2011).

There is a large body of data in the literature that shows how various SCMs affect the composition of the pore solution extracted from hydrated cement pastes (Longuet 1976; Diamond and Lopez-Flores 1981; Diamond 1981, 1983a,b; Glasser and Marr 1985; Canham 1987; Canham et al. 1987; Kollek et al. 1986; Duchesne and Bérubé 1992, 1994; Kawamura and Takemoto 1988; Page and Vennesland 1983; Kawamura et al. 1987; Andersson et al. 1989; Durand et al. 1990; Yilmaz and Glasser 1990; Rasheeduzzafar and Hussain 1991; Shayan et al. 1993; Wiens et al. 1995; Nagataki and Wu 1995; Shehata et al. 1999; Ramlochan et al. 2000; Shehata and Thomas 2002; Bleszynski 2002; Boddy et al. 2003). Studies on the effect of fly ash and slag cement on the pore solution of pastes have been reviewed by Thomas (1996), and studies involving silica fume have been reviewed by Thomas and Bleszynski (2001). These studies show that the incorporation of most SCMs leads to a reduction in the concentration of alkali hydroxides in the pore solution of pastes, mortar, and concretes, with the amount of reduction increasing with higher SCM contents. Figure 5.1.6.3 shows the evolution of the hydroxyl ion concentration of the pore solution extracted from sealed paste samples with $w/cm = 0.50$, and Fig. 5.1.6.3b shows the OH⁻ concentration at 2 years as a function of the SCM content (from Thomas [2011], using data from Shehata et al. [1999], Ramlochan et al. [2000], Bleszynski [2002], and Shehata et al. [2002]). The most efficient SCM in terms of reducing the

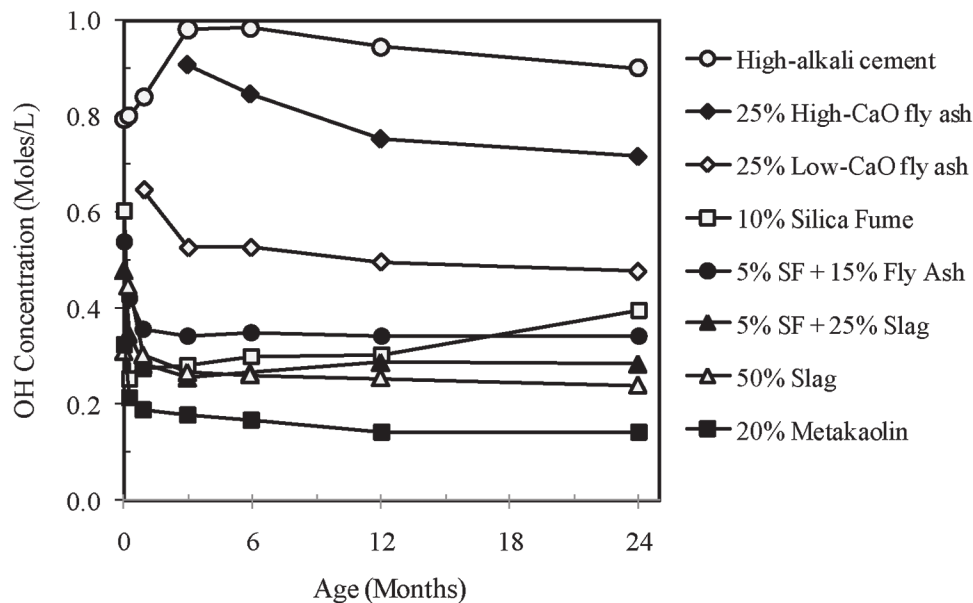


Fig. 5.1.6.3a—Evolution of the pore solution in pastes containing SCM (Shehata et al. 1999; Ramlochan et al. 2000; Bleszynski 2002; Shehata and Thomas 2002).

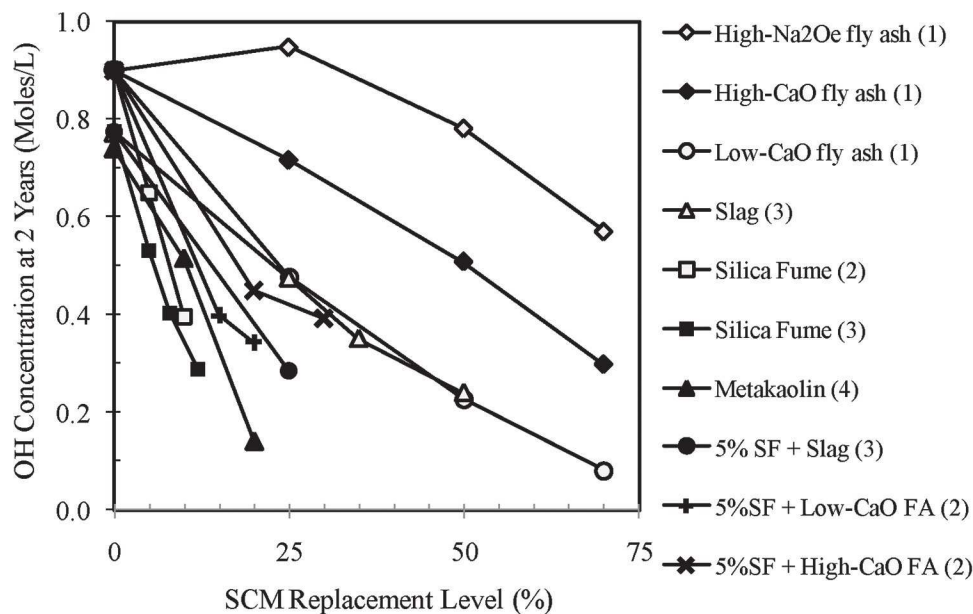


Fig. 5.1.6.3b—Effect of SCM type and replacement level on the pore solution hydroxyl ion concentration at 2 years ((1)—Shehata and Thomas 2002; (2)—Shehata et al. 1999; (3)—Bleszynski 2002; (4)—Ramlochan et al. 2000).

pore solution alkalinity is silica fume, followed closely by metakaolin and low-calcium fly ash. Slag cement and high-calcium fly ash are less effective and must be used at higher cement replacement levels. Thomas (2011) showed that the concentration of alkali in the pore solution is a function of the composition of the binder (cement + SCM), especially its alkali ($\text{Na}_2\text{O}_{\text{eq}}$), calcium (CaO), and silica contents. Figure 5.1.6.3c shows a strong correlation between the hydroxyl ion concentration in the pore solution and the chemical parameter $(\text{Na}_2\text{O}_{\text{eq}} \cdot \text{CaO})/(\text{SiO}_2)^2$ calculated from the chemical composition of the binder (cement + SCM). Thus, SCMs with higher silica contents and lower calcium and alkali

contents will be more efficacious in terms of controlling the alkali available for reaction.

The ability of SCMs to reduce pore solution alkalinity is linked to their effect on the composition and alkali-binding capacity of the hydrates. The introduction of SCMs reduces the Ca/Si ratio of the hydrates, which results in more alkali being bound (Bhatty and Greening 1978; Rayment 1982; Uchikawa et al. 1989; Thomas et al. 1991). Glasser and Marr (1985) explain the differences in alkali absorption on the basis of the surface charge on the C-S-H, which is dependent on the Ca/Si ratio. At high Ca/Si ratios, the charge is positive and the C-S-H tends to repel cations. As the Ca/Si ratio decreases, the positive charge decreases, becoming negative.

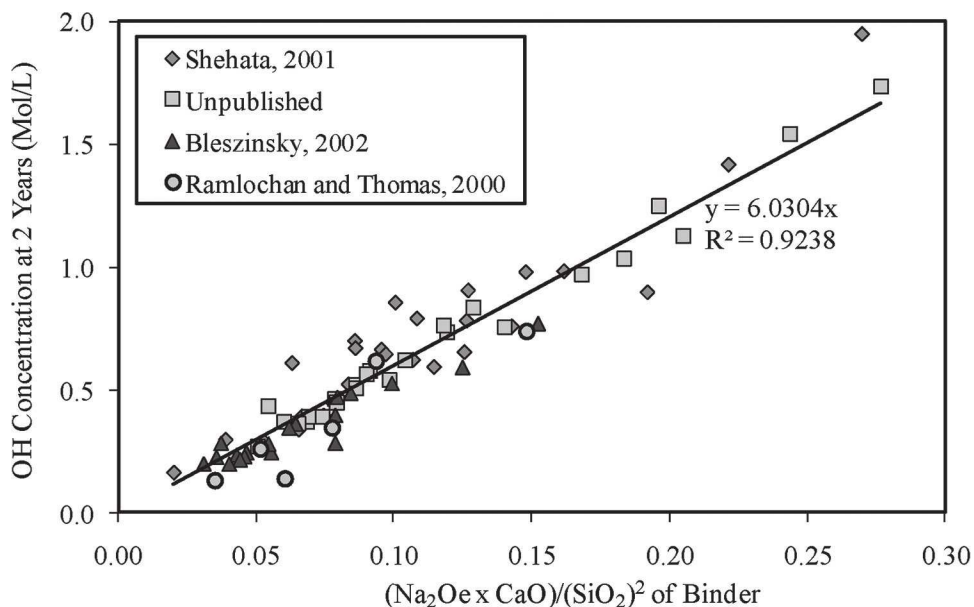


Fig. 5.1.6.3c—Relationship between pore solution composition and the chemical composition of the binder.

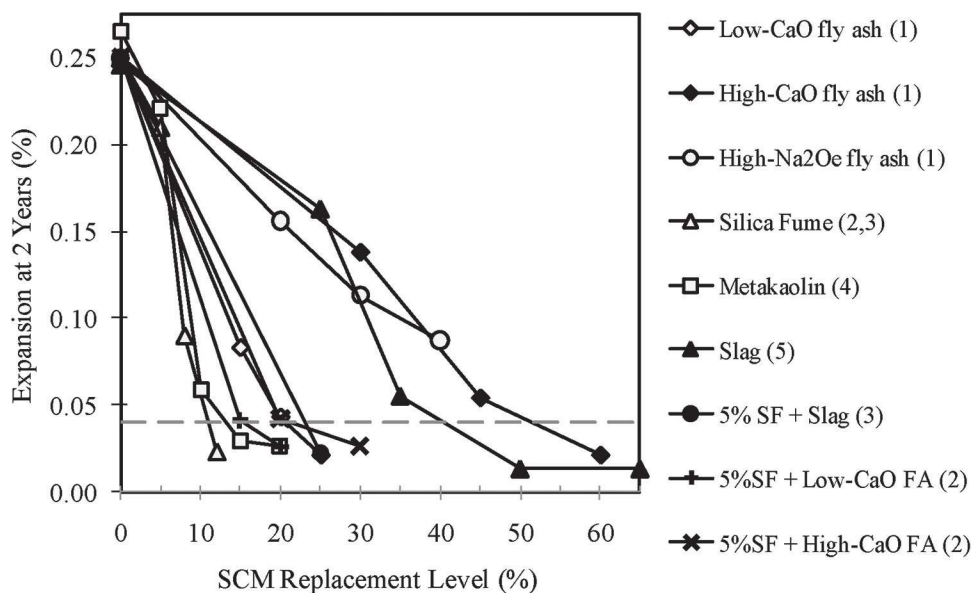


Fig. 5.1.6.3d—Effect of SCMs on 2-year expansion of concrete containing siliceous limestone ((1)—Shehata et al (1999); (2)—Shehata and Thomas (2002); (3)—Bleszynski (2002); (4)—Ramlochan and Thomas (2000); and (5)—Thomas and Innis 1998).

tive at Ca/Si ratios less than 1.3 (Glasser 1992). Negatively charged C-S-H has an increased capacity to absorb cations, especially alkalis. Hong and Glasser (1999) confirmed the importance of the Ca/Si ratio on the alkali-binding capacity of synthesized single-phase C-S-H, but subsequently showed that the binding capacity could be greatly increased by introducing alumina into the C-S-H to form C-A-S-H (Hong and Glasser 2002).

SCMs that are highly efficient at binding alkalis and reducing the alkali concentration of the pore solution are also found to be highly effective in controlling expansion of concrete containing reactive aggregate. Figure 5.1.6.3d shows the 2-year expansion of concrete prisms (ASTM C1293) as a function of the type and amount of SCM used (Thomas 2011). Once again it was found that

the SCMs with the most silica and the lowest Ca/Si ratio—silica fume, metakaolin, and low-calcium fly ash—are most effective and must be used at replacement rates of 10 to 30%, whereas slag cement and high-calcium fly ash must be used at higher replacement levels. With the exception of materials with very high alkali contents, all SCMs can be used to control ASR, provided that they are used at an adequate level of replacement. ASTM C1778 identifies high alkali fly ash as fly ash with greater than 4.0% $\text{Na}_2\text{O}_{\text{eq}}$ and high-alkali slag cement and silica fume as having greater than 1.0% $\text{Na}_2\text{O}_{\text{eq}}$. ACI 301 limits the alkali content of fly ash used as a preventive measure to 4.0%, unless testing using ASTM C1293 indicates innocuous levels of expansion.

The amount of SCM required to control ASR depends on the following (Thomas 2011):