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A review of salt scaling: I. Phenomenology

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Abstract

Salt scaling is a major durability issue for concrete, so the phenomenon has been the subject of an extensive research effort. Nevertheless, there is no agreement regarding the cause of this damage, so no means for preventing salt scaling can be identified. One of the primary reasons for this shortcoming is the lack of a critical review of the research in this field. Such a compilation is presented in the present series of articles. In Part I, we review the experimental studies that have revealed the phenomenology of salt scaling. In Part II, proposed mechanisms for scaling are discussed, and the adequacy of these mechanisms is judged based on their ability to account for the characteristics outlined here.

Keywords: Salt scaling; Phenomenology

Contents

1. Introduction

In cold climates, salts are regularly used to de-ice concrete roadways and walkways (Fig. 1). This practice leads to salt scaling, which is one of the major durability issues facing concrete in such climates. Salt scaling is defined as superficial

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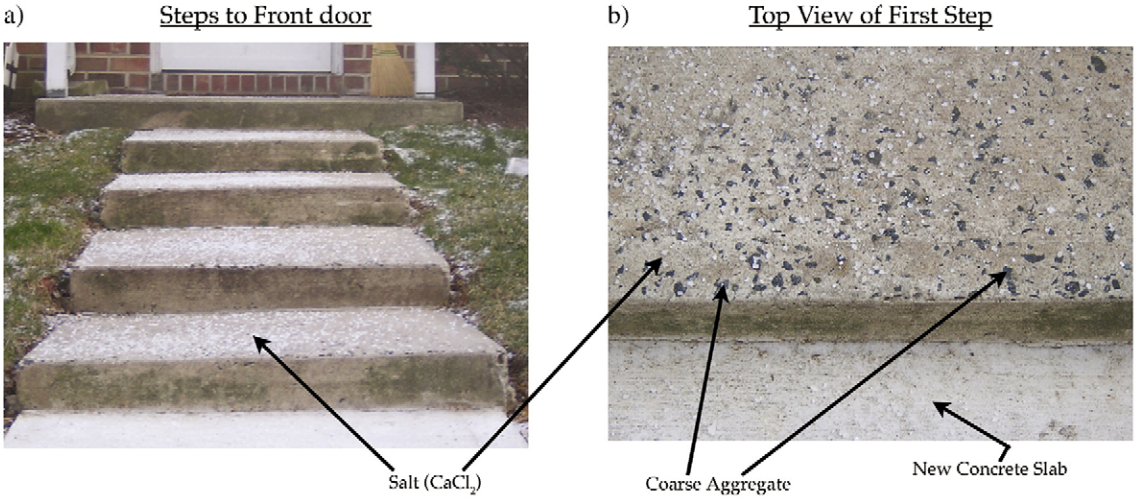

Fig. 1. (a) Picture of front walkway at a residence, where maintenance crews have applied salt in the wake of a light snowstorm. (b) Top view of first step in photo on left shows that salt scaling results in the exposure of coarse aggregate. The picture also shows the contrast between a new concrete slab, and a slab that has endured several winters of exposure.

damage caused by freezing a saline solution on the surface of a concrete body. The damage is progressive and consists of the removal of small chips or flakes of material. These characteristics were first revealed in the 1950s through laboratory testing [1,2], and they were later verified through field tests [3]. It is important to clarify that salt scaling is not analogous to conventional freeze/thaw damage, which is caused by internal crystallization and characterized by a reduction in stiffness and strength. Since salt scaling is superficial, it does not jeopardize the mechanical integrity of a concrete body. However, this damage renders the body susceptible to ingress of moisture and aggressive species that threaten overall durability. In addition, salt scaling is not aesthetically pleasing because it often results in the exposure of coarse aggregate (Fig. 1).

The characteristics of salt scaling were defined over the past 50 years through hundreds of laboratory and field studies. The most notorious characteristic is that a maximum amount of damage is achieved with a moderate amount of salt. This “pessimum” concentration is widely accepted to be at a solute concentration of ~3% by weight. In spite of the extent of research on salt scaling, none of the previously proposed mechanisms can account for all of the phenomenology. To demonstrate this, we present an exhaustive review of the experimental work in this field in which the characteristics of salt scaling are clearly revealed through laboratory testing and field performance. Several review articles provided insight into the literature that must be reviewed to obtain a comprehensive view of the state of the research in this field [4–6]. In Part II we evaluate the ability of the existing theories to account for the characteristics of salt scaling and conclude that only the glue-spall mechanism is completely successful [7].

In Section 2, we consider the laboratory test methods used to elucidate the characteristics of salt scaling and evaluate their reliability. The principle characteristics of salt scaling are discussed in Section 3. Analysis of the research reveals an underlying trend consisting of a greater susceptibility to scaling when the strength of the surface is compromised. For example, several researchers observed that brushing the surface prior to testing results in a significant decrease in the mass of scaled material [8–10]. Therefore, Section 4 considers the effect on salt scaling of additives that alter surface strength, such as entrained air and supplementary cementing materials. Finally, in Section 5 the influence of sample preparation and handling, including mix characteristics, curing conditions and the use of sealers, is examined.

2. Test methods

Most salt scaling experiments follow guidelines in the American Society for Testing and Materials (ASTM) standard C672 [11]. This method consists of confining a pool of 3 wt% NaCl solution with a depth of 6 mm on the surface of a concrete slab whose thickness is ≥75 mm (Fig. 2). The recommended temperature cycle consists of placing the specimen in a “freezing” environment where the temperature of the specimen is reduced to −17.8±2.8 °C in 16–18 h; then the specimen is removed to laboratory air at 23±3 °C for 6–8 h.

In addition to ASTM C672, two similar test methods are also employed: the capillary suction of deicing chemicals and freeze–thaw test (CDF) and the Swedish Standard SS 13 72 44. The CDF method is an “upside down” version of ASTM C672 developed in Germany. The concrete slab (thickness=50–75 mm) is equilibrated at 20 °C and 65% relative humidity (RH)

Fig. 2. Schematic of the ASTM standard C672 test method.

before setting up the experiment. The test configuration consists of supporting the slab 3 mm above the bottom of a stainless steel container (Fig. 3) that holds enough NaCl solution to submerge only a few mm of the test surface. The top of the slab (originally the bottom molded surface) is covered with 20 mm of insulation. The steel container is placed in a glycol solution that is circulated through a refrigerated bath. This configuration provides better control of the temperature in the salt solution by utilizing the insulating properties of air and providing conditions for efficient heat removal. Capillary rise of the salt solution is allowed to continue for a period of time sufficient to allow the weight to stabilize, before starting the freeze/thaw cycles. The thermal cycle consists of varying the temperature between −20 °C and +20 °C twice daily. The temperature of the salt solution and the glycol are monitored throughout the test.

The Swedish Standard SS 13 72 44 [12], also known as the Borås method, is very similar to ASTM C672. However, two modifications are incorporated to provide better control of the experiment: first, to promote unidirectional freezing ~20 mm of insulation is placed on the sides and bottom of the sample; second, a sheet of plastic foil is placed 20 mm above the salt solution to prevent evaporation. In the Borås method, the sample thickness is 50 mm and the salt solution depth is 3 mm. The thermal cycle consists of lowering the temperature to −15 to −20 °C in a period of 12 h and holding at the minimum temperature for a period of 4 h; then, the temperature is increased to 15–25 °C in a period of 8 h. The temperature in the salt solution is monitored throughout the experiment.

Based on a subjective analysis of the appearance of the surface, ASTM C672 uses a rating between 0 (no scaling) and 5 (severe scaling) to quantify the degree of scaling after every 5 freeze/thaw cycles. At this time, the mass of the specimen is also measured and the change in mass is calculated from the original mass. Neither of these observations accurately quantifies the degree of scaling, because the net change in mass is a result of water absorption and mass loss from the surface, and the rating system is subjective.

The best way to quantify the degree of scaling is to collect and measure the mass of scaled-off material. This quantity should be reported as the ratio of mass loss to the area of the test surface (m/L^2). Although it is not required, many recent projects that employed ASTM C672 monitored the mass of scaled-off material. Both the CDF and Borås methods require the determination of this quantity. This measurement is normally performed at frequent intervals throughout the experiment (ASTM C672: every 5 cycles, CDF and Boras: 7, 14, 28, 42 and 56 F/T cycles) by carefully removing the solution and lightly brushing the surface to remove all of the loose material. The material is then dried in an oven (~105 °C) before it is weighed.

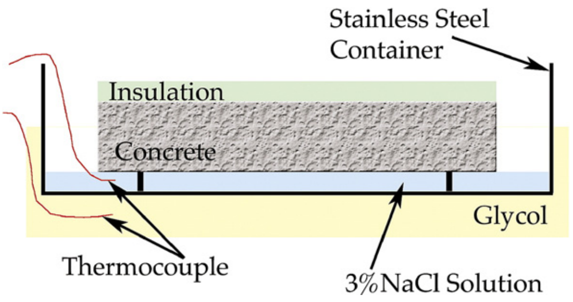

Fig. 3. Schematic of the CDF test method. Unidirectional freezing in the solution is promoted by utilizing the insulating properties of air. The temperature in the test solution is controlled by circulating refrigerated glycol around the stainless steel container.

Unfortunately, there has been no systematic study of the variability expected from the differences in the test methods. The temperature cycles used in all of the methods are similar, which renders use of results gathered from different test methods less questionable for identifying underlying trends. It has been widely agreed that unacceptable variation of results observed with a single method is largely due to poor control of specimen handling and the temperature cycle during the test [13,14]. In addition, the heterogeneity of concrete can contribute to some inherent, albeit minor, variability. To ensure uniform conditions during testing it is suggested that measures be taken to avoid excessive evaporation from the test solution, and that the temperature of this solution be monitored throughout the experiment.

3. Characteristics of salt scaling

Salt scaling is progressive [15] superficial damage of a cementitious surface. This damage consists of the removal of small chips or flakes [1,16] of binder with very few small aggregates removed [17]. The phenomenology that characterizes this damage is well known. The most surprising characteristic of salt scaling is the occurrence of a maximum amount of damage with a moderate amount of solute. This “pessimum” of solute concentration occurs at ~3 wt% [1,2,5,14,18–20] (Fig. 4). Two other notable trends are illustrated in Fig. 4: the pessimum is independent of the type of solute [1,2] and entraining air in the binder improves resistance to salt scaling [2,4,14,21–29]. In addition to the solutes studied by Verbeck and Klieger [2], Arnfelt [1] observed similar trends with barium chloride, potassium ferrocyanide and potassium ferricyanide. Several studies have indicated that no scaling occurs when the pool of solution is not present on the surface [2,14,19]. A discussion concerning why air entrainment is beneficial is presented in the next section.

A number of references report scaling caused by pure water [30–33]; however, these results are misleading. Although the experimental procedure used in these studies are less aggressive than freezing a saline solution on the surface of the slab [2], most of the results are reported after 100 freeze/thaw cycles, which is twice that used in a normal salt scaling test. Careful analysis of the results indicates that the observed damage is a result of a weak surface or extremely low-quality concrete. An example of the former is exhibited in reference [31] where the mixtures incorporated a 25% substitution of fly ash for cement. In the next section it is shown that fly ash substitution diminishes the resistance to scaling, and that this effect is attributed to a weak surface. The first scale rating was reported after 100 freeze/thaw cycles, and a majority of the mixtures yielded a rating of 2, with no rating greater than 3. For all mixtures, the scale rating reported after 200 and 300 freeze/thaw

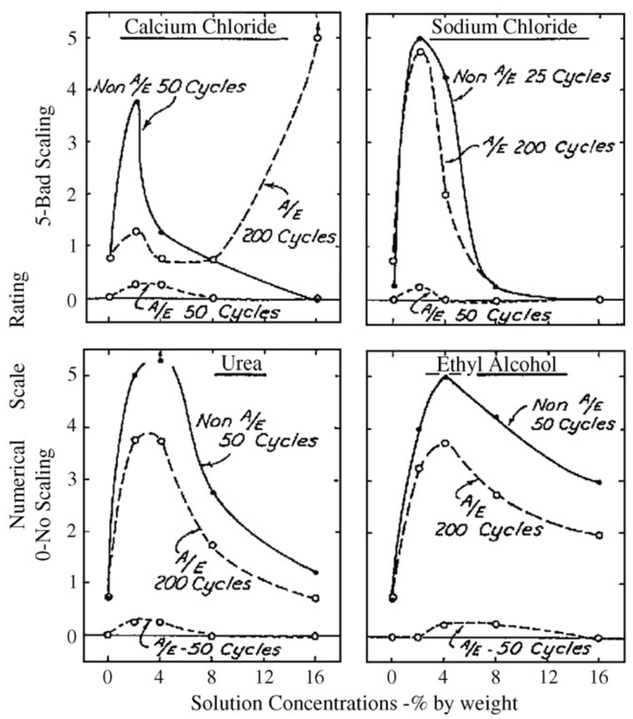

Fig. 4. Results from reference [2] indicate that a maximum amount of damage occurs at a solute concentration of ~3%, and that this trend is independent of the solute (Sodium Chloride, Calcium Chloride, Urea or Ethyl Alcohol). These results also illustrate the beneficial effect of air entrainment (A/E).

cycles was the same as that reported after 100 cycles. Therefore, once the weak surface was removed the material was resistant to further scaling. Moreover, it is reasonable to suggest that if the scale rating had been reported after 50 freeze/thaw cycles, the rating would have been lower, ~1, in agreement with that found using pure water in the classic scaling study by Verbeck and Klieger [2] (Fig. 4). In reference [30], the author reports scaling with pure water on extremely low-quality concrete. For example, the non-air-entrained mixtures that exhibited scaling were given a scale rating of 5 after 10–15 freeze/thaw cycles. The compressive strengths of most of the mixtures tested were less than 20 MPa. These values are not representative of cementitious materials in use today.

The influence of the temperature cycle has been investigated in experiments where the minimum temperature, time at the minimum temperature and rate of cooling were varied. It was demonstrated that damage is reduced when the minimum temperature of the thermal cycle is increased [5,14,19,34]. For example, Studer [19] showed that a greater reduction in damage occurs when the minimum temperature is increased from −18 °C to −16 °C, than when it is increased from −13 °C to −11 °C. This finding is consistent with the observation that no damage occurs when the minimum temperature is held above −10 °C [4,14]. Furthermore, it was shown that longer time at the minimum temperature results in more damage [14,17]. There are very few data on the effect of the freezing rate on surface deterioration; however, the available data indicate that the freezing rate has very little influence on the amount of damage [4,19].

In spite of the fact that chemically dissimilar solutes produce the same pessimum concentration, a number of researchers have investigated the role salt plays in salt scaling. The objective of these experiments was to determine how the salt concentration in the pore solution affects the salt scaling resistance of concrete. Accordingly, the experiments consisted of mixing the cementitious material with salt [18] or equilibrating specimens in salt solutions prior to testing [5,14,20]. All of these studies indicate that the salt concentration of the solution on the surface of concrete is more important than the composition of the pore liquid.

An air void system is known to prevent strength loss caused by internal frost action, if the distance between the voids is below a material-specific critical spacing factor [35–39]. These results, coupled with the evidence that entrained air improves scaling resistance, have led to the suggestion that internal frost action is the cause of scaling damage [5,23]. However, the presence of salt reduces the amount of ice formed [14,20,40]. Therefore, if internal frost action just beneath the surface were the cause of scaling, the most damaging solution would be pure water. Furthermore, it was reported that scaling damage is observed without a significant loss of strength [28,41–43], and that testing for susceptibility to internal frost action does not provide insight into the ability of the material to withstand salt scaling [8,31,34,44–46]. Therefore, different mechanisms are responsible for the loss of strength caused by internal frost action and the loss of material from salt scaling.

The evidence discussed above reveals the following reproducible characteristics of salt scaling:

1. Salt scaling consists of the progressive removal of small flakes or chips of binder.
2. A pessimum exists at a solute concentration of ~3%, independent of the solute used.
3. No scaling occurs when the pool of solution is missing from the concrete surface.
4. No damage occurs when the minimum temperature is held above −10 °C; the amount of damage increases as the minimum temperature decreases below −10 °C and with longer time at the minimum temperature.
5. Air entrainment improves salt scaling resistance.
6. The salt concentration of the pool on the surface is more important than the salt concentration in the pore solution.
7. Susceptibility to salt scaling is not correlated with susceptibility to internal frost action.

The next section considers how additives such as air entrainment or supplementary cementing materials affect the salt scaling resistance of concrete.

4. Effect of additives

4.1. Air entrainment

Fig. 4 illustrates that entrained air improves the salt scaling resistance of concrete. There is a clearly defined critical spacing factor of 250–300 μm, below which scaling resistance is satisfactory regardless of the type of concrete [22–24,45,47]. In

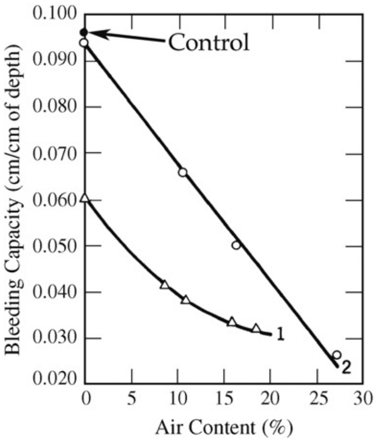

Fig. 5. Data from reference [53] obtained with cement paste (w/c ≈ 0.4–0.5). Bleeding is reduced by increasing the amount of entrained air. The data illustrate that some AEAs reduce bleeding without any entrained air (1—sodium abietate, 2—saponin).

addition, there is evidence that mass loss is proportional to the spacing factor, when the air void spacing is greater than the critical value [24,48,49]. In contrast, studies indicate that the critical spacing factor for internal frost action varies based on the type of concrete tested [38,39,46]. This contradiction provides further evidence that two different mechanisms are responsible for salt scaling and internal frost action. Entrained air could be beneficial to scaling resistance in two ways: (1) entrained air reduces bleeding; and (2) ice in the air voids sucks pore fluid from the surrounding matrix, which compresses the porous body.

To reduce the spacing factor, the volume fraction of entrained air is increased [39,50], which reduces bleeding of fresh cement paste (Fig. 5) [51–54]. Bleeding (or segregation) is important because it results in a variation in the water-to-cement ratio (w/c), and thus density, through the concrete thickness; the greatest density is found at the bottom of the sample [54–56]. This density variation yields a variation in strength, with the weakest concrete at the top. We suggest that air entrainment improves the resistance to salt scaling because it prevents bleeding from reducing the strength of the surface. The deleterious effect of segregation has been demonstrated by performing salt scaling experiments on the bottom, molded surface. The bottom surface was not damaged, while the top surfaces of companion slabs were [57,58].

Air bubbles reduce bleeding by adhering to cement particles, making the particles buoyant [53]. Owing to inter-particle interactions, this effect is not limited to the cement particles in contact with air bubbles (Fig. 6). Therefore, an increase in the average specific surface of entrained air bubbles (resulting in a smaller spacing factor) should result in less bleeding. Accordingly, there is an excellent correlation between scaling damage and volume of air voids with diameters less than 300 µm (Fig. 6), where the critical volume appears to be ≈1.5% [24,25,34]. Different surfactants produce populations of air bubbles with different bubble size distributions, which may explain why the two AEAs tested in reference [53] produce different relationships between bleeding and the air content (Fig. 5).

When care is taken to avoid the deleterious effects of bleeding, air entrainment still prevents salt scaling [59]. In this case the role of air entrainment is related to its influence on the dilatation of the body following nucleation of ice. Powers and Helmuth [35] showed that air-entrained concrete contracts, because ice nucleates in the voids and sucks liquid from the surrounding mesopores. As noted above, there is substantial evidence that salt scaling and internal frost action are caused by different mechanisms. Therefore, we expect that air entrainment affects these phenomena in different ways. Air protects against internal damage by causing contraction that offsets the crystallization pressure of ice crystals nucleated in mesopores [60]. In Part II of this series [7] we will discuss several mechanisms for salt scaling. For some of these mechanisms, like the glue-spall mechanism, compression caused by ice in the air voids offsets damaging tensile stresses.

4.2. w/c, strength and air entrainment

The most important characteristic of any cementitious mixture is the w/c, which governs material properties that

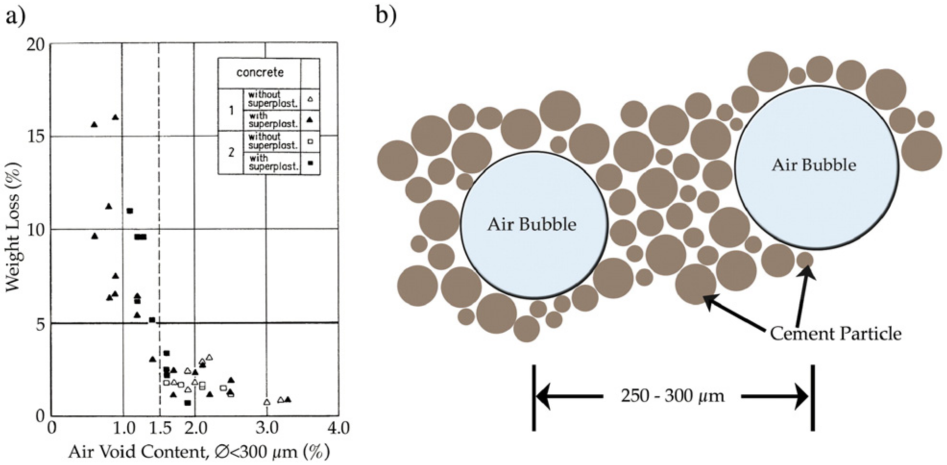

Fig. 6. (a) Data from reference [24] illustrate that the mass loss from scaling increases as the volume of voids with diameter smaller than 300 µm decreases. (b) Schematic illustrating how air bubbles make nearest neighbor cement grains more buoyant.

contribute to durability, such as strength and permeability [52,55]. In particular, lowering the w/c results in less bleeding [52,54,55] and increased strength [51,52]. Accordingly, lowering the w/c results in better resistance to salt scaling [18,27,29,34,44,45,61–66]. Concrete prepared at w/c ≤ 0.3 does not require air entrainment to resist salt scaling [34,45,46,67,68]. Reference [54] indicates that the bleeding capacity of a cement paste with w/c = 0.3 is very low and is similar to that of a paste with w/c ≈ 0.45 and 20% air (Fig. 5). In addition, at w/c ≤ 0.3 the strength of concrete is at least 50–60 MPa. It will be shown in the next section that a normal air-entrained concrete (w/c = 0.4–0.45) is resistant to salt scaling when the strength is 40–45 MPa. Therefore, low w/c concrete does not require air entrainment to prevent scaling because there is very little bleeding and the surface strength does not deviate greatly from the overall strength, which is normally greater than that which indicates a low susceptibility to salt scaling.

4.3. Supplementary cementing materials

Silica fume, fly ash and blast furnace slag, commonly referred to as supplementary cementing materials (SCM), are incorporated in a concrete mix by substitution for cement (5–50 wt%). Since these materials are generally finer than cement (Table 1), they increase the density of concrete by filling voids between adjacent cement grains and between cement grains and aggregate. When the SCM is substantially finer than cement, this effect results in an immediate strength increase.

In the presence of $Ca(OH)_2$ (CH) the amorphous silica (S) in silica fume and fly ash undergoes the pozzolanic reaction to form C–S–H gel:

$$x\,\mathrm{CH} + y\,\mathrm{S} + z\,\mathrm{H} \rightarrow \mathrm{C{-}S{-}H} \tag{1}$$

In concrete CH is liberated from the hydration of calcium silicates, which increases the pH of the pore solution to at least 12.5. The pozzolanic reaction requires high pH (~13) for the activation of the S, and the duration of moist curing necessary to realize a strength increase depends on the fineness of the supplementary material. Normally, the pozzolanic reaction will not commence until the concrete has aged for ~3 days, when enough alkali have been released to raise the pH to ~13. The subsequent strength increase occurs after prolonged moist curing. The silica content of the supplementary material determines the maximum substitution rate at which all the potentially available CH will be consumed. These maximum rates are roughly 10% for silica fume and 30% for fly ash [52]. At greater rates, the excess will be beneficial only if there is an increase in density that results from broadening the particle size distribution. Blast furnace slag is a latent hydraulic cement that hydrates after it is activated at high pH. The reaction products are basically the same as that produced by cement hydration, except for a lower CH content. The maximum effective slag substitution rate was determined to be 50% [52].

Table 1
Typical physical characteristics of ordinary Portland cement and supplementary cementing materials (SCM)

Material	Specific surface (m^2/kg)	Particle size (μm)	Silica (%)
Cement	150–250	3–100	
Silica fume	15,000–20,000	0.01–0.5	86–94
Fly ash	250–600	1–100	45–50
Blast furnace slag	350–500		20–30

As a result of the difference in particle sizes, SCM have different effects on the kinetics of strength development of concrete. For example, concrete incorporating silica fume exhibits an improved early strength (age <7 days) as a result of the extreme fineness of silica fume, which results in efficient packing and grain refinement due to nucleation of hydration products [69]. In addition, it takes much less time to dissolve the silica fume particles once the pore solution is saturated with CH. Therefore, the reaction of the SCM is not delayed by activation of the silica as it is with fly ash or slag. As a result, the rate of strength increase from continued hydration of relatively mature (>28 days) silica fume concrete is similar to that realized with ordinary Portland cement (OPC) concrete.

In contrast, fly ash particles are only slightly smaller than cement grains, so it takes longer for S in fly ash to be activated. Therefore, at early ages fly ash concrete has a lower strength than OPC concrete. However, after prolonged curing (1–2 months) the pozzolanic reaction of fly ash produces a very dense microstructure, so the strength of fly ash concrete will eventually be greater than OPC concrete. For these same reasons blast furnace slag concrete also exhibits low early strength, although the time necessary for the strength to rise above that realized with OPC concrete is much shorter (7–28 days). This is a result of the small particle size (silica fume < slag ≤ cement/fly ash) of blast furnace slag.

Salt scaling studies performed on concrete containing SCM are enlightening because the SCM affect the evolution of concrete strength. In general, if the strength approaches a value of 40 MPa at the time of testing, the salt scaling resistance of the material should be satisfactory. However, when SCM are used, the initial bound water demand (referred to as water demand hereafter) is reduced, so the actual w/c (not w/(c+s), where s is the amount of SCM) should be limited to avoid excessive bleeding. When this precaution is not taken, or the samples are prepared in a manner expected to magnify the effects of bleeding (discussed below), the strength of the surface may be compromised, despite the positive influence of air entrainment. When blast furnace slag is used, the concrete surface may be weakened by carbonation. As discussed in Section 4.1, reducing the surface strength results in a greater susceptibility to salt scaling.

4.3.1. Silica fume

Silica fume, also known as microsilica (MS) or condensed silica fume, is a by-product of the production of silicon metal or ferrosilicon alloys. Silica fume provides an increase in early strength because it provides nucleation sites for hydration products (resulting in grain refinement), reduces the porosity [70,71] and increases the fracture toughness [69] of the interfacial transition zone (ITZ). The ITZ is a volume of paste at the aggregate/paste interface that is generally more porous and weaker than the remainder of the concrete matrix [71]. This weak zone is a result of the cement grains' inability to pack efficiently against the aggregate surface [71]. Silica fume necessitates prolonged moist curing (~7–14 days) to realize the strength increase from the pozzolanic reaction.

The salt scaling resistance of concrete improves with the addition of silica fume, which can be attributed to the resulting strength increase. At w/c ≥ 0.4 the use of silica fume improves the salt scaling resistance when the resulting strength is greater than 40–45 MPa [26,28]. At lower w/c < 0.35, where strength is normally at least 40–45 MPa, silica fume has a marginal effect on the salt scaling resistance [14,27,72]. Experimental results that do not obey this trend have been reported. In these cases, the sample preparation technique is expected to result in a weak surface. For example, in reference [8] the authors present results from a series of ASTM C672 tests performed on concrete specimens with w/c = 0.45, silica fume additions of 0%, 5% or 10% and air void spacing factors below 200 μm. Companion mixes were prepared for each level of silica fume addition, one with a slightly greater spacing factor than the other. The results, presented in Fig. 7, indicate that silica fume addition is marginally detrimental. However, the samples were molded vertically so the test surface was a molded surface. The properties of a molded surface may be different than the remainder of the concrete body because of interactions with the mold release agent or bleeding towards the mold surface (wall effect [54,56]). In fact, Janeva et al. [58] verified that lateral molded surfaces have a reduced scaling resistance due the presence of excess moisture from bleeding.

The results in Fig. 7 (light bars) indicate that a majority of the scaling occurs in the first 20 cycles, and all of the mixes, except one, yield a final ASTM C672 rating of 3–4. This consistency was observed despite a variation in compressive strength between 30 (no silica fume) and 55 MPa (10% silica fume). The consistent magnitude of initial scaling (<20 freeze/thaw cycles) suggests that a weak surface is responsible for the early damage. For each of the companion mixes, the mix with higher strength always exhibits a better final rating (all mixes had adequate spacing factors, <200 μm).

In Fig. 7 the dark bars represent data from samples cured with a curing compound. After 1 day in the mold the compound was applied, and the samples were cured for 6 days. Then, the sample surface was "vigorously brushed with a metallic mechanized brush" to remove as much of the curing compound as possible. It is reasonable to suggest that the reduction in damage realized with the curing compound is actually achieved by removing the weak surface layer when the sample is brushed. Other researchers [9,10] have also recognized the positive effect of brushing the surface prior to testing.

Other studies yielded similar behavior [27] (Fig. 8). Although the experiment only consisted of 25 freeze/thaw cycles, it appears that several of the concrete mixes exhibit a lower scaling rate after the first 20 cycles. After casting, the slabs (20 × 20 × 6 cm) were covered with a plastic sheet until demolding 24 h later. This technique promotes a higher w/c ratio in the surface of the slab because the bleed water is not able to evaporate. Other researchers showed that this curing technique was detrimental to scaling resistance [57]. In fact, Neuwald et al. [73] showed that promoting evaporation for a short period after casting but prior to sealing (6 h), resulted in a drastic improvement in scaling resistance. Therefore, it is likely that the initial damage is the result of a weak surface. This conclusion is supported by the reduction in scaling achieved through air entrainment or decreasing the w/(c+MS) (Fig. 8). Both alterations reduce bleeding [51,52,54] and prevent the corresponding deleterious effects on surface strength. Increasing the silica fume content in the air-entrained samples results in more scaling. This is attributed to increased bleeding because the initial w/c ratio increases with fume addition (i.e., the silica fume acts as an inert filler until the pozzolanic reaction occurs). Considering the high surface area of silica fume (Table 1), this latter effect may appear counterintuitive. However, in this study all of the concrete mixtures were proportioned, including use of a high-range water reducer when necessary, to have a slump of

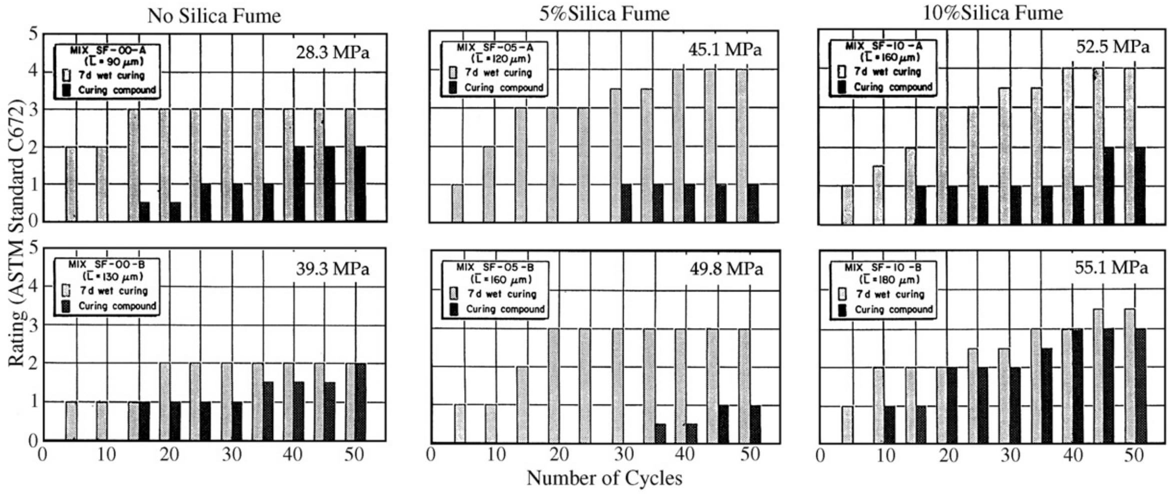

Fig. 7. Results from reference [8] indicate that a 10% silica fume addition to concrete (w/c = 0.45) is marginally detrimental to scaling resistance. Light bars represent data from samples moist cured for 7 days. Dark bars represent data from samples cured with a curing compound for 6 days.

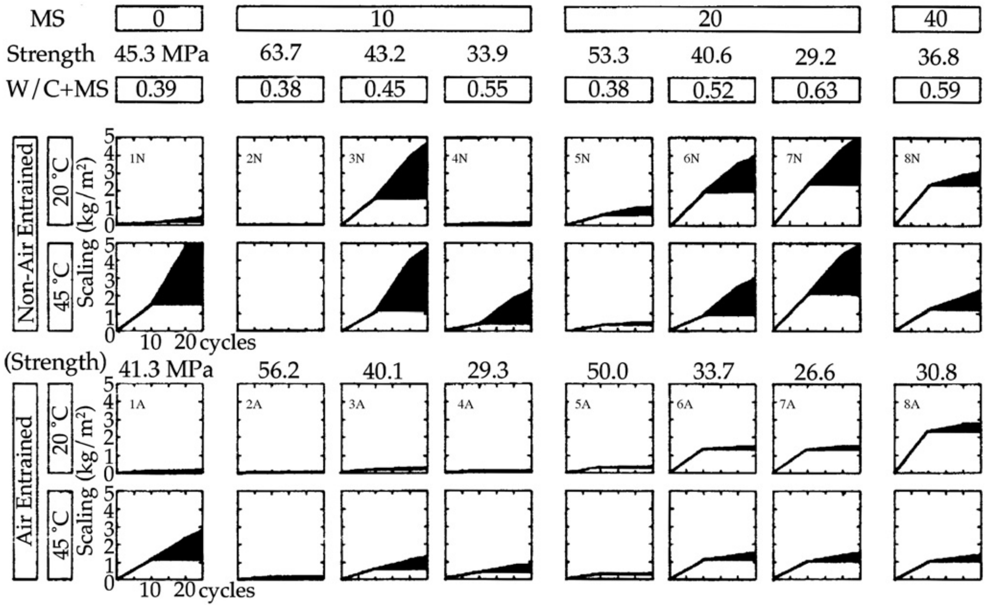

Fig. 8. Results from reference [27] illustrate rapid scaling during the first 20 freeze/thaw cycles. The results also indicate that scaling damage is reduced by air entrainment or lowering the w/(c+MS). Higher doses of silica fume result in an increase in the amount of initial scaling (air-entrained samples).

10 cm. Therefore, the fluidity of the fresh paste was constant, and the preceding interpretation is valid.

Evidence from a number of the studies on silica fume concrete indicates that prolonged freeze/thaw cycling results in accelerated, severe scaling when silica fume is used in concretes [14,17,18]. It is also shown that this increase is coincident with a reduction in the dynamic modulus [17]. This correlation suggests that scaling is a manifestation of the reduction in strength that accompanies internal frost action. At higher numbers (~100) of daily freeze/thaw cycles, the sample is prone to becoming saturated [74–76]. As a result, the sample is highly susceptible to internal frost action [77]. The mass loss always concludes with total disintegration of the specimen [17,18]. It should be noted that prolonged testing is not representative of natural exposure because it is very unlikely that a cementitious body will have a pool of fluid on its surface for 100 days.

4.3.2. Fly ash

Fly ash is a by-product of the coal-fired power industry. The ash, precipitated from the exhaust gas, consists of spherical particles with diameters in the range 1–100 μm. As Table 1 indicates, fly ash particles are in the same size range as unhydrated cement grains. Therefore, fly ash particles are at least two orders of magnitude bigger than silica fume particles, which results in a slower pozzolanic reaction rate and prevents the immediate increase in density realized with silica fume. In addition, fly ash contains a significantly lower fraction of reactive silica (~50%) than silica fume (~90%). As a result of these differences, the beneficial effect on strength is not realized until the concrete cures for extended periods (1–2 months). Fly ash addition may also hinder the ability to entrain air, resulting in high air void spacing factors [41,52,78,79]; however, satisfactory spacing factors are obtained by increasing the AEA dose [41,64,78,80,81]. All of the results discussed in this section were obtained on concrete with an adequate air void system.

Salt scaling experiments on concrete incorporating fly ash indicate that fly ash addition diminishes the resistance to salt scaling [10,31,44,64,65]. Fly ash is detrimental in part because short moist curing periods (3–28 days) result in lower strength [10,64,65]. Two studies performed by Bilodeau et al. [10], and Bilodeau and Malhotra [65] indicate that scaling damage is greatly reduced if the 28-day strength approaches 40 MPa, or alternatively if w/c ≤0.5 (Fig. 9).

The large difference in scaling illustrated in Fig. 9 is a result of the different substitution rates used in the two studies. In reference [10], fly ash substitutions of 20% and 30% were investigated, while substitution of 58% was investigated in reference [65]. Fly ash reduces the water demand and retards the initial set time. Excessive addition rates, like those used in reference [65], exaggerate these effects; therefore, more bleeding and a corresponding reduction in scaling resistance are expected (Fig. 9). In fact, Neuwald et al. [73] demonstrated that the amount of bleeding increases with an increase in fly ash substitution. The detrimental effect of high fly ash substitution (>30%) was observed by other researchers and in practice [57,64].

The results from reference [65] (Fig. 10) indicate that a majority of the scaling occurs in the first 20 freeze/thaw cycles. With the exception of Mix 9 and Mix 5, concrete that exhibits high total mass loss (Mixes 1–9) also exhibits the worst abrasion resistance. Therefore, the initial scaling occurs in a surface weakened by segregation. After the first 20 freeze/thaw cycles, greater scaling rates are observed for materials with relatively low 28-day strength (Fig. 10; Mixes 1, 4, 7, 8 and 9) [9]. Of these, Mixes 1, 4 and 7 have the highest actual w/c (~0.9), and Mixes 7, 8 and 9 include fly ash that exhibits the

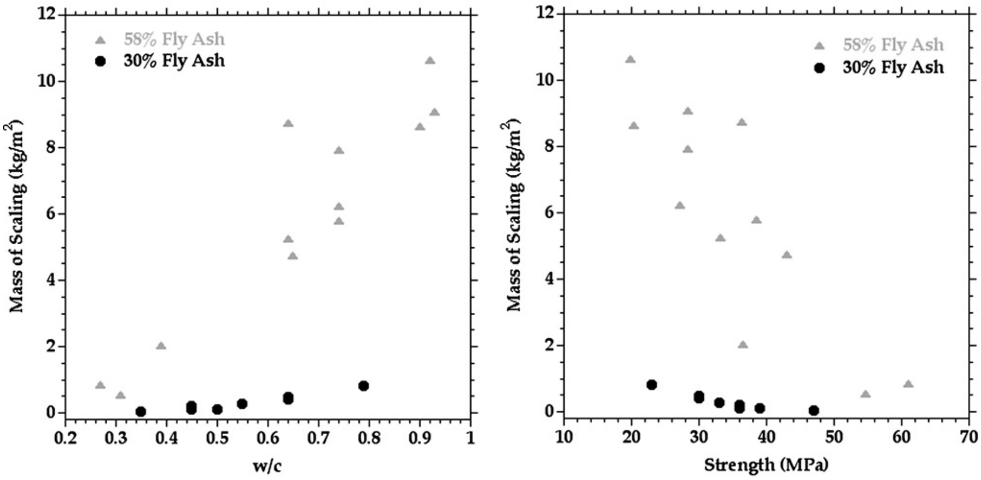

Fig. 9. Results from references [10] and [65]. The mass of scaling is reduced by keeping the actual w/c below 0.5 or alternatively achieving a 28-day strength of 40 MPa.

lowest pozzolanic activity. The concrete samples that do not exhibit rapid initial scaling and exhibit a marginally satisfactory resistance to scaling (Mixes 10, 11, 12) do not contain fly ash (reference mixtures).

4.3.3. Blast furnace slag

Blast furnace slag is a waste product of the production of pig iron. About 300 kg of slag is produced for every 1000 kg of pig iron. For use in concrete, slag must be quenched to produce granulated glass. The glass is highly reactive, while crystals of the same composition are not. Slag consists of the same oxides as Portland cement: lime, silica and alumina. However, different proportions of these compounds are found in slag. The fineness of slag is not specified because it can be ground to any level of fineness depending on how much energy the producer is willing to invest, although slag is normally ground finer than OPC. Once the material is quenched and ground to a high fineness, it is called “ground granulated blast furnace slag” (ggbs).

The hydration of ggbs is slow because the glass must be broken down by hydroxyls [82]. As a result of the delayed hydration, ggbs concrete has less strength than ordinary concrete when it is young (7–14 days). However, after longer curing periods (28 days) the slag hydrates and the concrete microstructure becomes very dense, resulting in stronger concrete (Fig. 11).

Unlike silica fume and fly ash there are very few studies on the salt scaling resistance of ggbs concrete. The available data indicate that ggbs reduces the salt scaling resistance of concrete [9,25]. These studies show that the use of slag results in an increase in the amount of scaling during the first ten freeze/thaw cycles (Fig. 12). The rapid scaling is not caused by a difference in strength because the samples are tested at an age of 28 days (Fig. 11); for example, reference [9] indicates that the ggbs and ordinary concrete used in the scaling study have similar 28-day strengths. Therefore, rapid scaling of ggbs concrete must occur because the use of slag results in the formation of a weak surface.

When ggbs is used, the amount of bleeding may increase because the water demand is related to the amount of cement used. For example, in reference [9] more bleeding is expected when slag is used, because the actual w/c is 0.55, 0.73 and 1.1 at the substitution rates of 0%, 25% and 50%, respectively. Therefore, the amount of rapid scaling (depth of weak surface) increases with the amount of slag used. As discussed in the previous section, Neuwald et al. [73] observed a similar trend for fly ash substitution. Fig. 12 illustrates this relationship, where the amount of material removed in the first 10 freeze/thaw cycles increases with the amount of slag used. Other researchers have observed similar trends [25,57].

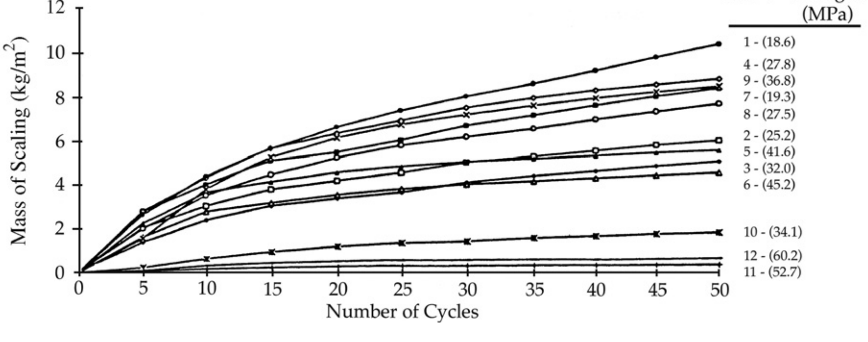

Fig. 10. Plot from reference [9], data from the experiments discussed in reference [65]. The results show that concrete containing fly ash (fa/(fa+c)=58%) exhibits rapid scaling in the first 20 freeze/thaw cycles. Concrete with low strength (<30 MPa) exhibits greater scaling rates after the first 20 cycles.

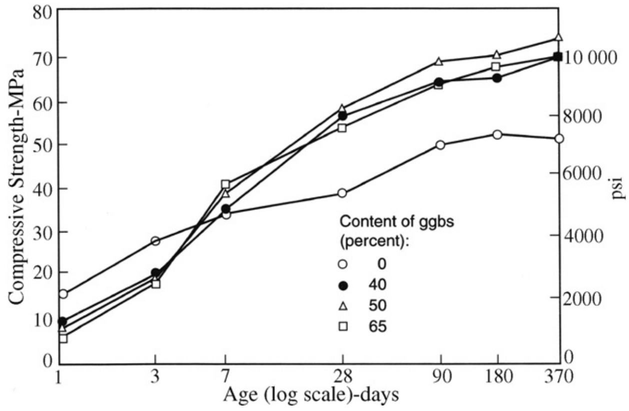

Fig. 11. Plot from reference [52]. Plot shows strength evolution of concrete containing various amounts of ground granulated blast furnace slag (ggbs).

When calcium hydroxide in concrete is exposed to carbon dioxide (CO_2) it undergoes carbonation:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2}$$

In ggbs concrete, carbonation results in the formation of two polymorphs of calcium carbonate ($CaCO_3$), aragonite and vaterite [82], that are ~20% and ~90% more soluble than calcite [83], respectively. In addition, since ggbs consumes CH through the pozzolanic reaction, it is likely that carbonation in ggbs concrete will decalcify the C–S–H [84,85]. Both of these effects will result in a coarser microstructure, whereas dissolution of calcite is only relevant in the field after long-term exposure. In contrast, carbonation of ordinary concrete yields a denser microstructure [32,86]. Fig. 13 illustrates the effect of carbonation on the microstructure of ordinary and ggbs cement pastes. The same trends were observed on concretes exposed in the field for 20 years [86] and in other lab studies [84]. The results presented in Fig. 13 were obtained on material that was not exposed to moisture prior to characterization. Therefore, the coarsening of the porosity in this ggbs paste is presumably wholly the result of decalcification of C–S–H. Upon exposure to moisture, the carbonate polymorphs will dissolve away, further degrading the surface. The strength of a cementitious surface is affected by these microstructural changes. As expected, after nearly 20 years of field exposure, carbonation of ggbs concrete reduces the tensile strength of the surface [86]. Accordingly, references [82] and [87] indicate that after carbonation the scaling resistance of ordinary concrete is improved, while that of slag concrete is reduced. In addition, both references show that the depth of scaling is equivalent to the depth of carbonation, illustrating that the surface strength governs the susceptibility to damage.

4.4. Summary

At low substitution rates, silica fume (<10%) improves the resistance to salt scaling when the strength approaches 40 MPa; however, there is no benefit to using silica fume in concrete at low w/c (<0.35). Fly ash will not be severely detrimental to scaling resistance, if the substitution rate does not exceed 30% [10,57]. As in silica fume concrete, a satisfactory resistance to salt scaling is achieved if the strength approaches 40 MPa. Available data indicate that ggbs reduces the resistance to salt scaling.

The initial bound water demand is reduced when SCMs are used, especially at high substitution rates of fly ash and slag. Figs. 8 and 9 indicate that satisfactory scaling resistance is achieved by limiting the actual w/c of air-entrained concrete to 0.5. The improved durability at these w/c may be partly attributed to the strength increase realized by lowering the w/c. However, bleeding is also reduced at lower w/c, ensuring that the strength of the surface does not significantly differ from the overall strength.

The results discussed above provide overwhelming evidence that the strength of the surface layer is crucial to scaling resistance. The importance of bleeding is highlighted by the beneficial influence of entrained air and the detrimental influence of sample preparation techniques that magnify the reduction of the surface strength. The deleterious effect of carbonating a ggbs concrete surface and the related strength loss further demonstrate that it is necessary to ensure the integrity of the concrete surface to produce salt-scaling resistant concrete.

5. Curing, drying and heating

Several experimental series were performed to determine the effect of sample handling on salt scaling resistance. The investigations included varying the moisture state and temperature during curing and the use of sealers or curing compounds. The effect of curing conditions is discussed in Section 5.1 and surface treatments in Section 5.2.

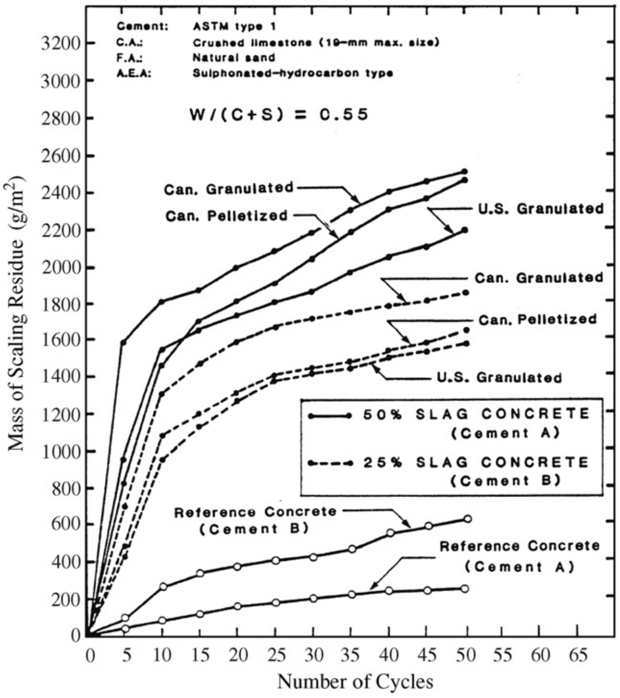

Fig. 12. Data from reference [9] clearly illustrate that the use of slag increases the amount of scaling during the first 10 freeze/thaw cycles, and that a substitution of 50% is worse than 25%.

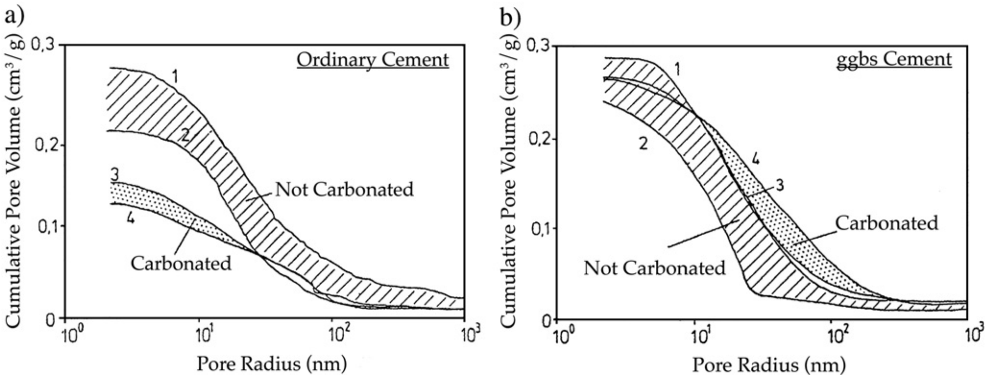

Fig. 13. Results from reference [32] show the effect of carbonation on microstructure of cement paste made with (a) type I cement and (b) paste with ggbs at a 75% substitution rate. Curve 1: age 7 days, no carbonation. Curve 2: age 6 months, sample taken from interior, no carbonation. Curve 3: age 6 months, sample taken from surface exposed to atmosphere with 0.03% CO_2. Curve 4: age 1 month, sample taken from surface exposed to atmosphere with 2.0% CO_2.

5.1. Curing and handling

The moisture state and temperature affect the morphology of the products of cement hydration and the resulting cement microstructure [52]. Longer moist curing promotes continued hydration resulting in a denser microstructure and higher strength. In contrast, drying [88–90] or curing at elevated temperature [91–96] produces a coarse microstructure and low strength.

Immediately after fabrication, curing at elevated temperature for short periods (~24 h) results in less resistance to salt scaling [47,68]. The resulting durability is inversely related to the curing temperature [68]. Reference [97] indicates that curing for 1 day at 38 °C results in a 10% reduction in the 28-day strength, while reference [47] indicates that 18 h at 70 °C results in a 25% reduction. Therefore, elevated curing temperatures lower strength, which results in a greater susceptibility to salt scaling.

Experimental studies indicate that longer moist curing periods improve the resistance to salt scaling [47,72]. This improvement is only realized by ASTM type I cement, presumably because type III cement exhibits a high early strength [34,72]. The influence of drying after moist curing (3–14 days) depends on the drying temperature and the type of concrete. Ordinary concrete dried at 45 °C [27] (Fig. 8) or 100 °C [66] is more susceptible to salt scaling. In contrast, other experiments indicate that drying at room temperature (~23 °C) has a marginal effect on the scaling resistance [2,10,64].

When a saturated porous body dries, menisci form in the surface pores to prevent the formation of a solid/vapor interface. The fluid just beneath a meniscus is under negative pressure, $p_{\mathrm{surf}}=\gamma_{\mathrm{LV}}\kappa$, proportional to the interfacial free energy of the liquid/vapor interface, γ_{LV}, and the curvature, $\kappa=2/r$, of the meniscus [98], where r is the (negative) radius of curvature. This suction pulls fluid from the interior of the body according to Darcy's law [99,100]:

$$J=-\frac{k}{\eta_L}\nabla p|_{\mathrm{surf}}=\dot{V}_E \tag{3}$$

where J (m/s) is the flux of fluid from the interior, k (m^2) is the permeability, η_{L} (Pa/s) is the fluid viscosity and $\dot{V}_{\mathrm{E}}$ is the evaporation rate ($m^3/m^2/s$). In a rigid body the curvature of the menisci will increase until $r=r_{BT}-\delta_W$, where r_{BT} is the breakthrough radius [101,102] and δ_{W} is the thickness of a water film that remains on the pore wall [103,104]. (The breakthrough radius is the radius of the largest sphere that can traverse a body through the porosity [105]. The radius roughly corresponds to the peak of the pore size distribution measured by mercury intrusion [106], nitrogen desorption [107] or thermoporometry [104], and it is the pore size that controls the rate of fluid flow in a porous body [108].) In the case of the slabs used for salt scaling experiments, k is low and the thickness, L is large. Therefore, the menisci will quickly retreat into the body at all likely evaporation rates. As a result, the greatest stress that arises in the concrete surface depends only on capillary pressure: $p_{BT}\approx-2\gamma_{LV}/(r_{BT}-\delta_W)$.

As a result of the suction in the pore fluid, the drying surface tends to shrink. On the contrary [101,102], the interior is not significantly stressed, so it resists the shrinkage of the surface, which results in tensile stress in the surface. This tensile stress is the main cause of surface cracking reported by many researchers [89,90,109,110]. Even in the absence of a gradient in pore pressure, cracking may also result from local resistance to shrinkage by aggregate and crystal phases (most notably CH) near the concrete surface [109]. In addition, elevated temperatures result in dehydration of ettringite (AFt) and monosulfoaluminate (AFm) [89,111], which produces more cracking and cracking to a greater depth [110]. Therefore, drying at elevated temperature or at extremely low (<30%) relative humidity weakens the concrete surface and is therefore expected to result in a greater susceptibility to salt scaling.

Fig. 8 (air-entrained samples only, for reasons discussed in Section 4.3.1) indicates that drying silica fume concrete at 45 °C is not detrimental to durability [27]. In contrast, drying silica fume concrete at 100 °C does reduce the durability [66]. Silica fume concrete has a finer microstructure than ordinary concrete, resulting in a smaller breakthrough radius [112] and greater suction at the surface. However, silica fume increases the tensile strength by up to 50% of that realized with a similar OPC concrete [113], which may prevent cracking at the surface. In addition, silica fume consumes calcium hydroxide in the

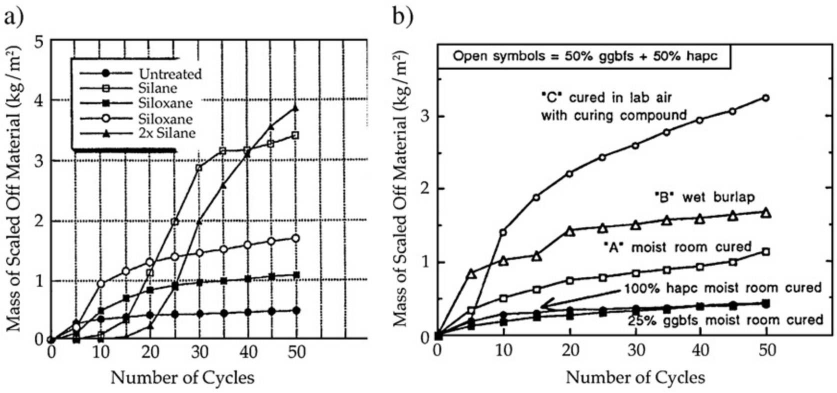

Fig. 14. Results from scaling experiments on concrete surfaces treated with (a) sealer [116] or (b) curing compound [57]. The results show that the surface treatments delay the onset of deterioration, followed by an abrupt and large mass loss.

pozzolanic reaction, Eq. (1), so there is less CH available to resist surface shrinkage [114]. Furthermore, silica fume favors the formation of AFt over AFm [115]; the latter is more susceptible to dehydration under less aggressive conditions [89], such as drying at 45 °C. The increased tensile strength, reduced resistance to shrinkage on a local scale and lower susceptibility to cracking from decomposition of AFm render silica fume concrete less susceptible to surface damage during mild drying. However, the propensity for AFt formation and the susceptibility of this phase to decomposition during drying at higher temperature (~100 °C) render silica fume concrete prone to damage under these conditions.

5.2. Curing compounds and sealers

Field and laboratory scaling studies performed on concrete surfaces treated with curing compounds or sealers are limited. Of the studies performed after the use of curing compounds [47,57,10] only one consists of scaling experiments on a surface where the curing compound was not removed by brushing the surface prior to testing [57]. The beneficial effect of brushing the concrete surface prior to testing was previously noted. Therefore, only data from experiments performed on a material whose surface was not brushed will be considered here. The use of sealers has been investigated in the laboratory [116,117] and the field [118].

The only discernable trend from laboratory experiments is that sealers or curing compounds delay the onset of surface deterioration. After this delay, in some cases, an abrupt and considerable loss of mass occurs (Fig. 14). Two studies showed that sealers delay the onset of surface deterioration; however, in both cases the eventual deterioration of the surface occurs at a rate similar to that observed on an untreated sample [25,117]. Field studies indicate that the use of sealers on bridge decks has no influence on the ability of the surface to resist scaling [118].

In reference [116], three sealers were investigated: a silane, an oligomeric siloxane and a polymeric siloxane. In reference [57] a commercial curing compound, Sealtight® 1220, was used, which is a waterborne, resin-based titanium dioxide emulsion. Upon application, these treatments (including the sealer discussed in reference [25]) render the surface hydrophobic, which delays moisture ingress during a scaling test. Using a similar silicone surface treatment, it was shown that the moisture content of a treated sample nearly equilibrates with that in an untreated sample after 1 day of immersion, and the difference is nullified after 3 days of immersion [33]. Thus, the ability of a surface treatment to prevent the onset of scaling during the first ~5–10 daily freeze/thaw cycles does not appear to be a result of the ability to prevent moisture ingress. In fact, Cleland and Basheer [117] demonstrated that increasing the depth of the treated surface results in a greater delay for the onset of scaling. This trend was attributed to the removal of the treated surface during the initial freeze/thaw cycles [117].

The results from reference [57] were obtained on a concrete with 50% ggbs substitution, which is known to result in rapid scaling, owing to its weak surface. The significant amount of mass lost upon scaling (Fig. 14) is attributed to the treatment's ability to bind the surface together, resulting in the removal of larger chunks of material. Stated differently, when the surface is treated with these chemicals, the cracking that occurs during scaling is routed through paths with little or none of the treatment present. This is expected because the residue of these treatments toughens the surface. The most likely scenario is that the cracks penetrate to a depth below the extent of the treatment, whereupon the entire treated surface is removed.

Therefore, the reliable trend from experiments and field studies concerning the effect of surface treatments on scaling resistance is that treatments delay the onset of deterioration [25,57,116] but ultimately have no effect on the scaling resistance [25,118,117]. The results from the field study are not surprising because the massive live loads experienced on roadways will quickly remove the residue from the surface. Coupled with the laboratory results, this implies that regardless of the magnitude or intensity of traffic, surface treatments comparable to those discussed above will not result in an improved scaling resistance.

6. Conclusions

In light of the experimental results and trends discussed above, it is clear that the material strength can be used as a predictor of durability. More specifically, the results from the studies on silica fume and fly ash concrete indicate that concrete with strength on the order of 40–45 MPa will be resistant to salt scaling. However, this level of strength is necessary, but not sufficient, for resistance to salt scaling. If the strength of the surface is compromised by improper preparation or handling, or exposure to aggressive conditions, then the resistance to scaling damage is diminished. Thus, the strength of the surface ultimately governs the ability of a cementitious body to resist salt scaling. Therefore, the revised list of characteristics of scaling damage that any satisfactory mechanism must account for is:

1. Salt scaling consists of the progressive removal of small flakes or chips of binder.
2. A pessimum exists at a solute concentration of ∼3%, independent of the solute used.
3. No scaling occurs when the pool of solution is missing from the concrete surface.
4. No damage occurs when the minimum temperature is held above −10 °C; the amount of damage increases as the minimum temperature decreases below −10 °C and with longer time at the minimum temperature.
5. Air entrainment improves salt scaling resistance.
6. The salt concentration of the pool on the surface is more important than the salt concentration in the pore solution.
7. Susceptibility to salt scaling is not correlated with susceptibility to internal frost action.
8. The strength of the surface governs the ability of a cementitious body to resist salt scaling.

Acknowledgments

In Part II [7], the characteristics listed above are used to judge the adequacy of previously proposed mechanisms for salt scaling. This work was supported by National Science Foundation Grant CMS-0200440.

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