

Ability of the Glue Spall Model to Account for the De-Icer Salt Scaling Deterioration of Concrete

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1 Introduction

Exposure to freezing and thawing cycles in the presence of de-icing chemicals (such as sodium chloride and calcium chloride) remains one of the principal causes of degradation of concrete surfaces in cold climates [1, 2]. Mixtures inadequately protected against this type of degradation typically suffer mass loss as small pieces of mortar spall away from the concrete surface, eventually leaving coarse aggregate particles exposed. This phenomenon is usually referred to as de-icing salt scaling [3].

The mechanisms leading to the degradation of concrete are still nowadays not fully understood. This has resulted in numerous practical problems. For instance, it has impeded engineers in developing practical solutions to fully protect concrete (even air entrained mixtures) against this phenomenon [3]. This is particularly the case for mixtures produced with supplementary cementing materials. Laboratory investigations invariably indicate that partial replacement of Portland cement with fly ash or slag markedly reduces to an unacceptable level the frost resistance of concrete in the presence of de-icing chemicals [1, 4-11].

The lack of basic understanding has also prevented the development of reliable test procedures to discriminate between durable and de-icer salt scaling susceptible concrete mixtures. According to some authors, most existing test procedures are much too severe, and cannot be used to evaluate the performance of concrete in service [1, 9-11]. Furthermore, the ASTM C 672 test has been criticized for the intrinsic variability of its results often attributed to the lack of precise control of the temperature regime and the absence of any device to impede the evaporation of the test solution during the test [12, 13].

2 Review of the degradation mechanisms proposed

The cause of salt scaling is clearly different from that responsible for internal cracking during freezing, as indicated by the fact that tests often produce one kind of damage without the other [14-18]. A variety of mechanisms have been proposed to explain scaling, but they generally fail to account for some of the phenomenology, as explained in recent reviews [19-21]. The most comprehensive model to date is the “glue spall” mechanism [19, 22-25], which attributes the damage to cracking of the

superficial layer of ice, owing to thermal expansion mismatch with the concrete. The thermal expansion coefficient of ice is about 5 times larger than that of cement or concrete, so the ice goes into tension as the temperature decreases; if the ice cracks, the crack penetrates the surface of the substrate, then turns and removes a chip. The trajectory of the crack (i.e., whether it penetrates and how deeply it extends before turning) can be predicted on the basis of fracture mechanics [26-28]. This theory accounts for the following essential features of salt scaling [19]:

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° 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.

The explanation for the pessimum concentration of solute is as follows [23]. Ice formed from pure water is too strong to fail from the stresses generated during cooling to -20°C ; in fact, those stresses are much smaller than what would be predicted by an elastic analysis, owing to the rapid creep of ice [25]. However, when a small amount of solute is present in the water, regardless of the chemical nature of the solute, freezing results in the formation of pure ice with small pockets of unfrozen brine. Those pockets act as flaws that facilitate cracking, and the cracks in the ice lead to damage to the underlying surface [23]. If the solute content is high (for NaCl, $> 5 \text{ wt}\%$), then the frozen layer is too soft to exert significant stress on the surface. The fracture mechanics analysis indicates that the depth of penetration of the cracks increases with the thickness of the ice, and with the mismatch in fracture toughness of the ice and substrate; that is, the weaker the surface, the greater the damage. Air entrainment has been observed to reduce scaling damage, even though it weakens the material. To explain this in terms of the glue spall mechanism, it has been proposed that the air bubbles reduce bleeding [29-32], so that air entrained materials have a stronger surface that resists cracking. Detailed discussion of the ability of the glue spall model to

account for experimental observations is provided in references 19-21. Support for the model is also provided by finite element simulations by Copuroglu et al. [33]. The least certain aspect of the model is its ability to explain the effect of air entrainment; the most controversial experimental observations (which the model purports to explain) are the role of surface strength and the relationship between the thickness of the ice and the depth of the scaling damage. Therefore, the present experimental program was designed to test those factors.

3 Materials and experimental procedures

3.1 Materials and mixture characteristics

All mortars were produced with an ASTM Type I ordinary Portland cement. A low percentage (20% by volume) of Ottawa sand type C-109 was used as fine aggregate to improve mixture homogeneity. Mixtures were prepared at two water/binder ratios (0.40 and 0.55) and three different air contents (0%, 3% and 6%) by volume using a synthetic detergent air-entraining agent (AEA) (Microair by BASF). Batching was done using a counter-current pan mixer. A welan gum-based viscosity modifying agent (VMA) was added at the end of the mixing sequence. The VMA, commercialized by Euclid was used to minimize internal bleeding.

Six cylindrical specimens ($\varnothing 100 \times 200$ mm) and six cubes (50 x 50 mm) were cast from each batch. Mortar was consolidated in the molds by vibration. After casting, the specimens were covered with wet burlap and left as such for 24 hours. At the end of this period, specimens were demolded and placed in a wet room kept at 100% relative humidity (r.h.) and 23°C prior the testing. Mortar mixture characteristics are summarized in Table 1.

Table 1: Mixture characteristics

Mixture	Cement (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	AEA (ml/kg cement)
W/B 0.40, 0% air	1110	442	528	-
W/B 0.40, 3% air	1110	432	525	3
W/B 0.40, 6% air	1110	422	533	5.9
W/B 0.55, 0% air	919	504	528	-
W/B 0.55, 3% air	919	495	526	1.5
W/B 0.55, 6% air	919	487	523	2.8

Viscosity modifying agent : 2.73 ml/kg of cement for all mixture

3.2 Specimen conditioning

All specimens were kept in moist storage until the age of testing. Cylinders for the scaling test were kept in the moist curing chamber for 28 days. At the end of the curing period, the cylinders were cut in 16 pieces, each having a thickness of 20 mm and a diameter of 100 mm. The top and the bottom sections were discarded. The specimens were placed in a room kept at 23°C and 50% r.h. for 14 additional days. At the end of the drying period, the specimens were placed in a Styrofoam mold that insulates the specimen's lateral surfaces from the cold environment and maintains the brine on the top of the specimens (Fig.1). The test surface of each specimen was recovered with a solution made with deionized water and 3% NaCl for at least 10 days.

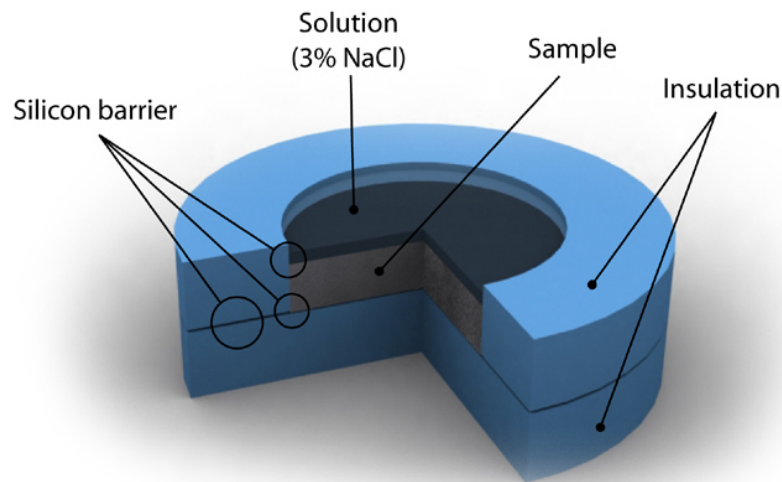


Figure 1: Scaling specimen preparation

3.3 Testing procedures

Fresh properties of mortars, such as air content and slump were measured according to ASTM C231 and C143. The compressive strength of all mixtures was performed after 28 and 56 days on three cubes in accordance with ASTM C109. The air-void characteristics of all mixtures were determined in accordance with ASTM C457 - Modified Point-Count Method.

The mechanical properties of the mortar surface were investigated using the Brinnell hardness test. All tests were run with a 500 -kg load on companion samples that had been cured for 28 days and subjected to a drying period of a few weeks. All samples were tested in a dry state.

All de-icer salt scaling tests were performed in accordance with NQ-2621-900-1¹ and ASTM C672 procedures² to evaluate the influence of the

¹ This procedure is recommended by the “Bureau de Normalisation du Québec” that defines the standards in Québec.

thickness of the solution layer. Four replicates were tested for each of the four testing conditions. At the end of the resaturation period, the solution on top of each specimen was flushed and replaced by a fresh one. The right amount of solution was used to meet the specified thickness (i.e. either 2, 4 or 8 mm). A last series of specimens was also tested with no solution on top (thickness = 0 mm). In this case, the saturation solution was simply flushed and the surface left as such without sponging. In order to prevent evaporation and maintain constant the thickness of the test solution, all test specimens were covered with an airtight plastic film. The specimens were subjected to 56 daily cycles of freezing and thawing. Previous calibrations have indicated that the characteristics of the freezing and thawing cycle are not significantly affected by the location of the test specimens within the freezing chamber. These calibrations show that the precision of the minimum temperature is $\pm 1^\circ\text{C}$. A typical freezing and thawing cycle, as measured at the solution-mortar interface, is given in Figure 2. Each week, after seven cycles, the salt solution was changed and scaled-off particles were collected, dried and weighed.

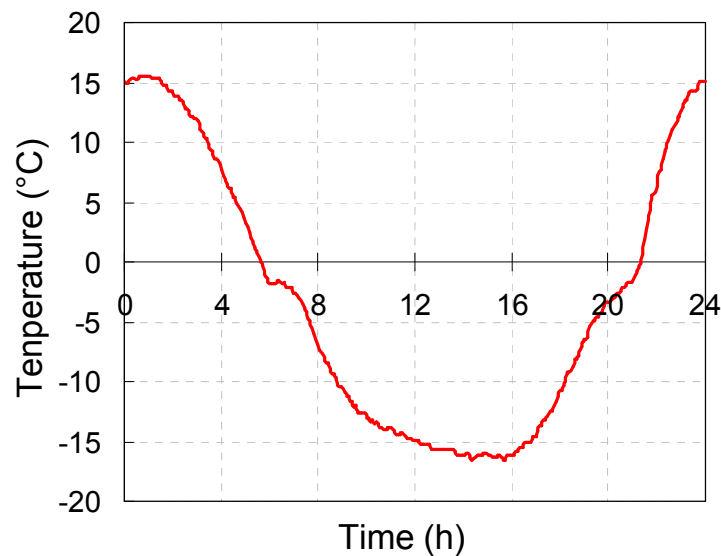


Figure 2: Typical freezing and thawing cycle

4 Results

4.1 Properties of the fresh mortar

The properties of the fresh mortar are summarized in Table 2. Air entrained mortars were more fluid than those produced without an AEA. However, the dosage in AEA did not have a significant effect on workability. Mixtures with water/binder ratio of 0.55 were also more fluid than those produced at a water/binder ratio of 0.40.

² The test surface was however smaller than the minimum surface area specified by the standards.

Table 2: Fresh mortar properties

Mixture	Air Content (%)	Slump (mm)
W/B 0.40, 0% air	0.4	95
W/B 0.40, 3% air	3	210
W/B 0.40, 6% air	6	200
W/B 0.55, 0% air	0.4	100
W/B 0.55, 3% air	3	> 210
W/B 0.55, 6% air	6	> 210

4.2 Properties of hardened mortar

The air-void characteristics of all mixtures are given in Table 3. As it is often the case, the air content measured on the hardened samples is higher than the one determined on the fresh mixtures. Good spacing factors ($< 250 \mu\text{m}$) were obtained for all air-entrained mortars.

Table 3: Hardened mortar properties

Mixture	Air void characteristics		Compressive strength		Indentation hardness
	Air Content (%)	Spacing factor (μm)	28 days (MPa)	56 days (MPa)	
	W/B 0.40, 0% air	0.9	748	47.0	
W/B 0.40, 3% air	5.1	128	40.0	51.1	40.2
W/B 0.40, 6% air	7.7	85	37.4	44.9	32.5
W/B 0.55, 0% air	1.5	863	32.2	39.8	31.5
W/B 0.55, 3% air	5.0	200	28.6	39.5	26.5
W/B 0.55, 6% air	5.8	85	27.2	33.6	23.2

As could be expected, the presence of air reduces the compressive strength of the mortars. A reduction of the water-cement ratio also contributes to increase the compressive strength of the mixtures. The surface hardness test results follow the same tendency.

4.3 De-icer salt scaling results

Figure 3 show the evolution of the mass of scaled particles with the number of daily freezing and thawing cycles. The curves are the mean of three or four replicates.

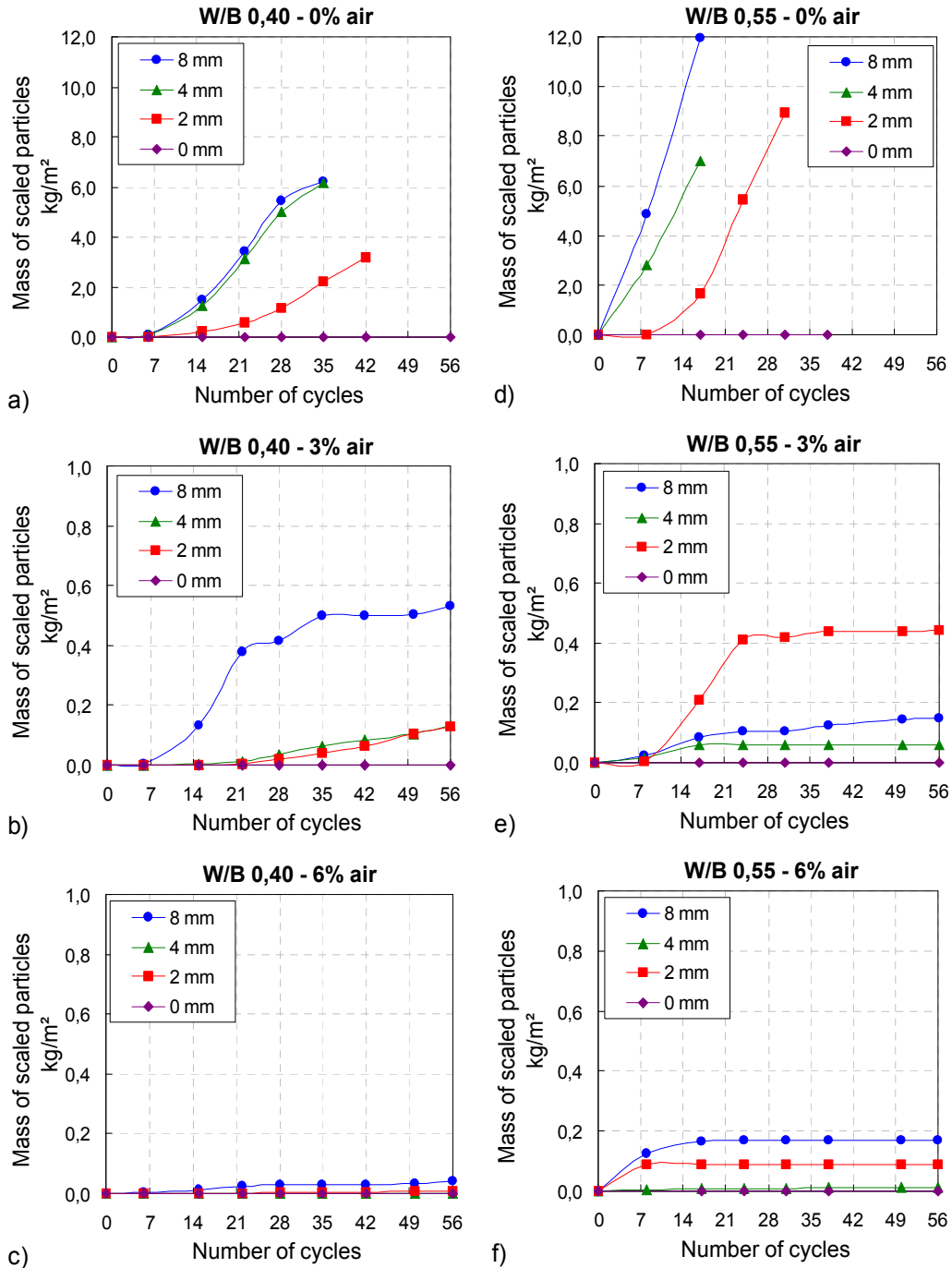


Figure 3: De-icer salt scaling test results

Note that the scale of the ordinate for mixtures without air (Fig.3 a.d) is an order of magnitude greater than that for the air-entrained mixtures.

4.3.1 General observations

Mixtures with water/binder ratio of 0.55 (Fig.3 d.e.f) suffer generally more scaling than mortars with water/binder ratio of 0.40 (Fig. 3 a.b.c). The test was stopped before the end of the 56 cycles for mixtures without air

because degradations were too severe to continue. The other mixtures tend to stabilize after a few weeks. There were no noticeable differences in the shape of debris for mixtures with or without air.

4.3.2 Air content

The non air-entrained mixtures tested with a 4-mm and 8-mm thick solution layer suffered severe degradation (reaching 5 kg/m² to 12 kg/m²) in less than 35 daily cycles (Fig.3 a.d). For these mixtures, degradation extended into the sample interior, indicating that internal frost action contributed to disintegration of the specimen (see Figure 4). After 56 daily cycles deterioration was limited to 0.5 kg/m² with the air entrained mixtures. Air content and spacing factors do not seem to make any significant difference on the performance of the air-entrained mortars (Fig. 3 b.c – e.f).



Figure 4: Degradation of the mixture prepared at a W/B 0.55 and 0% Air after 17 cycles

4.3.3 Solution layer thickness

No scaling is observed when the solution is absent from the sample surface. With the exception of Figure 3e the results show that the 8-mm layer of solution causes the most severe scaling, and the overall trend is that scaling increases with the thickness of the solution layer.

5 Discussion

This experimental program was designed to test the following results of the glue spall theory:

- 1) Entrained air reduces bleeding and thus prevents the formation of a weak surface susceptible to scaling.
- 2) The amount of scaling increases with the depth of the salt solution.
- 3) Surface strength governs the susceptibility to scaling.

Figure 3, clearly shows that entrained air improves the scaling resistance of both series of mixtures. These data are consistent with the field studies by Fournier et al. [34], and Laroche et al. [35], which indicated that air

entrained concretes with a spacing factor of less than 250 μm were much more resistant to scaling. The results also indicate that the reduced compressive strength and surface hardness realized with entrained air, is much less influential than the beneficial effect of air entrainment. Although, it is well known that air entrainment reduces bleeding, this phenomenon is unlikely to have had any influence in this case because the mixtures were produced with a VMA that minimizes bleeding. Moreover, the cylinders were sawed in such a way to obtain test surfaces that were not significantly affected by bleeding or mold effects.

Calculations indicate that the glue spall stress at low temperatures is roughly equivalent to the tensile strength of mortar [19, 23]. Therefore, any mechanism that reduces the overall stress on the surface will reduce, if not prevent the occurrence of scaling. If ice forms in the surface air voids, and compresses the surrounding matrix as it tries to penetrate the intersecting pores [20], then air entrainment could prevent salt scaling in much the same way that it prevents internal frost action. This point needs to be further investigated.

Considering the relative importance of air entrainment, it is necessary to compare results obtained from samples with the same level of air in order to ascertain the effect of surface strength on scaling resistance. Comparing Figure 3a&d, and Figure 3c&f, and cross referencing the results of the Brinnell hardness test (Table 3), one can see that a reduction in surface strength leads to an increase in scaling.

With the exception of figure 3e, it appears that 8 mm of salt solution results in more scaling than the other thicknesses. This trend is in qualitative agreement with the prediction of the glue spall theory, and tends to confirm that the interaction of the ice layer with the surface of the material has a significant influence on the mechanisms of deterioration. This conclusion is further emphasized by the fact that no scaling occurs when the solution is absent from the surface (i.e. Figure 3 - 0 mm). This observation is valid for all mixtures including those without entrained air. In this case, surface evaporation is probably not responsible for the absence of scaling because care was taken to keep the surface moist prior to the onset of freezing.

In accordance with the glue-spall theory [19,23], this work highlights the relevance of the ice layer/test surface interaction. This advance represents an important contribution to the community interested in salt scaling. Testing laboratories usually pay little attention to the thickness of the solution layer placed on the surface of the specimens. Such a lack of control could be partially responsible for the variability in scaling test results that are often reported in the literature.

6 Conclusion

The experimental program was designed to test the predictions of the glue spall theory, and the suggestion that air entrainment is beneficial due to its ability to reduce bleeding. In accordance with the predictions of the theory, the results indicate that salt scaling increases with the thickness of the ice layer, and a reduction in surface strength. However, the results indicate that air entrainment is not beneficial due to a corresponding reduction in bleeding. In addition, the results indicate that internal frost action is not the cause of salt scaling. Therefore, more work is necessary to determine the means by which air entrainment reduces the susceptibility to salt scaling.

7 References

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