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Evaluation of de-icer deterioration of concrete

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Evaluation of de-icer deterioration of concrete

by

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ABSTRACT

The work presented in this thesis involves the study of deterioration of concrete caused by using deicers. This thesis includes two papers resulting from the study: 1). Scaling resistance and evaluation of concrete containing slag cement and 2). Effect of the Interfacial Transition Zone on Joint Deterioration of Concrete Pavements. In the first paper, an alternative test method was proposed to evaluate scaling resistance of concrete containing SCMs, which is believed to better represent the field performance, and both standard method and alternative method was performed and compared. The relationship between air system and scaling resistance and the methods to test air system are also studied. In the second paper, deicer deterioration of interfacial transition zone is observed by Scanning Electron Microscopy, to study the mechanism behind the deterioration of joint of concrete pavements.

In Paper 1, Scaling resistance and evaluation of concrete containing slag cement has been studied. Slag cement (slag), has long been used as a supplementary cementing material in concrete mixtures. With the addition of slag, concrete generally exhibits good long-term strength and durability. However, various authors have expressed concern about the scaling resistance of concrete containing slag cement, especially when the dosage is high. Much of the concern to appears to be based on the results from laboratory scaling tests (ASTM C672), which tend to overestimate damage when compared to field observation and results. The reasons for this are thought to be because at high replacement levels, SCM mixtures can take longer to set and develop their properties, but neither of these factors is considered in the finishing and curing procedure of laboratory tests. As a result, a modified test which takes these variables into account has been drafted and used in this project (Hooton 2012).

The experimental research focused on the evaluation of scaling resistance tests, including the new test and the ASTM C672 test with normal curing and an accelerated curing regime used by VA DOT. A total of 28 concrete mixtures were studied using high alkali cement and low alkali cement, Grade 100 and Grade 120 slag with 0, 35, and 50 percent slag replacement by mass of total cementing materials. The objective of the paper is to recommend a test method that is more representative of field performance for concrete in a salt scaling environment. It is recommended that the proposed test method be submitted to ASTM for acceptance as a new test method.

In Paper 2, Effects of the Interfacial Transition Zone on Joint Deterioration of Concrete Pavements is studies. In the Midwestern region of the U.S., some concrete suffers from deterioration of sawn joints, generally related to freezing and thawing of saturated concrete. One form of the distress occurs as cracks forming about one inch from, and parallel to, the free surface. These cracks are observed to go around the coarse aggregate and leave little or no paste adhering to it.

It is hypothesized that a mechanism for this observation is that when joints are sawn, the cut exposes the interfacial transition zone (ITZ) around coarse aggregate particles. Water or salt solution subsequently held in the saw-cut can be wicked around the coarse aggregate particles through the ITZ. Subsequent freezing and thawing action can lead to the aggregate being separated from the paste, and a crack propagating to the surface. Once the now-loose piece is removed by traffic loading, the cycle is repeated. The mechanisms behind the separation of aggregate and paste are not clear and may include freezing expansion of water, salt crystallization and dissolution of the ITZ. This paper describes an experimental program

aimed at investigating this hypothesis and to assess what mechanism(s) can be responsible or

the observed behavior. It was found that chemically induced expansion of the paste likely

caused a stress concentration around the non-expanding aggregate, so resulting in a crack in

the ITZ.

CHAPTER 1. INTRODUCTION

General Introduction

In Midwest region of U.S., concrete suffers from durability problem because of coldness and snowing. Beside Freeze-Thaw problem brought by winter, deicer deterioration also causes troubles to concrete pavements. F-T damage, scaling, D-cracking, and deicer deterioration, with different mechanisms, these phenomenon cause a huge problem in Midwest area, and it is critical to study the mechanisms and cause behind these deteriorations.

Deicer is widely used in cold regions to melt the ice on the pavement. As efficient as deicer is, problems regarding durability of concrete were raised because of deicers. One of the major problems is scaling, the removal of small flakes of concrete at the exposed surface. Though scaling does not damage the integrity of concrete, it increases the access of moisture, which offers a preferred environment for calcium leaching and C-S-H gel decomposition to occur. At the same time, the ingress of moisture due to scaling will increase the susceptibility of concrete to physical frost damage due to fluctuating temperature (Beckett 1983, Sellevold and Farstad 1991). Concrete containing slag cement generally exhibits good long-term strength and durability characteristics. However, concern has been expressed about the deicer scaling resistance of concrete containing slag, especially when the dosage of slag exceeds 50% of the total cementitious material in the mixture (TRB 1990, Klieger and Isberner 1967, Marchand et al. 1994.1995, Luther et al. 1994). Much of the concern appears to be based on the results of laboratory scaling tests based on ASTM C 672, despite indications that such mixtures often perform well in the field. This thesis include a paper to evaluate alternative

test methods, including finishing and curing practices, to develop an alternative laboratory test method to ASTM C 672 that would better represent the field performance of concretes containing slag cement. A test method already in use by the Quebec Ministry of Transportation was evaluated, and several modifications were tested. As a result, a new draft test method has been proposed (Hooton et al. 2012).

The other major problem related with deicer is joint deterioration, which is the distress in pavement exhibited in the form of cracks that appear and grown in this area. And these cracks are observed to go around the coarse aggregate and leave little or no paste adhering to it. One paper of this thesis describes an experimental program aimed at investigating this hypothesis. Previous phase of this project already investigated the factors that may impact the property of ITZ. This phase of the project will try to explore if this sort of joint deterioration is related to both salt solution and F-T cycles, or salt solutions along will cause damage in ITZ.

Objective of Thesis

The main purpose of this work is to perform a comprehensive study of two different aspects of the deicer deterioration to concrete. In order to achieve this purpose, the following objectives are included in this thesis:

- Investigation on determining the effects of different replacing level of slag, type of slag, and type of cement on scaling resistance.
- Determine the rate of scaling damage through F-T cycles.
- Evaluation of different laboratory scaling test methods, including finishing method, curing method, and deicer that applied.
- Determine the deterioration of deicers to concrete joint without F-T cycles

- Determine the effects of different deicer solutions to ITZ without F-T cycles.

Thesis Organization

This thesis is divided into five chapters. Chapter 1 provides a general introduction and thesis objectives.

Chapter 2 provides a brief literature review of mechanisms of deicer scaling damage and ITZ deterioration, factors affecting scaling and ITZ deterioration, and how to prevent each deterioration. The review is aiming to provide background and information about deicer deterioration of concrete.

Chapter 3 and 4 includes selected papers that have been either submitted for publication or ready for submission to peer reviewed journals. The results and conclusions of this thesis are presented in these two chapters.

Chapter 5 summarizes the major findings of the study and the recommendations for future research and industrial applications.

CHAPTER 2. LITERATURE REVIEW

Introduction

Premature deterioration of joints in concrete pavements is reportedly primarily caused by saturated freeze thaw cycling, but Zhang and Taylor (2013) have also reported some added impact of freezing salt solutions on the interfacial transition zone (ITZ). This review discusses current thinking related to the ITZ, freeze thaw and salt scaling distress.

Premature deterioration of sawn joints in pavements in cold regions has been the focus of some study in the past 10 years. The motivation for this effort has been to address the needs of agencies to reduce the maintenance costs in their pavements. While the deterioration is limited in terms of the total miles of pavement, some local agencies have been significantly impacted by the phenomenon.

Typically the distress starts as a shadowing near sawn joints that subsequently leads to loss of material. Cores taken from such locations typically contain small flakes of concrete due to cracking parallel to and at about 1-mm spacing below the exposed surface. This is likely due to water that has penetrated about 1 mm into the paste subsequently freezing and expanding, with layers of flakes being generated with freeze-thaw cycles (Taylor, Sutter and Weiss, 2012). Deicing salts likely add to this distress by a number of mechanisms (Giergiczny et al., 2009).

However, it was observed in the field in a number of locations that the distress resulted in cracks forming in 1" steps rather than 1 mm steps (Figure 1). These cracks were observed to go around the coarse aggregate particles leaving little or no paste adhering to

them, leading to the hypothesis that the interfacial transition zone was a part of the mechanism.

Figure 1. **Joint deterioration in Eau Claire, WI (Zhang and Taylor, 2013)**

Since the last century, the mechanisms behind deicer and F-T related deterioration have been extensively studied by researchers around the world. A number of different mechanisms have been proposed by these researchers.

Mechanisms of Freeze Thaw Distress

F-T deterioration is believed to occur in the pore structure of cement paste and aggregate particles in concrete and is related to the expansion of water as it freezes, among other mechanisms discussed below.

As water freezes, tensile stresses are generated in the paste due to its 9% increase in volume. When this occurs in a saturated cavity, the unfrozen water is driven toward nearby voids. The resistance to this flow will develop hydraulic pressure dependent on the distance between the cavity and the void. If there is an insufficient pore distribution, permanent damage may occur (Powers 1945, Pigeon and Pleau 1995).

The pores in portland cement paste range in size from those within the hydrated cement paste that are of molecular dimension (known as gel pores), through capillary pores (average 0.5 microns) that are initially filled with un-hydrated water, up to bubbles of entrained air (5 microns to 5 mm)(Cordon 1966). The freezing temperature of water is influenced by size of the pores in which it is contained. It is reported that for gel-pores the freezing temperature is as low as -40° C (Pigeon and Pleau1995).

Mechanisms of Salt Scaling Distress

Characteristics:

Scaling does not damage the integrity of concrete below the surface, but it increases the access of moisture, which offers a preferred environment for calcium leaching and C-S-H gel decomposition to occur. At the same time, the ingress of moisture due to scaling will increase the susceptibility of concrete to physical frost damage due to fluctuating temperature. (Sellevold and Farstad 1991, Beckett 1983)

There are many field and laboratory studies have been done regarding characteristics of salt scaling. Valenza and Scherer (2007) reviewed these characteristics in details:

1. Salt scaling is progressive deterioration of a cementitious surface, which consists of the removal of small chips or flakes of binder.

2. Instead of high concentrated solution, the maximum of this damage occurs at 3 wt. %, and it's independent of the solution. (Verbeck and Klieger 1957, Sellevold and Farstad 1991)

3. Without the pool of solution, no scaling will occur on the surface.(Verbeck and Klieger 1957, Sellevold and Farstad 1991)

4. Entraining air in the binder improves resistance to salt scaling. (Stark 1989, Siebel 1989)

5. As long as the minimum temperature is held above -10 C, no damage will occur. At the same time, the amount of damage will increase as the minimum temperature decreases bellow – 10 C and with longer time at the minimum temperature. (Sellevold and Farstad 1991, Studer 1993)

6. Comparing with composition of the pore liquid, the slat concentration of the solution on the surface of concrete is more important. (Sellevold and Farstad 1991, Lindmark 1998)

7. Scaling damage is observed without a critical loss of strength. (Powers 1945, Aitcin and Pigeon 1986)

8. Salt scaling resistance of concrete dose not correlate with susceptibility to internal frost action (Gebler and Klieger 1986, Pigeon and Perraton 1987)

9. Majority of the scaling occurs in the early cycles instead of later (Sorensen 1983, Pigeon et al. 1987)

Osmotic pressure

In 1975, Powers and Helmuth proposed an osmotic pressure theory on the effects of solutions containing salts.

Water in pores does not necessarily freeze when the temperature falls below 0°C due to the presence of dissolved chemicals and the small size of the pores. When temperature reaches the freezing point, instead of freezing all at once, some water freezes, causing concentration of the dissolved ions in the remaining solution to increase, thus suppressing freezing temperature further. Osmosis is the movement of ions seeking to reach local equilibrium, particularly between small, non-frozen pores and larger partially frozen pores, thus setting up potentially significant pressures.

Salt crystallization

Higher potential energy is contained by solute in its supersaturated condition than in a corresponding saturated solution. When this solute crystallizes, this potential energy may be released as expansive pressure. The state of saturation is critical for crystallization in a closed system because critical crystallization pressures are not developed in an unsaturated system. The pressure generated by crystallization from supersaturated deicing salts may be up to 16 MPa, which is 5 to 10 times the tensile strength of concrete (Thaulow and Sahu 2004).

Glue spalling

In 2005, Valenza proposed the glue spalling theory (Valenza 2005, Valenza and Scherer 2006) based on observations of interactions between epoxy and glass. A thin layer of epoxy spread over the surface of sandblasted glass at high temperature, then cooled, will tend to contract more than the glass, which places the surface in tension causing the epoxy will break into smaller pieces and so reflecting cracks into the glass. A similar action is likely when salt solutions freeze on a concrete surface. As temperatures drop, the ice layer will tend to contract up to five times more than the underlying concrete so initiating cracks in the concrete (Pounder 1965, Scherer 2004).

Chemical Effects

Formation of MSH

The effect of magnesium chloride on concrete materials is complicated and aggressive because magnesium and chloride are considered the most aggressive ions to concrete (Biczok 1967). Magnesium and chloride ions may substitute in $Ca(OH)_2$ to form $Mg(OH)_2$ (brucite) and $CaCl_2$ (Catinaud 2000, Lawrence 2008, Xianming and Laura 2009, Monosi 1992, Larry and Thomas 2006, Lawrence and Karl 2008). Also, $MgCl_2$ may convert C-S-H to M-S-H (which has no binding capacity) because M-S-H and $Mg(OH)_2$ are thermodynamically more stable than C-S-H and $Ca(OH)_2$ (Xianming and Laura 2009). Xianming and Laura also concluded that the expansive force from formation of $Mg(OH)_2$ would accelerate the concrete deterioration process.
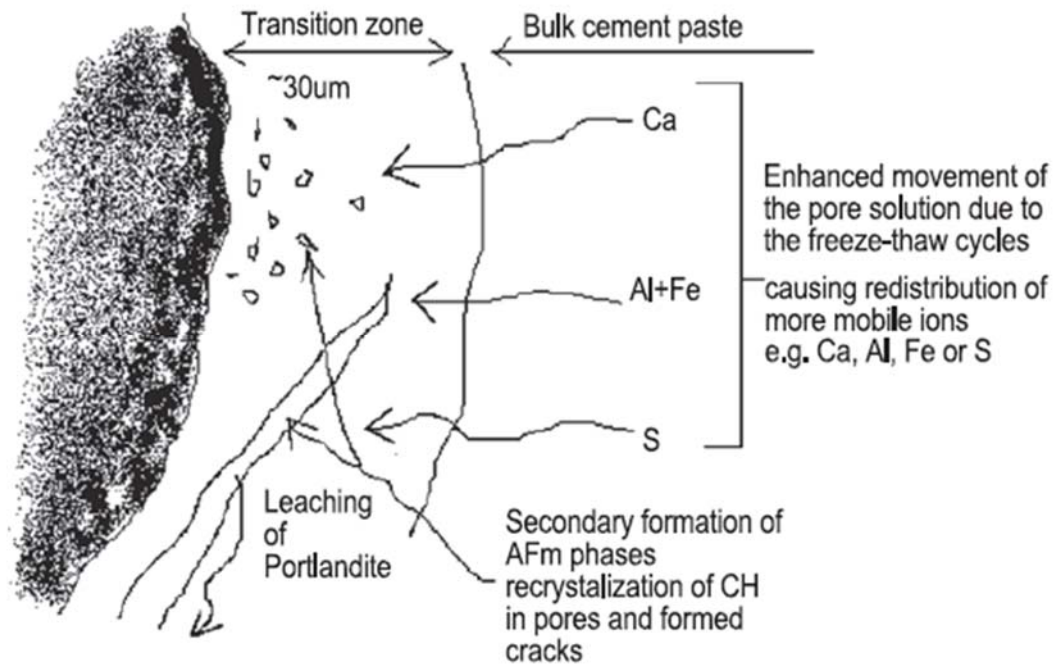
Figure 2. **Phenomena taking place in transition zone (Andrzej, Vesa. 2004)**

Formation of calcium oxychloride

Expansive calcium oxchloride is believed to be a significant cause of deterioration due to reactions with chloride deicers. Both $CaCl_2$ and $MgCl_2$ will cause formation of calcium oxychloride. Chloride ions can penetrate into the hydrated cement pastes relatively quickly (Geout and Revertgate 1992), and leach out $Ca(OH)_2$ (Fig 2), so increasing porosity and susceptibility to freezing (Dirk 1984). Chlorides can also react with the hardened cement paste causing formation of new products such as calcium oxychloride, that may be expansive (Larry and Karl 2006) Reportedly expansion is least for NaCl and greatest for $MgCl_2$. Similarly chloroaluminiate and Friedal's salt may be formed with chloride penetration (Geout and Revertgate 1992, Dirk 1984, Wang and Daniel 2006, Lawrence and Karl 2006, Xianming and Laura 2009).

More detailed formation of magnesium oxchloride formation was described by Gustavo (2009). Low PH of magnesium chloride solution caused instability in concrete pore fluid, leading a leaching of hydroxyl ions and chloride ions' penetration. To balance the large penetration of chloride ions, calcium hydroxide occurs to dissolute to provide more hydroxyl ions. At the same time, because of binding of chloride ions by aluminate phases, AFm, formation of Friedel's salt occurs. In the early age, rapid formation of brucite, Mg (OH)$_2$ limited penetration of magnesium to surface layers of concrete. Meanwhile, penetration of chloride ions causes dissolution of more calcium hydroxide, and this dissolution would saturate the pore fluid with hydroxyl and calcium ions as mentioned above. Eventually, binding capacity of chloride to concrete is met and pore fluid is saturated with chloride. A saturated pore fluid of calcium, chloride, and hydroxyl creates a favorable environment for ion exchange, an exchange between sulphate from ettringite and hydroxyl ions, and this kind of exchange would continue till all sulphate form of ettringite is reacted. Sulphate ions released from ettringite will react with calcium and water to produce gypsum, $CaSO_4.2H_2O$. With enough of calcium, chloride, and hydroxyl ions, formation of calcium oxychloride could also happened. While calcium oxychloride is not stable in solutions unless in highly concentrated calcium chloride solutions, so it tends to dissolve and then release hydroxyl ions for the crystallization of magnesium oxychloride, which is believed to cause concrete to swell and expansion. Leaching of calcium hydroxide may cause lack of calcium hydroxide in pore fluid, as a result, another chemical reaction would begin. Pore fluid with magnesium ions would generate an ion to exchange C-S-H. And this will cause C-S-H to be replaced of calcium by magnesium ions, which will cause the concrete seriously impaired. This whole process depends on temperature, concentration of solution, and pH. When these requirements

are not satisfied, formation of magnesium oxychloride would contribute instead of calcium oxychlroide, and the deterioration process by magnesium oxychloride would be quite severe.

Formation of ettringite

Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is a mineral which is widely found in the mineralogy of hydrated production. Primary ettringite is formed from gypsum and C_3A with appearance of calcium hydroxide. And without sufficient sulfate concentration, the rest C_3A will react with newly formed ettringite to monosulfate and other solutions (Stark 1997). These reactions usually occur in initial hydration and does no harm to concrete since the system is still plastic (Stark 1997, Lee and Cody 1998). The formation of ettringite after concrete hardened is called delayed ettringite formation, and Stark claimed different forms of ettringite are found in concrete, spherical cluster crystals, felt-like or parallel needles with different sizes. The size variation could be cause by composition, pH value of pore solution, the inclusion of ions, etc.

Concretes undergoing DEF suffer a general loss in dynamic elastic modulus (Diamond, 1996). Stark claimed different forms of ettringite are found in concrete, spherical cluster crystals, felt-like or parallel needles with different sizes. The size variation could be cause by composition, pH value of pore solution, the inclusion of ions, etc. small crystals formed by ettringite tend to recrystallize in any voids or cracks that may exist in concrete, while large crystals may not indicate distress (Famy 2001). The existence of DEF-induced ettringite could be in air voids, complete fillings or as linings, and it also could be observed in the paste and interfacial transition zone (Heinz and Ludwig, 1986)

The expansion of ettringite is what makes it a big concern in concrete. The mechanism of its expansion is not fully understood. One possible explanation is that this expansion is caused by the recrystallization (Taylor, Famy and Scrivener, 2001). Monosulfate and ettringite are both intermixed with C-S-H, and if crystal grows in a limited space at high supersaturation would generate substantial pressure. Monosulfate replaced by ettringite recrystallization would generate expansive pressure, especially in confined space, which may cause damage. At the same time, when leaching CH discussed above happened, a reducing pH may cause recrystallization of ettringite, and the crystallization pressure also would damage the microstructure.

Parameters that Impact Scaling

Cementitious materials

The normal used cementitious materials include fly ash, silica fume, and slag. Fly ash has a larger particle size than silica fume, and this causes a slower pozzolanic reaction rate. As a result, slow strength gain is expected. Partially this caused the reduction of scaling resistance for concrete containing fly ash (Gebler and Klieger 1986, Johnston 1987). Studies done by Bilodeau (1991, 1992) et al. indicate that scaling damage will reduce if the 28-day compressive strength reaches 40 MPa. At the same time, more bleeding will cause by fly ash due to the reduced water demand, which also cause a deduction in scaling resistance (Bilodeau et al. 1990)

Slag cement contains the same oxides as portland cement, but in different proportions. The hydration of slag is slow, since the glass must be broken down by hydroxyls

(Stark and Ludwig 1997). As a result, concrete containing slag has a lower strength than OPC in younger age (7-14 days), but after longer curing period, it becomes much denser and stronger. It was proposed that slag would reduce the scaling resistance of concrete (Bilodeau and Malhotra 1993, Setzer 1993). Bilodeau and Malhotra claimed that the difference in strength between concrete containing slag and OPC is not the cause of the rapid scaling occurs in slag concrete, which has an increasing amount of scaling damage in the early F-T cycles. Bleeding could the reason for rapid scaling occurring. Adding slag would increase bleeding since water demand is related to the amount of cement used. With high replacement level of slag, w/c ratio will increase when w/b ratio keeps the same, which will lead to more bleeding and cause a rapid scaling damage.

W/C ratio

Water-cementitous materials ratio (w/cm) impacts the porosity of the paste, in both paste and interfacial transition zone, which means it controls both strength and durability of concrete. Low water-cementitious ratio will have less bleeding and higher strength, and because of these reasons, lowering w/cm ratio results in better scaling resistance (Sorensen 1983, Peterson 1986). Concrete prepared at w/c< 0.3 does not even need air entrainment to have scaling resistance (Foy and Pigeon 1988, Hammer and Sellevold 1990) and its bleeding capacity of cement paste is similar to w/c=0.45 with 20% air. As conclusion, due to low bleeding, low w/cm ratio concrete has a low susceptibility to salt scaling.

Construction procedure

Finishing

Improper finishing practices are common causes for scaling, and those would leave a bad surface for a concrete with good air voids system, which will decrease the scaling resistance of concrete. Commonly improper practices include: a). Start finishing operations before cessation of bleeding, and as a result, bleeding water would trapped beneath the finished surface; b.) Softening of surface by addition of water during finishing, or finishing with bleed water; c.)Loss of air and distortion of air voids at surface relative to that in the body, by prolonged finishing. (Dipayan 2007)

For premature finishing, the surface would seem ready for finishing, but inside of concrete the bleeding is still occurring. This is quite common especially when the rate of evaporation of surface water is higher than the rate of bleeding. Industry recommendation is not to initiate finishing till the footprint impression on the surface to be finished is less than ¼ in.

For softening of surface by addition of water during finishing, finishing operations on a surface containing extra water, no matter from water added during finishing to improve workability, or bleed water sheen that has not been evaporated, both of them will increase the w/cm ratio at the surface, which as a result, reduce the strength, hardness, and scaling resistance. Application of water reducer would benefit the workability while no additional water is adding.

For loss of air and distortion of air voids at surface relative to that in the body, by prolonged finishing, to get an acceptable finished texture and appearance of a surface,

finishing operations may carry on after the period between initial and final set of concrete. This sort of over-finishing may reduce the air content of air-entrained concrete at top of concrete.

Curing

Curing at elevated temperature for short periods will result less scaling resistance (Lanlois and Beaupre 1989), since drying or curing at elevated temperature will produce a coarse microstructure and low cement. Thus, a long moist curing would promote continued hydration, which as a result, a denser microstructure, higher strength, and stronger scaling resistance.

No so much on deterioration of ITZ, but the influence of curing and finishing to scaling resistance is critical for concrete in cold regions. In paper one 'Scaling resistance and evaluation of concrete containing slag', both evaluation method and factors of scaling resistance is studied, and a new test method proposed by Hooton (2012) was evaluated.

Interfacial Transition Zone

To fully understand the mechanisms behind ITZ deterioration, a better understanding of formation and characteristics of the ITZ is necessary. This section reviews both the formation of ITZ, and also the characteristics and parameters that may impact ITZ formation,

Formation of ITZ

The initial formation of Interfacial transition zone, is a cement particle packing process, is considered to be more likely a physical process than a chemical process. This

initial packing of cement particles against aggregates is mainly a physical process from mixing dry ingredients with water, causing adhesion between them (Zimbelmann, 1985).

Two mechanisms have been proposed to explain the formation of the ITZ. One is the wall effect (Maso 1995, Scrivener and Pratt 1994). During placing, the spatial arrangement of unhydrated cement grains becomes looser in the vicinity of aggregate particles. As a result, the porosity and local w/c ratio increase near the surface of aggregate particles. The other side of the wall effect is that hydration products growing away from one cement grain may meet those coming from another cement grain, so mixing and bonding with each other. On the other hand, hydration product growing toward an aggregate particle is one sided and consequently has a different chemistry and morphology from the bulk paste. This wall effect has been confirmed by observing mortars using back-scattered electron imaging (BSEM) (Escadeillas and Maso 1991).

The other mechanism proposed is that of micro bleeding (Chatterji and Jensen 1992). In this mechanism, aggregate particles have a lower submerged weight than cement paste, so settle at a slower rate than cement particles. The void between aggregate particles and paste will be filled by bleeding water. Later, during compaction, the relative movement between aggregates and cement paste particles during vibration will encourage formation of a water-rich layer round aggregate particles. Porosity near the aggregates has been measured to be higher than in the bulk (Goldman and Bentur 1992). Variations in hardness between the different parts of specimen were reported by (Hoshino 1988), but Scrivener and Pratt (1994) observed little difference in the microstructure above and below aggregate particles.

Characteristics of ITZ

Thickness

The thickness of interfacial transition zone has been studied by researchers using various methods. Snyder and Winslow estimated a 15-20 μm transition zone in mortar using mercury intrusion porosimetry (MIP) (1992). A similar result was observed by Scrivener and Pratt (1994) and Bentz and Garboczi (1999) using backscattered electron imaging (BSE). Concrete reportedly has a generally larger transition zone of 30-50 μm around coarse aggregate in high performance concrete (Andrzej and Vesa 2004).

Permeability

The existence of ITZ impacts permeability and strength of concrete (Mehata and Monteiro 2002). Because of its high connectivity and preferential permeability, it impacts transport processes in the concrete, and this kind of influence would facilitate movement of the chloride ions (Delagrave et al. 1997). Chloride solutions ($NaCl$, $CaCl_2$, and $MgCl_2$) are more likely to be applied by agencies as deicer, and chloride solutions would deteriorate concrete both physically and chemically, promoting scaling, map cracking, and paste deterioration. The existence of interfacial transition zone may enhance this kind of influence.

Structure and components

As discussed above, the chemical reactions near the aggregates are slightly different from those in the bulk paste (Ollivier and Maso 1995). This leads to different hydration products forming near the aggregate as detected using micro analysis in a scanning electron Microscope (SEM) (Liao et al. 2004).

Components in the interfacial transition zone (Figure 3) vary with age as hydration proceeds. A 1 to 3 µm thick film is formed in direct contact with aggregate, with a portlandite inner side and a C-S-H gel outer part (Barnes et al. 1978, Yuan and Odler 1987, Olliver and Maso 1995). Others observed a similar thin layer formed directly on the aggregate surface but identified this as C-S-H (Javels et al. 1974, Scrivener and Pratt 1994). In terms of CH, researchers detected not just more, but larger CH crystal in the zone. (Douglas and Menashi 1994, Olliver ans Maso 1995). High C-S-H content could also be found but the amount of monosulfate is similarly to bulk in ITZ (Kjellsen and Wallevik 1998).

As for porosity and pore structure, ITZ has a significant higher porosity than bulk paste (Ollivier and Maso 1995, Yuan and Odler 1987, Scrivener and Pratt 1994). Not only is the amount of pores greater in the ITZ, but the pores are larger (Olliver and Maso 1995, Kjellsen and Wallevik 1998). It is also believed that small cement particles will dissolve and react rapidly, then leave hollow shells inside the ITZ, leading to coarser pores (Douglas and Menashi 1994, Kjellsen and Wallevik 1998).
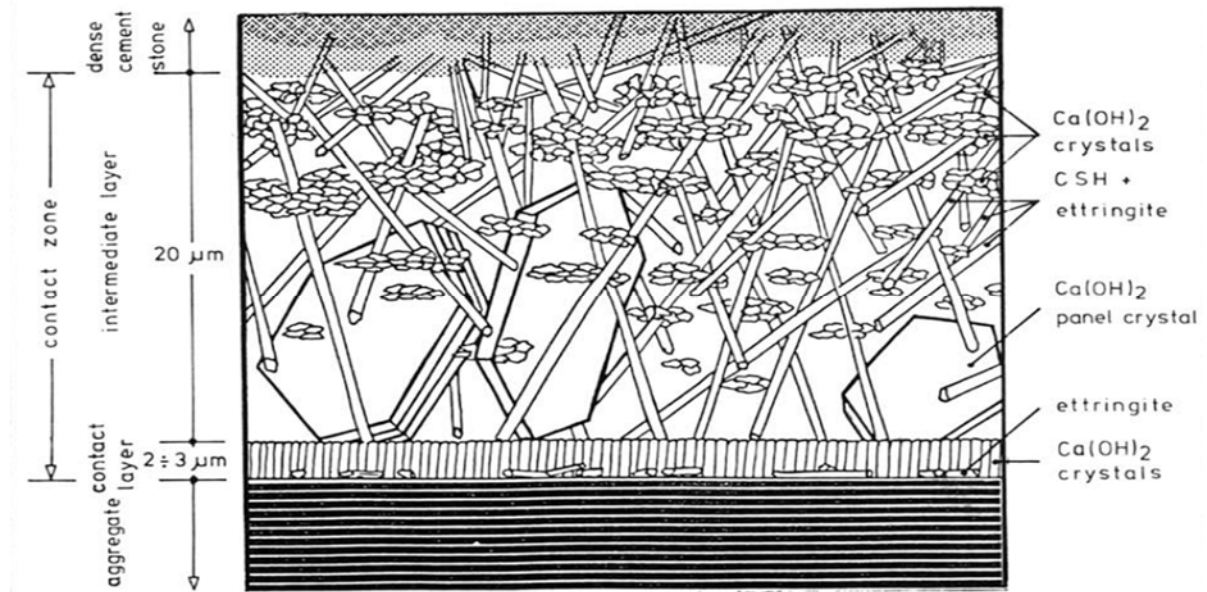
Figure 3. **Model of Interfacial Transition Zone (Zimbelmann 1985)**

Parameters that impact ITZ

Aggregate

The aggregate type is reported by some as having relatively little effect on the microstructure (Crumbie 1994, Older and Bentur 1994), while others demonstrated that mineralogical nature of aggregate had a measurable impact (Odler and Zurz 1995, Minhong and Odd 1990, Ping and Beaudoin 1991). The reaction between calcite and paste can result in an improvement in the aggregate-cement bond (Olliver and Maso 1995) due to calcite reaction with tricalcium aluminate to form calcium carboaluminate phases in the ITZ (Yuan and Odler 1995). The influence of aggregate size on interfacial transition zone is less complex. Reducing aggregate size tends to reduce the thickness of interfacial zone. (Amir E. Menashi D. Jan O 2003, Xie P and J.J B 1991, Tulin and Mustafa 2003)

Water to cement ratio, and cement type

The water cement ratio impacts the microstructure and composition of the interfacial transition zone. Low water/cement ratio enhances the efficiency of cement grans' packing and so minimizes the width of the ITZ (Crumbie 1994, Sidney and Huang 2001, Andrzej and Vesa 2004, Kjelleson et al. 1998, Amir et al. 2003). However, this kind of impact only effects the about first 5 um from the aggregate (Crumbie).

However, there are researchers who found that w/c ratio had little or no effect on the extent of the ITZ (Bentz and Garboczi 1992, Diamon and Huang 2001).

Silica fume, fly ash, blast slag are incorporated in a concrete mix by substitution of cement. And due to the finer grain size, it was believed that pozzolanic and supplementary cementitious materials increases impermeablity, density, and other microstructure related properties. There were some field and laboratory studies showing a potential of scaling by adding SCMs. But there are also studies show that scaling resistance of concerts may increase with cementitious materials. In fact, the inadequate curing and lack of maturity are often found to be the cause of high salt deterioration potential than material itself.

Salt deterioration resistance will improve with the more silica fume, which was believed to be attributed to the strength increase (Aitcin and Pigeon 1986, Jacobsen and Farstad 1991), since it reduces porosity and increases the fracture toughness. The impaction of silica fume to scaling resistance depends on w/c ratio. For lower w/c ratio (w/c<0.35), silica fume has a miner effect on scaling resistance (Sorensen 1983), but for higher w/c ratio (w/c>0.4), silica fume improves the salt scaling resistance (Jacobsen 1991). Some experimental results do not show this trend, and it was believed that sample preparation

technique causing a weak surface, which leads to a low scaling resistance (Janeva et al. 2002, Valenza and Scherer 2007). Adding silica fume also decreases the permeability of ITZ, increase the density of ITZ, which as a result, decrease the possibility of ITZ deterioration by deicers.

Problematic

The interfacial transition zone is considered the weakest region of concrete, and can have significant impact on both mechanical properties and durability of concrete (Tasong et al. 1998). While the effects of ITZ on bonding have been studied extensively, few researchers considered the influence of deicer on the ITZ. Because of the high porosity and permeability, there is a potential that the ITZ would be impacted by the ingress of deicer ions.

In 2013, Zhang and Taylor hypothesized that the ITZ around coarse aggregate particles exposed by saw-cutting in slabs on grade may be deteriorated under the action of deicing salts in cold weather (Figure 1). Three mechanisms may be responsible for this damage: 1) water expansion when freezing, 2) salt crystallization or 3) dissolution of the ITZ.

Valenza and Scherer (2006) suggested that osmotic pressure caused by freezing salt solution is about 160 psi, and the crystallization pressure is about 374 psi according to Correns (1949), but the typical tensile strength of concrete with w/c ratio 0.45 is about 650 psi (Bhanja and Sengupta 2005). These figures indicate that the first two mechanisms then are unlikely to be dominant. Due to this, chemical dissolution during F-T cycles is also a factor of this deterioration. Calcium hydroxide could be dissolved with the presence of deicing salt solution (Sutter et al. 2006). The combination of three damage discussed above

could cause the dissolutions observed in Fig 1 and Fig 4. The mechanism behind this

deterioration would be studied in this thesis.

A   **B**

Figure 4.   **Test results from Zhang and Taylor (2013)**

A: Sample in water during freezing and thawing showing paste pushed above the aggregate
B: Sample exposed in 3% NaCl solution shown washed aggregate on concrete

Figure 4A shows that paste around the aggregate in the middle of the sample

separated from the aggregate after F-T cycles. Figure 4B shows that the aggregate on the top

is partially exposed by deterioration from NaCl solution.

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CHAPTER 3. DEICER SCALING RESISTANCE AND RESISTANCE AND EVALUATION OF CONCRETE CONTAINNG SLAG CEMENT

Xin Wang[1], Kejin Wang[2], and Peter Taylor[3]

Abstract

Slag cement (slag), has long been used as a supplementary cementing material in concrete mixtures. With the addition of slag, concrete generally exhibits good long-term strength and durability. However, various authors have expressed concern about the scaling resistance of concrete containing slag cement, especially when the dosage is high. Much of the concern to appears to be based on the results from laboratory scaling tests (ASTM C672), which tend to overestimate damage when compared to field observation and results. The reasons for this are thought to be because at high replacement levels, SCM mixtures can take longer to set and develop their properties, but neither of these factors is considered in the finishing and curing procedure of laboratory tests. As a result, a modified test which takes these variables into account has been drafted and used in this project (Hooton 2012).

The experimental research focused on the evaluation of scaling resistance tests, including the new test and the ASTM C672 test with normal curing and an accelerated curing regime used by VA DOT. A total of 28 concrete mixtures were studied using high alkali

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cement and low alkali cement, Grade 100 and Grade 120 slag with 0, 35, and 50 percent slag replacement by mass of total cementing materials. The objective of the paper is to recommend a test method that is more representative of field performance for concrete in a salt scaling environment. It is recommended that the proposed test method be submitted to ASTM for acceptance as a new test method.

Keywords: concrete scaling, slag cement, deicer, ASTM C672

Introduction

Concrete containing slag cement generally exhibits good long-term strength and durability characteristics. However, concern has been expressed about the deicer scaling resistance of concrete containing slag, especially when the dosage of slag exceeds 50% of the total cementitious material in the mixture (Klieger and Isberner 1967, Luther et al. 1994). Much of the concern appears to be based on the results of laboratory scaling tests based on ASTM C 672, despite indications that such mixtures often perform well in the field.

The initial phase of this project consisted of field surveys of portland cement concrete pavements and bridge decks containing slag cement. These surveys were conducted to evaluate whether the addition of slag cement to the concrete mixtures increased the surface scaling caused by the routine application of deicer salt. From this study, it appeared that construction-related issues played a bigger role in the observed scaling performance than did the amount of slag in the concrete mixture (Schlorholtz et al. 2008). The work also indicated that the ASTM C 672 test method may be more severe than most environments.

A second phase was undertaken to evaluate alternative test methods, including finishing and curing practices, to develop an alternative laboratory test method to ASTM C

672 that would better represent the field performance of concretes containing slag cement. A test method already in use by the Quebec Ministry of Transportation was evaluated, and several modifications were tested. As a result, a new draft test method has been proposed (Hooton et al. 2012).

This paper contains the results of scaling tests discussed above, and also contains air parameter test results. The purpose of the work was to investigate the new draft test method, and also the impacts of slag replacement levels and cement alkali contents on scaling resistance. Air parameter tests (AVA, ASTM C 457 Rapid Air) were performed to evaluate air system in concrete samples

Experimental Work

Materials

Cementitious materials used in this work were similar to those used in the work reported by Hooton (2012). Aggregates used were local Iowa materials.

Cementitious materials

Two ASTM Type I Portland cement types were utilized: low alkali (LA), and high alkali (HA). Two slag cements representing ASTM C989 Grades 100 and 120 were obtained. Results of XRF analyses of the cementitious materials are presented in Table 1.

Table 1. Chemical analysis of the low and high alkali cements

	High Alkali Cement	Low Alkali Cement	Slag Cement
	%	%	%
SiO_2	20.15	20.39	37.2
Al_2O_3	5.44	4.71	9.48
Fe_2O_3	2.35	2.79	0.47
CaO	62.33	63.55	40.1
Na_2O	0.21	0.19	0.26
K_2O	1.2	0.5	0.41
MgO	2.44	2.6	10.99
P_2O_5	0.12	0.09	0.01
SO_3	3.54	2.44	1.11
TiO_2	0.27	0.22	0.43
SrO	0.08	0.07	0.36
Mn_2O_3	0.07	0.16	
ZnO			0.95
LOI	1.94	2.26	

Chemical admixtures:

The air-entraining admixture was a rosin based material and the water reducing

admixture was a polycarboxylate based high range water reducer.

Aggregates:

The aggregates used were 1" crushed limestone (Table 2) and a river sand from

(Table 3).

Table 2. Coarse aggregate properties

Sieve Size	Cumulative percent retained by mass
1"	0.74
3/4"	17.55
1/2"	55.05
3/8"	69.78
No. 4	92.95
Pan	99.88
Relative density	2.66
Absorption %	0.77

Table 3. Fine aggregate properties

Sieve size	Cumulative percent retained by mass
3/8 in	0
No.4	2.5

No.8	12.2
No.16	28.6
No.30	62.7
No.50	93.0
No.100	99.7
Pan	-
F.M.	2.98
Relative density	2.68
Absorption %	0.6

Deicing solutions:

Two solutions were prepared for deicer scaling tests:

- 4 wt% CaCl2 for the ASTM C 672 method

- 3 wt% NaCl for the new method.

Concrete mixtures

Matrix

The matrix of mixture variables included:

- Cement type, high alkali or low alkali

- Slag cement type, Grade 100 or 120

- Slag cement dosage, 0, 20, 35 or 50%

- Curing, as per ASTM C 672 or VA DOT (7days at 73ºF (23ºC) followed by 21 days at 100ºF (38ºC)

The fixed parameters were:

- Cement content, 564 pcy (338 kg/m3)

- w/cm, 0.42

- Target air, 6 to 7%

- Target slump, 4 to 6 inches

Mixture proportions are reported in Table 4.

Batching and mixing

Moisture content of the aggregates was determined according to ASTM C 566 prior to batching and water contents of mixtures were adjusted accordingly.

Mixtures were prepared in accordance with ASTM C192/C 192M.

Four 11.3-in. x 11.3-in. x 3.1-in. slabs were formed and finished in plastic containers from each mix in accordance with ASTM C 672 or the new method as required. A 4x8-in. cylinder was prepared for hardened air void analysis.

Table 4. Concrete mixture proportions

Mix	Cement	Slag	Slag Dose, %	Curing	Cement, pcy	Slag, pcy	Water, pcy	Coarse, pcy	Fine, pcy	AEA, oz/cwt	WRA oz/cwt
1	High Alkali	-	0	Standard	564	0	236	1471	1661	1.08	8.96
2	High Alkali	G100	20	Standard	451	113	236	1464	1654	1.08	8.96
3	High Alkali	G100	35	Standard	367	197	236	1460	1649	1.08	8.96
4	High Alkali	G100	50	Standard	282	282	236	1455	1644	1.08	8.96
5	High Alkali	G120	20	Standard	451	113	236	1464	1654	1.08	8.96
6	High Alkali	G120	35	Standard	367	197	236	1460	1649	1.08	8.96
7	High Alkali	G120	50	Standard	282	282	236	1455	1644	1.08	8.96
8	Low Alkali	-	0	Standard	564	0	236	1471	1661	1.08	8.96
9	Low Alkali	G100	20	Standard	451	113	236	1464	1654	1.08	8.96
10	Low Alkali	G100	35	Standard	367	197	236	1460	1649	1.08	8.96
11	Low Alkali	G100	50	Standard	282	282	236	1455	1644	1.08	8.96
12	Low Alkali	G120	20	Standard	451	113	236	1464	1654	1.08	8.96
13	Low Alkali	G120	35	Standard	367	197	236	1460	1649	1.08	8.96
14	Low Alkali	G120	50	Standard	282	282	236	1455	1644	1.08	8.96
15	High-Alkali	-	0	VDOT	564	0	236	1471	1661	1.08	8.96
16	High-Alkali	G100	20	VDOT	451	113	236	1464	1654	1.08	8.96
17	High-Alkali	G100	35	VDOT	367	197	236	1460	1649	1.08	8.96
18	High-Alkali	G100	50	VDOT	282	282	236	1455	1644	1.08	8.96
19	High-Alkali	G120	20	VDOT	451	113	236	1464	1654	1.08	8.96
20	High-Alkali	G120	35	VDOT	367	197	236	1460	1649	1.08	8.96
21	High-Alkali	G120	50	VDOT	282	282	236	1455	1644	1.08	8.96
22	Low Alkali	-	0	VDOT	564	0	236	1471	1661	1.08	8.96
23	Low Alkali	G100	20	VDOT	451	113	236	1464	1654	1.08	8.96
24	Low Alkali	G100	35	VDOT	367	197	236	1460	1649	1.08	8.96
25	Low Alkali	G100	50	VDOT	282	282	236	1455	1644	1.08	8.96
26	Low Alkali	G120	20	VDOT	451	113	236	1464	1654	1.08	8.96
27	Low Alkali	G120	35	VDOT	367	197	236	1460	1649	1.08	8.96
28	Low Alkali	G120	50	VDOT	282	282	236	1455	1644	1.08	8.96

Samples were either cured in a standard fog room (ASTM C192) or in accordance with the VA DOT accelerated procedure (7days at 73ºF followed by 21 days at 100ºF).

Tests

Air void analysis

Fresh concrete air voids analysis (Air Voids Analyzer)

Air contents were determined in the fresh concrete in accordance with ASTM C 231.

At the same time, a small amount of mortar sample (20 milliliters) was extracted from fresh concrete by a vibrating cage and a syringe. The extracted mortar was injected into an assembly containing liquids with controlled viscosities. As the mortar was injected, stirring released air bubbles, which rose through the liquids toward a buoyancy recorder at the top of the assembly. The rate that the bubbles rise is a function of their size. A data collection system tracked the change in buoyancy over time, and software determined the size distribution of the bubbles. The entrained air content, spacing factor, and specific surface were calculated from these data by an algorithm built into the device.

Hardened concrete air voids analysis (ASTM C 457)

Air void analysis was performed on one 100 mm x 200 mm concrete cylinder for each mix that had been cured for at least 28 days. The cylinder was cut longitudinally in half so that two specimens approximately 100 mm x 75 mm could be polished. After polishing, surfaces were blackened and the voids filled with barium sulfate, then the air void parameters were measured using the RapidAir 457 image analysis equipment.

Deicer scaling tests

Two primary scaling procedures were evaluated in this study: ASTM C672 and the new method (Hooton 2012). Two curing methods were used: standard curing and, VA DOT

accelerated curing. A summary of the differences between these tests and curing conditions is provided in Table 5. For each mixture, four slabs were tested in each method, two under each curing regime.

Table 5. Comparison of the scaling test methods

	ASTM C672	New method
Specimens	Surface area 72 in^2. Depth 3 in. 2 specimens / mix	Unchanged
Finishing	Finishing after the concrete has stopped bleeding and then brush with a medium-stiff brush	Finishing after consolidation
Curing	14 days at 100% RH + 14 days at 50% ± 5% RH	Mix 1, Mix 8, Mix 15, Mix 22 : 14 days at 100% RH+14 days at 50% ± 5% RH Mix 2-7, Mix 16-21 SCM 28 days at 100% RH+14 days at 50% ± 5% RH Mix 9-14, Mix 23-28: 7 days at 100 RH+ 21 days at 38°C 100% RH + 14 days at 50% ± 5% RH All samples are saturated in solution for 7 days before temperature cycling
Solution	4% CaCl$_2$	3% NaCl
Freezing and thawing cycles	50 cycles Freezing at -18 ± 3°C for 16 ± 1h Thawing at 23°C ± 2°C for 8 ± 1h	50 cycles Freezing at -18 ± 3°C for 16 ± 1h Thawing at 23°C ± 2°C for 8 ± 1h

Evaluation of Surface quality	Every 5 cycles Visual assessment Mass Loss	Every 5 cycles Visual assessment Mass loss

After each 5 cycles, mass loss was determined by measuring the mass of the flakes loosened from the surface. At the same time, a visual rating was assessed according to Table 6.

Table 6. Visual rating of surface from ASTM C 672

Rating	Condition of Surface
0	no scaling
1	very slight scaling (3 mm [⅛ in.] depth, max, no coarse aggregate visible)
2	slight to moderate scaling
3	moderate scaling (some coarse aggregate visible)
4	moderate to severe scaling

Results

Air system test

Air parameters from both AVA and ASTM C 457 rapid air are given in Table 7. Air parameter results from University of Toronto are also presented in Table 8 (Hooton et al. 2012) for comparable mixtures.

Scaling test

Results of the scaling test are given in Table 9 and Table 10, both from this work and as reported by Hooton for comparable mixtures.

The procedure followed in this work was based on the recommendations developed by Hooton et.al (2012). This means there are differences between the procedures because the final procedure was developed after they completed their laboratory work. For the standard curing set, the mixtures containing supplementary cementitious materials (SCMs) were wet-cured by Hooton et al. for 14 days while, in this work, they were wet-cured for 28 days. For the VDOT accelerated curing set, Hooton et.al. did not dry samples between the end of the accelerated curing and the start of soaking, but this step reportedly made scaling worse (Hooton, 2012)

Table 7. Air parameters from AVA and rapid Air

	Iowa State University				University of Toronto	
Mix	Spacing factor		Specific surface		Mix	Spacing factor
	AVA	Rapid Air	AVA	Rapid air		Rapid Air
1	0.305	0.164	15.00	27.70	1	0.247
2	0.444	0.225	12.40	27.04	8	0.239
3	0.326	0.403	17.50	14.62	9	0.283
4	0.644	0.324	9.50	17.66	10	0.155
5	0.357	0.445	13.80	11.91	14	0.214
6	0.391	0.341	15.00	13.02	15	0.253
7	0.443	0.243	12.10	19.85	16	0.23
8	0.579	0.086	11.20	29.71	1	0.247
9	0.432	0.071	13.50	26.71	8	0.247
10	0.392	0.169	14.90	23.42	9	0.239
11	0.351	0.110	14.30	27.87	10	0.283
12	0.472	0.151	11.60	23.52	14	0.155

13	0.321	0.118	16.20	26.33	15	0.214
14	0.609	0.142	8.70	25.43	16	0.253
15	0.235	0.150	18.90	28.06	4	0.278
16	0.165	0.136	21.90	21.83	5	0.165
17	0.395	0.109	11.30	28.13	6	0.253
18	0.249	0.160	20.40	22.35	7	0.252
19	0.290	0.166	14.30	20.90	11	0.181
20	0.351	0.120	12.90	21.10	12	0.264
21	0.495	0.132	9.50	25.12	13	0.228
22	0.564	0.070	13.90	19.52	4	0.278
23	0.530	0.084	9.20	24.75	5	0.165
24	0.650	0.052	57.30	34.77	6	0.253
25	0.652	0.042	12.70	23.65	7	0.252
26	0.274	0.091	16.00	25.36	11	0.181
27	0.480	0.154	11.50	24.07	12	0.264
28	0.656	0.171	10.90	27.97	13	0.228

Table 8. Air content of fresh and hardened concrete

Curing method	Mix	Cement type	Slag Type	Slag content (%)	ASTM C23 (%)	AVA (%)	Rapid Air (%)	Slump (in.)	Mix	ASTM C23 (%)	Rapid Air (%)
					Iowa State University				University of Toronto		
Standard curing	1	HA	X	0	6.5	5.1	5.33	4.5	1	6.0	4.84
	2	HA	G100	20	4.0	3.4	3.09	5.5	8	6.2	4.50
	3	HA	G100	35	4.0	3.2	3.39	4.0	9	7.0	4.91
	4	HA	G100	50	7.0	2.7	3.53	5.5	10	7.0	6.80
	5	HA	G120	20	6.0	4.4	4.37	3.0	14	6.2	5.83
	6	HA	G120	35	5.5	3.0	5.15	3.5	15	6.0	6.70
	7	HA	G120	50	6.0	3.6	4.82	4.0	16	6.0	4.52
VDOT curing	8	HA	X	0	6.5	5.5	5.81	3.0	1	6.0	4.84
	9	HA	G100	20	7.0	5.9	8.56	6.0	8	6.0	4.84
	10	HA	G100	35	6.0	5.4	7.67	7.0	9	6.2	4.50
	11	HA	G100	50	6.5	4.1	7.31	6.5	10	7.0	4.91
	12	HA	G120	20	6.5	6.0	7.70	6.0	14	7.0	6.80
	13	HA	G120	35	7.5	5.3	9.99	8.0	15	6.2	5.83
	14	HA	G120	50	5.0	4.8	7.59	9.0	16	6.0	6.70
Standard curing	15	LA	X	0	6.0	2.3	10.47	4.0	4	6.1	3.36
	16	LA	G100	20	6.0	5.5	13.67	7.0	5	7.5	7.77
	17	LA	G100	35	6.0	3.0	6.40	5.5	6	7.0	6.70
	18	LA	G100	50	7.0	4.2	8.23	6.5	7	6.1	4.95
	19	LA	G120	20	6.0	3.5	7.17	3.0	11	7.0	5.92
	20	LA	G120	35	7.0	3.9	8.07	5.5	12	6.5	5.05
	21	LA	G120	50	6.5	3.7	5.94	6.0	13	6.4	5.63
VDOT curing	22	LA	X	0	7.0	1.5	18.64	6.0	4	6.1	3.36
	23	LA	G100	20	6.0	4.5	12.63	7.0	5	7.5	7.77
	24	LA	G100	35	6.0	7.3	14.46	5.0	6	7.0	6.70
	25	LA	G100	50	7.0	1.4	11.45	3.0	7	6.1	4.95
	26	LA	G120	20	6.0	5.5	10.95	4.0	11	7.0	5.92
	27	LA	G120	35	5.0	3.4	6.91	2.5	12	6.5	5.05
	28	LA	G120	50	5.5	1.9	4.85	3.5	13	6.4	5.63

Table 9. Scaling test results from Iowa State University

ISU Data			Scaling test method			
			ASTM C672		New Method	
			4% CaCl2		3% NaCl	
Curing method	Mix No.	Fresh air (%)	Mass	VR	Mass	VR
Standard curing	Mix 1	6.5	391	5	629	5
	Mix 2	4	574	5	636	4
	Mix 3	4	192	4.5	517	4
	Mix 4	7	317.19	4.5	638	4
	Mix 5	6	263.7	4	481	4.5
	Mix 6	5.5	517	3	445	2.5
	Mix 7	6	1118	4.5	1861	5
VDOT curing	Mix 8	6	1467	4	1149	4
	Mix 9	6	1886	5	1863	5
	Mix 10	6	815	5	896	5
	Mix 11	7	1233	4	2063	5
	Mix 12	6	1396	5	2475	5
	Mix 13	7	1650	4.5	1822	5
	Mix 14	6.5	1122	3.5	1761	4
Standard curing	Mix 15	6	286	2.5	779	2
	Mix 16	6	351	2	437	3
	Mix 17	6	323	3	460	3
	Mix 18	7	450	5	1019	5
	Mix 19	6	155	4	138	4
	Mix 20	7	366	3	875	3.5
	Mix 21	6.5	645	3.5	1147	4
VDOT curing	Mix 22	7	927	3	2725	5
	Mix 23	6	2671	4	2475	5
	Mix 24	6	1090	5	1719	5
	Mix 25	7	1943	5	1594	5
	Mix 26	6	1213	5	1824	5
	Mix 27	5	870	3	811	3
	Mix 28	5.5	1517	5	1956	5

Table 10. Scaling test results from University of Toronto

Toronto Data			Scaling test method	
			ASTM C672	New Method
			4% CaCl2	3% NaCl
Curing method	Mix No.	Fresh air (%)	Mass	Mass
Standard curing	Mix 1	6	1064	3692
	Mix 8	6.2	944	934
	Mix 9	7	897	1101
	Mix9 Redo	6.4	290	1013
	Mix 10	7	2568	1698
	Mix 14	6.2	777	761
	Mix 15	6	546	1018
	Mix 16	6	637	1683
VDOT curing	Mix 1	6	1064	3692
	Mix 8	6.2	944	934
	Mix 9	7	897	1101
	Mix9 Redo	6.4	290	1013
	Mix 10	7	2568	1698
	Mix 14	6.2	777	761
	Mix 15	6	546	1018
	Mix 16	6	637	1683
Standard curing	Mix 4	6.1	409	3966
	Mix 4 Redo	9.4	170	487
	Mix 5	7.5	268	78
	Mix 5 Redo	6.8	205	116
	Mix 6	7	527	197
	Mix 7	6.1	580	1221
	Mix 11	7	399	545
	Mix 12	6.5	730	1563
	Mix 13	6.4	1575	2042
VDOT curing	Mix 4	6.1	409	3966

|				
Mix 4 Redo	9.4	170	487	
Mix 5	7.5	268	78	
Mix 5 Redo	6.8	205	116	
Mix 6	7	527	197	
Mix 7	6.1	580	1221	
Mix 11	7	399	545	
Mix 12	6.5	730	1563	
Mix 13	6.4	1575	2042	

Discussion

Air system test

Air content

The relationship between reported air contents from each test method is plotted in Figure 5. The correlations of air content between AVA and other methods (Figure 5a, Figure 5b) are poor. From Figure 5a, most mixes yield a higher air content in the pressure meter than in the AVA, and the similar trend is observed in Figure 5b, where the air content from ASTM C 457 Rapid air is generally higher than AVA. Figure 5c and 1d showed a good correlation between C 231 pressure meter and C 457 Rapid air, both in Iowa State and Toronto. The results from Figure 5 are consistent with the literature (Jian and Jiang 2013, Lazniewska 2012, Wang and Mohamed 2008, Magura 1996, Hover 1993).

The major reason that AVA reports a lower air content result than the pressure meter and rapid air is likely that the AVA only counts voids smaller than 3mm, thus under-reporting the total air content (Jian and Jiang 2013, Wang and Mohamed 2008, Magura

1996). Research conducted by Wang and Mohamed (2008) suggested that 5% air content from the pressure meter is equivalent to 2.3% to 3% total air content measured by AVA.

Spacing factor is a preferred indicator of frost resistance of concrete and is a measure of the distance between bubbles, where a smaller number is desirable. Specific surface represents the number and size of air voids in concrete, where larger value indicates a smaller air void. Both AVA and Rapid-air report these two factors, and the results are presented in Table 8. The relationships between the data reported by AVA and Rapid-air are presented in Figure 6. Spacing factor from AVA is larger than from Rapid-air, and specific surface from AVA is smaller than from Rapid-air. Both results are consistent with previous research (Jian and Jiang 2013, Giergiczny and Glinicki 2009, Wang and Mohamed 2008, Magura 1996).
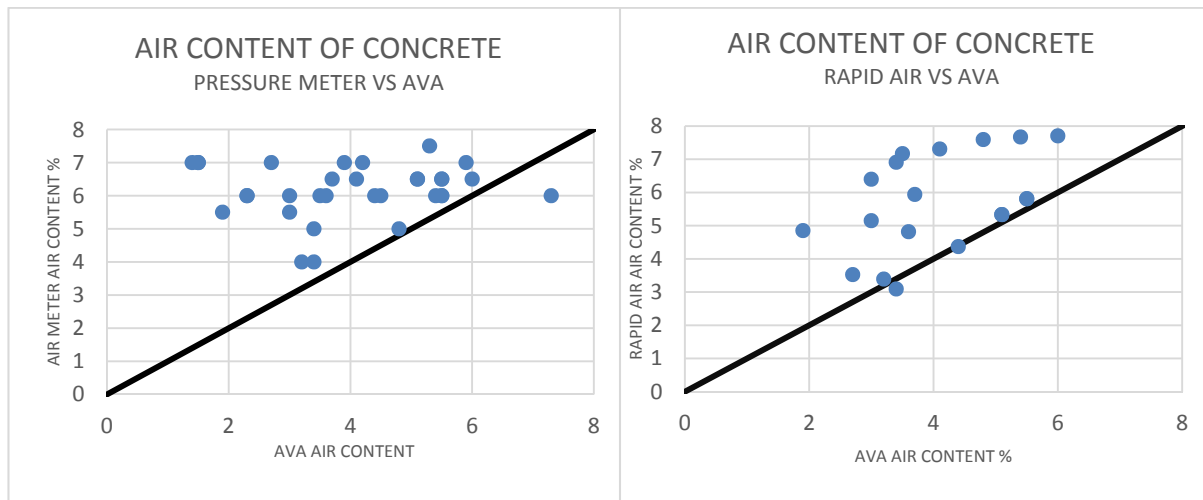
a).   b).
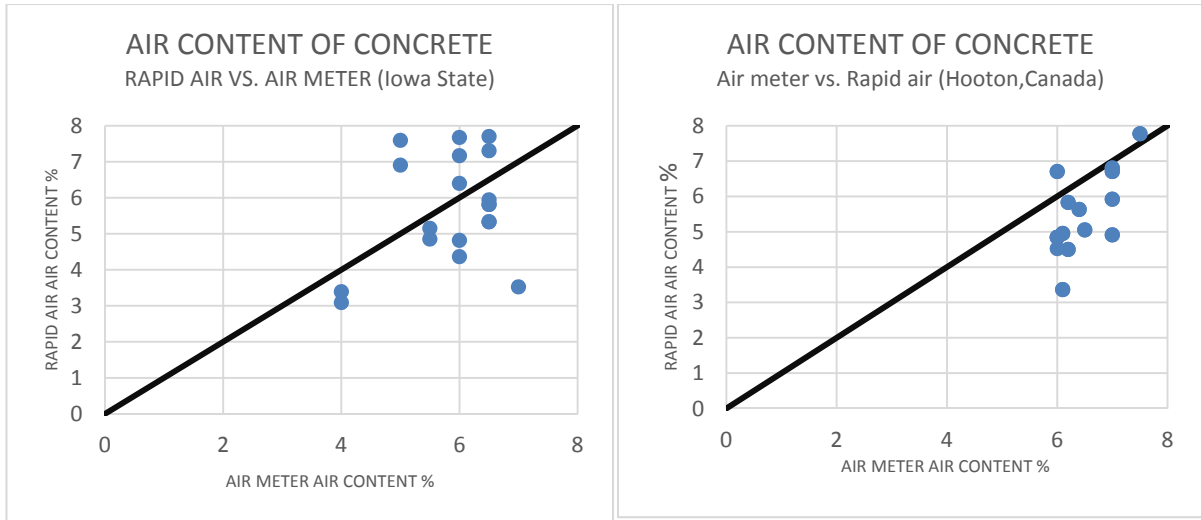
c).   d).

Figure 5. **Relationship of air content % between each method a). Pressure Meter VS. AVA; b). Rapid Air VS. AVA; c). Rapid Air VS. Air Meter; d). Air Meter VS. Rapid Air (Hooton, Canada)**
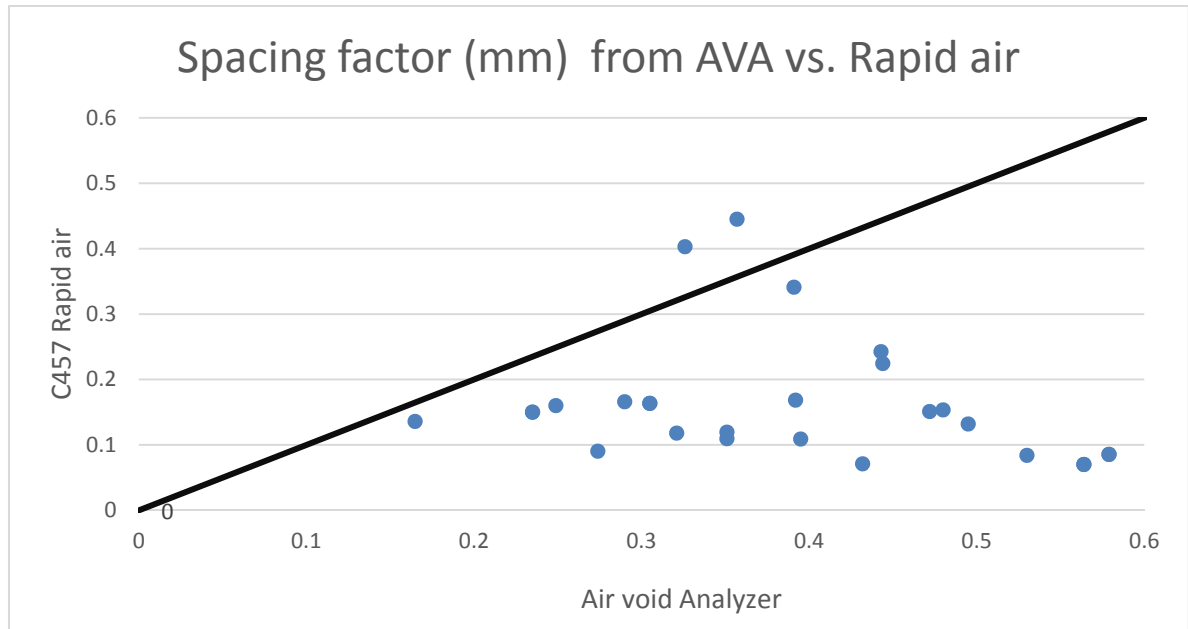

Figure 6. **Relationship between Spacing factor from AVA and Rapid air**

Scaling test

Deicer scaling tests were conducted according to ASTM C 672, the new method with standard and accelerated curing. The average accumulative scaling mass loss and final visual rate is presented in Table 9 for each testing method and mix design.

Rate of mass loss

To evaluate the severity of scaling in different stages of F-T cycles, the maximum mass loss from each increment of 5 cycles was determined and plotted in Figure 7. The horizontal axis shows the cycle in which maximum mass loss was found, and the vertical axis shows the mass loss in gram per square meter.

Regardless of differences between the test methods, it is noticeable that maximum mass loss generally occurred between cycles 10 and 25.

A similar result was found by Stark and Ludwig (1997), where the heavy mass loss occurred early on in slag-cement concretes, both with and without air entrainment. They proposed a chemical cause for this early age scaling tied to carbonation. Metastable modifications of $CaCO_3$ (vaterite and aragonite) are dissolved by frost and chloride, which leads to an extensive erosion of the concrete surface. As a result, in the deeper layer the dissolution of $CaCO_3$ may lead to the new formation of calcite in microstructure. The change in volume may enhance the damage of this dissolution. When the entire carbonated layer has been scaled off, the speed of damage decreases in latter age, since there is not much more modification of $CaCO_3$. This explanation could not be used to explain that the same phenomenon was observed in OPC, which only has calcite instead of vaterite and aragonite.

A weaker surface of concrete slab may also contribute to this increased early age mass loss. A concrete surface may have a higher w/c ratio because of bleeding (Panesar and Chidiac, 2006), at the same time, carbonation shrinkage, if it occurs, would significantly reduce elastic modulus and possibly tensile strength (Valenza and Scherer, 2007). Valenza and Scherer also found that with increasing cycles, the salt concentration would increase in solution, so moving away from the pessimum.

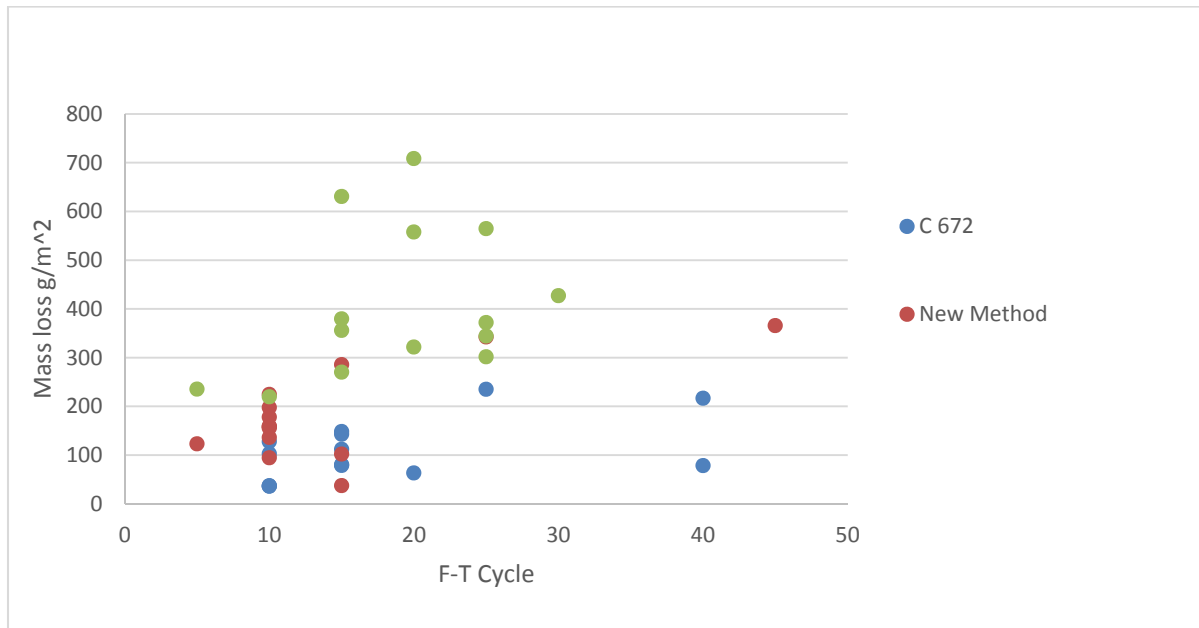The differences between three methods are discussed in the following sections.

Figure 7. **Maximum mass loss per 5 F-T cycles**

Cumulative mass loss and visual rating

One of the limitations of ASTM C 672 is that assessment is by applying a visual rating to the extent of damage to the sample surface. Such an approach is inherently subjective and open to variation.

It was interesting to find that there is a rough linear relationship between mass loss and visual rate. Figure of mass loss vs. visual rate is given in Figure 8. For most samples, such relationship could be found with R^2 over 0.9. This linear relationship would be a good way to estimate scaling damage in the long time period.
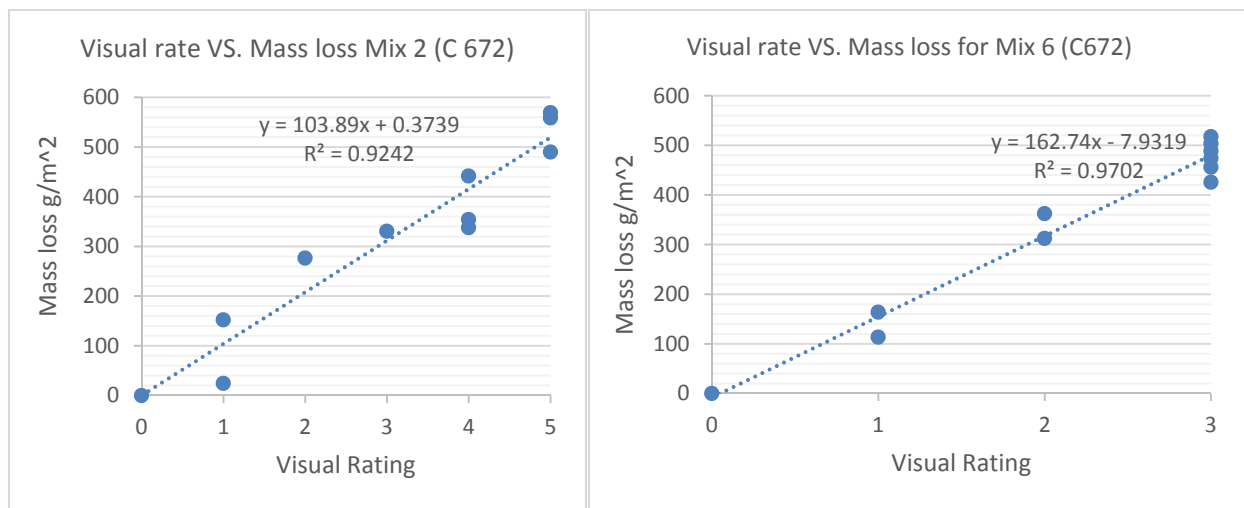

Visual rate VS. Mass loss Mix 2 (C 672)

$y = 103.89x + 0.3739$
$R^2 = 0.9242$

Visual rate VS. Mass loss for Mix 6 (C672)

$y = 162.74x - 7.9319$
$R^2 = 0.9702$

Figure 8.   **Mass loss vs. visual rating**

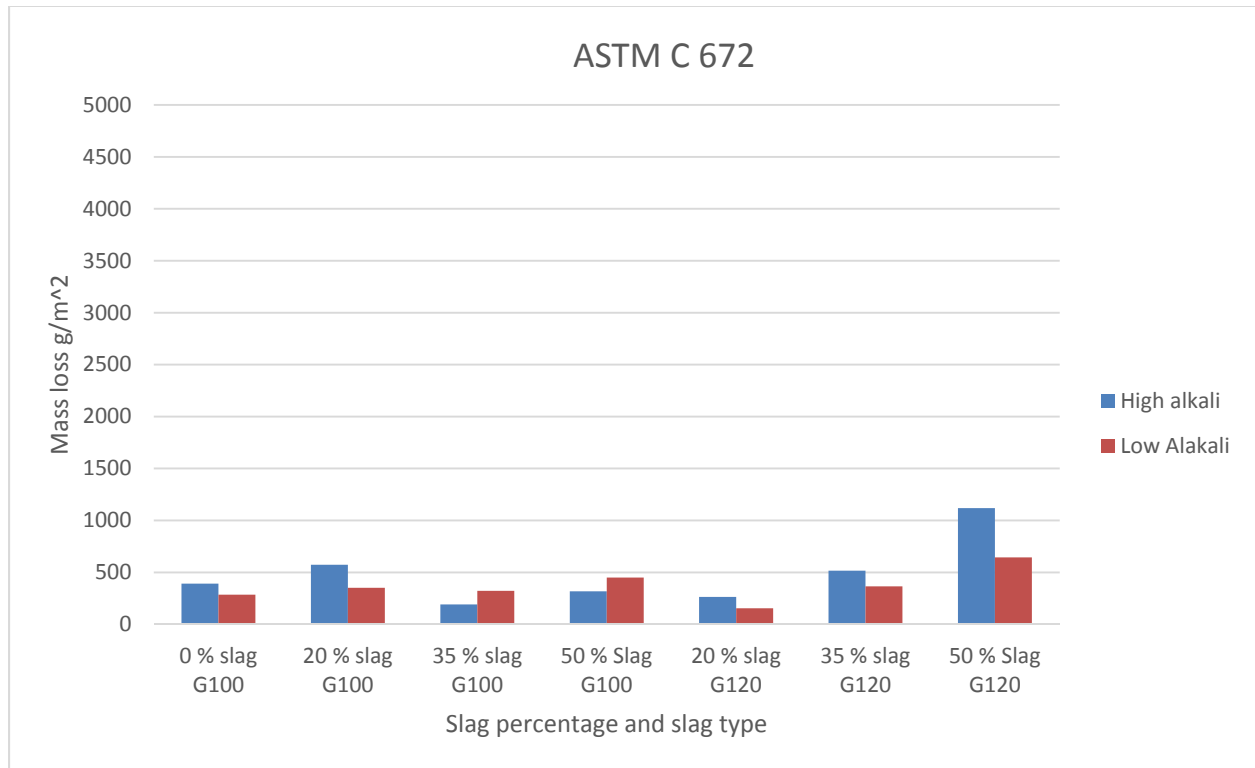*Slag type and replacement level, and cement type*

Figure 9. **Cumulative mass loss of ASTM C672 (High alkali vs. Low alkali, ISU)**
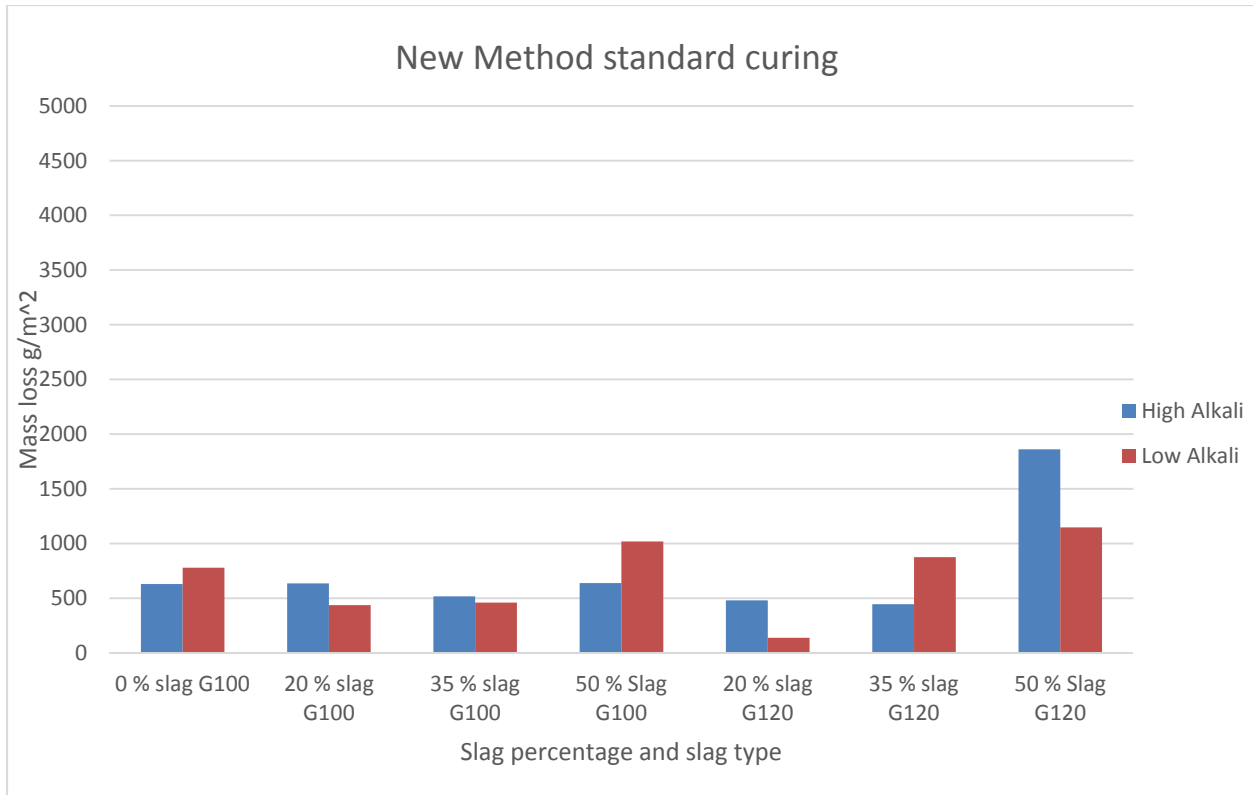
Figure 10. Cumulative mass loss of new method (High alkali vs. Low alkali, ISU)
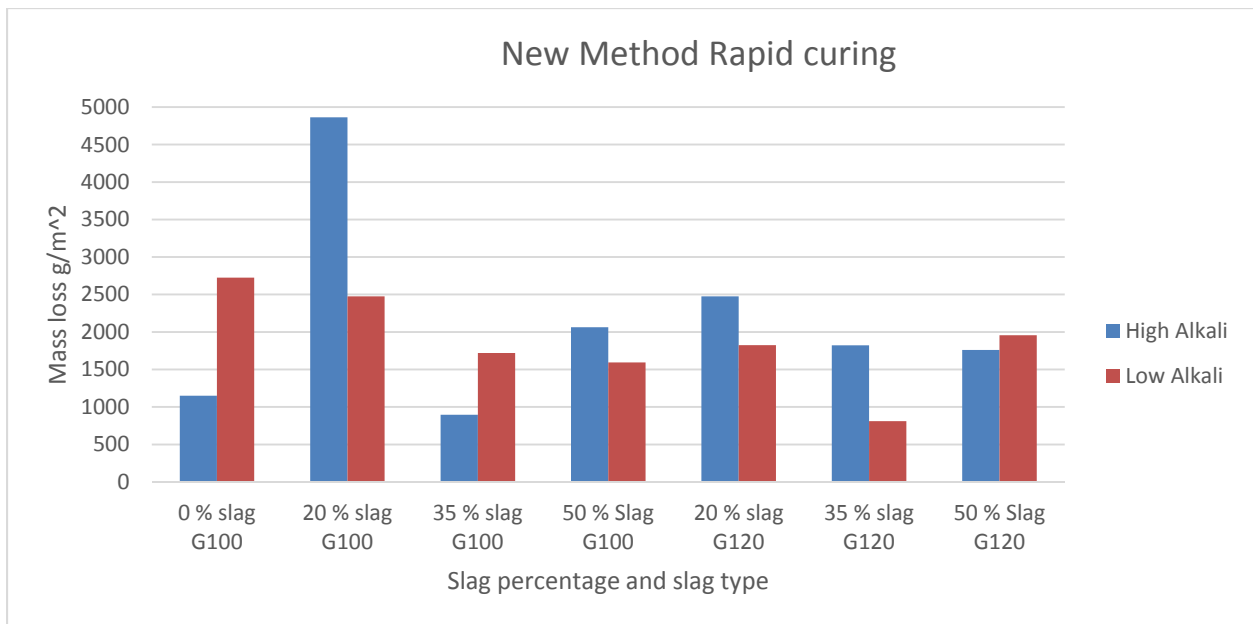

Figure 11. Cumulative mass loss of new method + accelerated curing (High alkali vs. Low alkali, ISU)
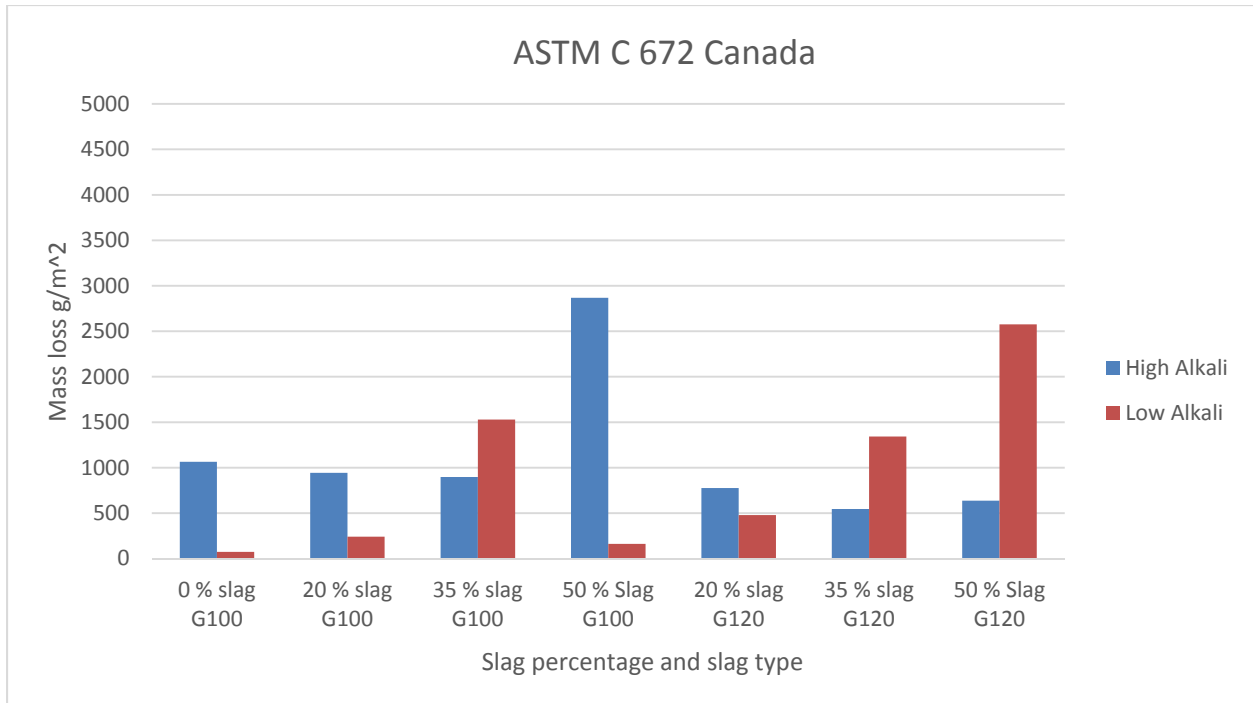
Figure 12. Cumulative mass loss of new method + accelerated curing (High alkali vs. Low alkali, Hooton, Canada)
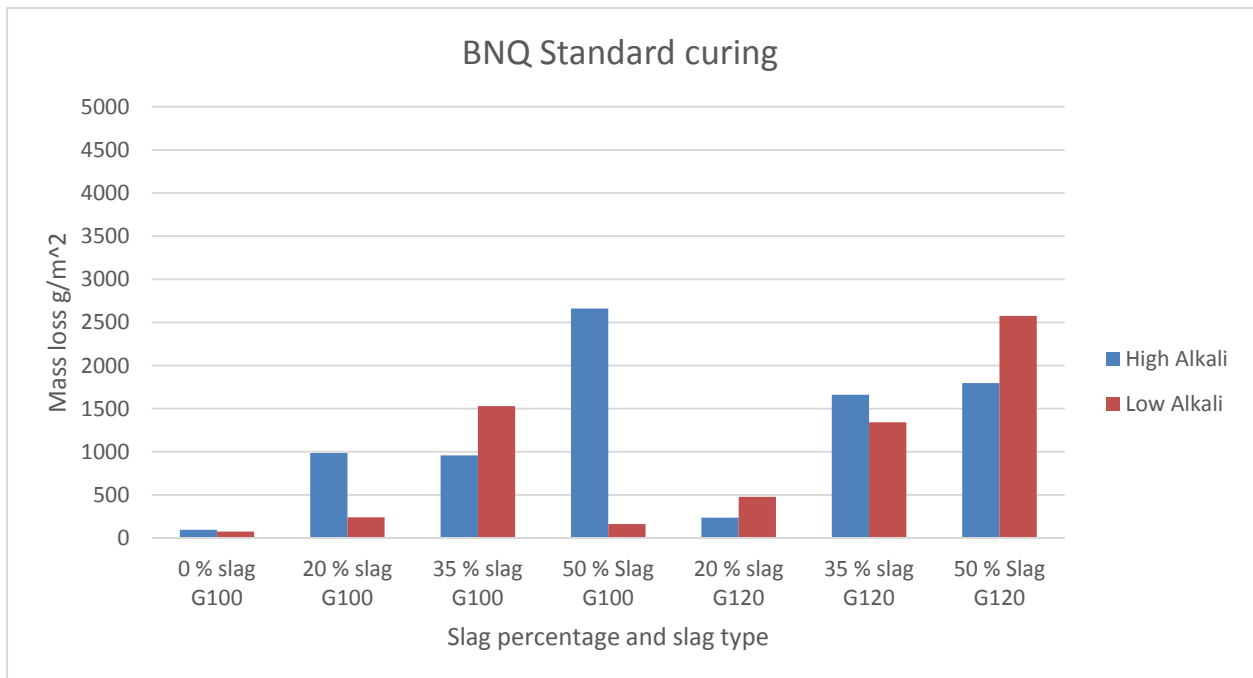

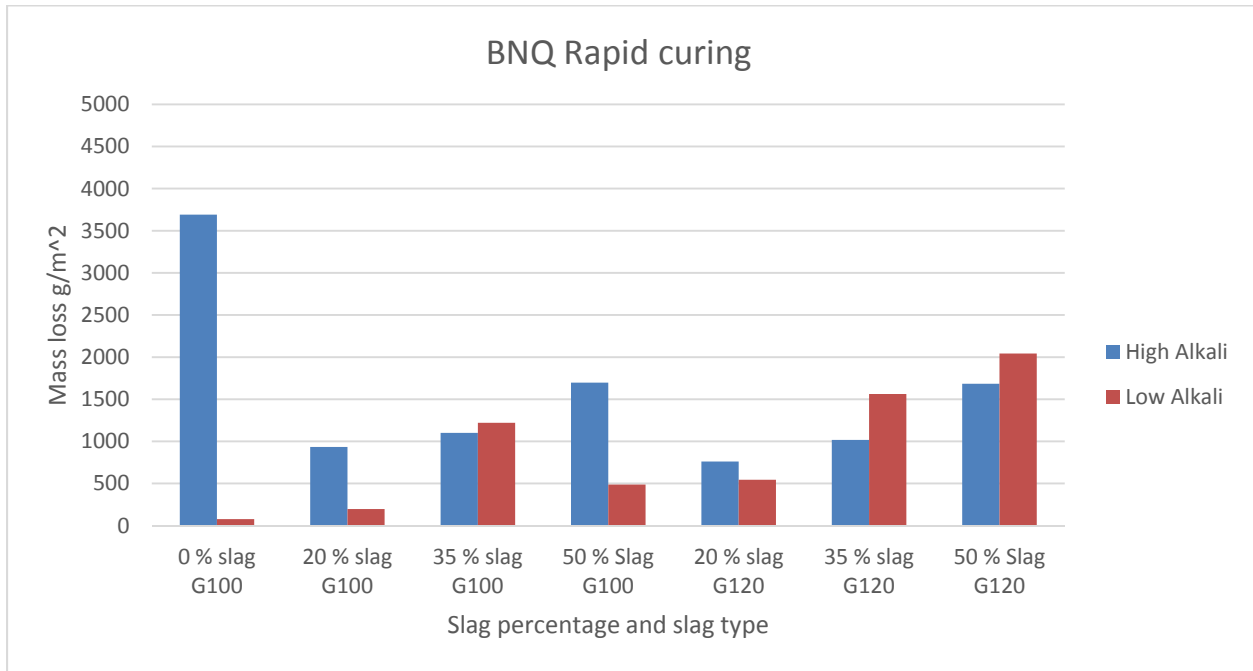**Figure 13. Cumulative mass loss of BNQ method (High alkali vs. Low alkali, Hooton, Canada)**

Figure 14. Accumulative mass loss of BNQ method+ rapid curing (High alkali vs. Low alkali, Hooton, Canada)

To compare the effects of the cementitious system on scaling resistance, mass-loss results after 50 F-T cycles from this work and those reported by Hooton are presented in Figures 9-14.

No consistent trend was found regarding replacement level. Results from Hooton showed that mass loss did increase with raising dosage of G120 slag.

With the same replacement level and same cement, concrete using G100 slag had a higher mass loss than concrete using G120 slag in most of cases, which is different from the findings in maximum mass loss each 5 cycle. G 120 was found to have a higher maximum mass loss per cycle, but lower accumulative mass loss in 50 cycles. This could be the result of higher compressive strength of G120 slag if there is a relationship between compressive strength and scaling resistance. In general, concrete contains G 120 slag would have a better scaling resistance than G 100.

These two phenomena of slag type and replacement level raised an interesting question regarding the mechanism of scaling. It is agreed that carbonation has a significant role in scaling (Osborne, 1998 Jochen and Horst, 1997). Zhang and Zhou (2013) concluded that slag has minor effect on carbonation in low replacement level (under 60%). The findings of this paper indicate that both slag type and replacement level would impact scaling resistance.

Alkali content of cement also has an impact on scaling resistance. In general, low alkali cement concrete showed a higher scaling resistance than high alkali cement in this work and by Hooton (2012).

Testing methods

Cumulative mass loss results from each method are presented in Figure 15 It can be seen that in general, the ASTM test yielded lower mass loss results than the new method in most cases. When rapid curing was applied, samples suffered the most severe scaling damage. This section will discuss these results in terms of salt type and curing method.

Deicers

One of the major differences between new method and ASTM C 672 is that ASTM uses calcium chloride while new method uses sodium chloride. Sodium chloride is believed to be the least destructive among conventional deicers (Darwin, Browing 2007, Sutter and Peterson 2006, Lee and Cody 2000), but from Figure 15, it appear s that sodium chloride caused more severe scaling damage in the method under both curing regimes.

Crystallization pressure is believed to be the main cause of frost damage (Powers and Helmuth 1962), indicating that the variety of salt solution may cause a different degree of damage. Sodium chloride is believed to result in the lowest crystallization pressure (Catinaud

2000, Julio-Betancourt 2009). It is also discussed that sodium chloride would react with calcium hydroxide (CH) and cause the dissolution of CH (Larry and Thomas 2006, Dirk, Kejin and Daniel 2006, Catinaud 2000, Lea 1998), which may result in increasing porosity and permeability of the concrete. There are also researchers who have observed formation of ettringite-like needles (Andrzej and Vesa 2004), loss of calcium ions from Aft and Afm and reactions between NaCl and portlandite which leads to a higher PH (Shi and Fay 2009). These mechanisms could all contribute to the findings observed in this experiment.

Curing method

It has been proposed that ASTM C 672 tends to be in poor agreement with field observations because it is overly aggressive, especially for concrete containing SCMs. (Hooton and Vassilev 2012). One of the reasons is that at high replacement levels SCM mixtures can take longer to develop their properties. The new method allows more curing time than ASTM C 672. However, from Figure 15, it can be observed that the new method results in a larger mass loss than ASTM C 672. The result is consistent with Hooton and Vassilev's work. A longer curing time should not decrease the durability of mixes, which is the case here.

After 50 cycles, VA DOT curing indicated the largest mass loss in most of mixes. It was expected that after 14 day drying period, VA DOT accelerated curing regime would exhibit less scaling because of the higher maturity achieved. However it appears that during curing, slabs subjected to VA DOT accelerated curing regime become more saturated, thus leading to accelerated damage. Moreover, because of the low solubility and low diffusibility of cement products, it is hard for them to diffuse to a significant distance from the cement grain in the short time provided by rapid curing. As a result, highly non-uniform distribution of solid phases were likely produced. At the same time, a coarser pore structure was established because of the

uneven distribution of the solid phases, which would lead to an increased permeability. Coarse pores and higher permeability could contribute to poor scaling resistance of samples cured by the accelerated curing method.
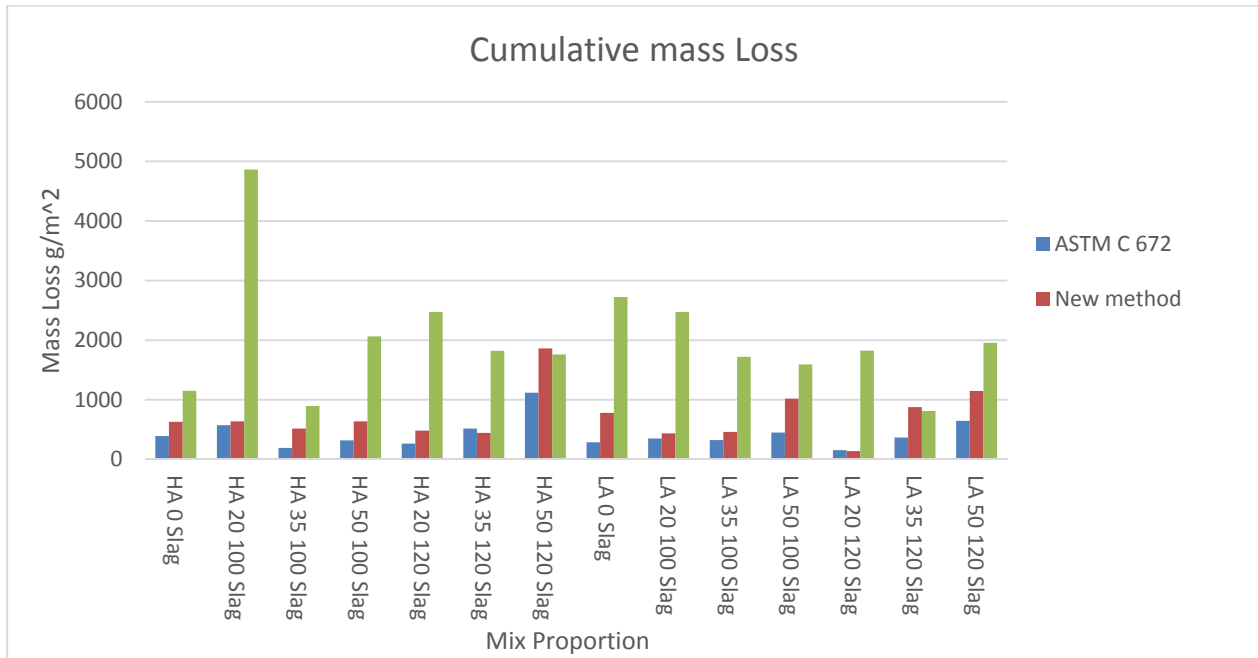

Figure 15. **Cumulative mass loss of each method**

Requirements of air parameters for scaling resistance

Air parameters

Air content, spacing factor and specific surface are commonly used as parameters to assess the air-void-system and so predict F-T resistance. 5% air content from C 231 measurements is considered acceptable for fresh concrete (Wang and Mohamed, 2008), as is a spacing factor of 0.008 in (0.2 mm) is considered acceptable. As discussed above, air parameters from AVA would be lower than C 457, therefore a maximum spacing factor of 0.012 in (0.3 mm) reported by the AVA may be considered equivalent. For specific surface, a minimum value

of 25 mm^{-1} is normally required. Figure 16 to Figure 17 presents results of air tests and if they satisfied the limitations discussed above.

Figure 16 a) and Figure 17 a) gives the air parameters from AVA. When spacing factor of 0.3 mm spacing factor is applied, some mixes pass the limitation, but still most of them would not provide adequate scaling resistance. In Figure 13 a), all test results fail to pass the minimum specific surface of 25 mm^{-1}.

Figure 16 b) and Figure 17 b) presents the air parameters ASTM C 457 tests. All mixes except mixes 2 to 7pass the 0.2 mm spacing factor requirement. From Figure 12 7), some passed the 25 mm^{-1} requirement while others did not.
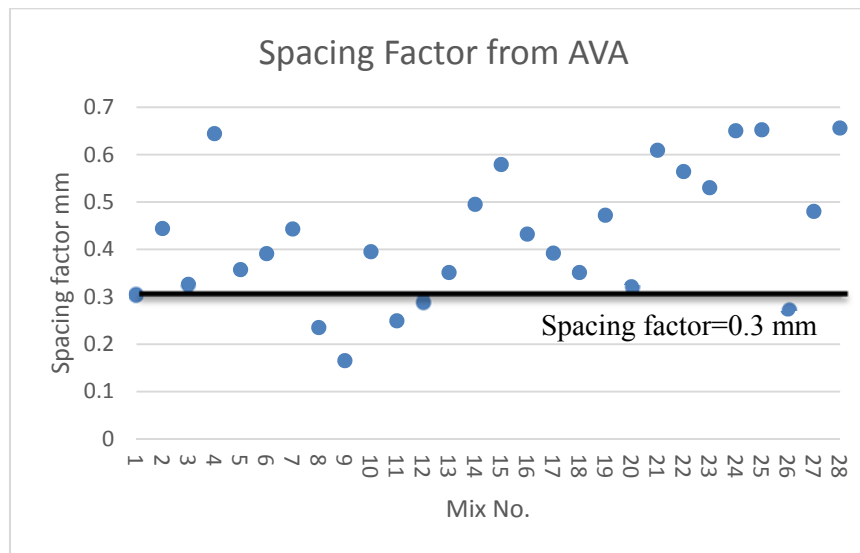
a).
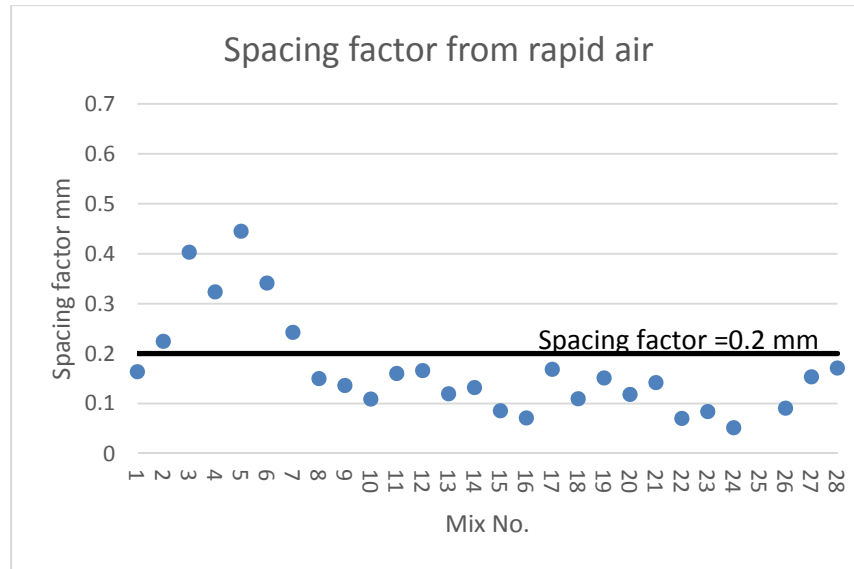
b).

Figure 16. **Spacing factor a). Spacing factor from AVA; b). Spacing factor from rapid**
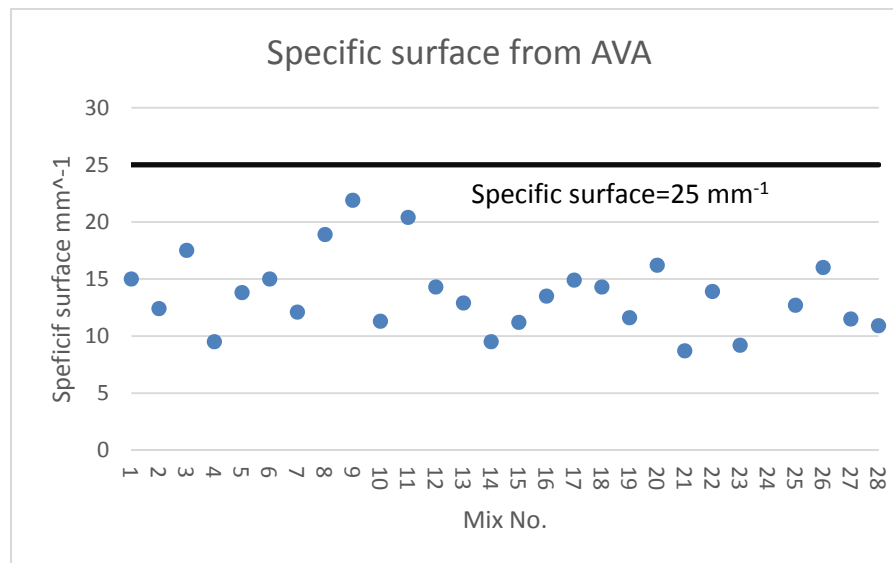

a).

Specific surface from rapid air
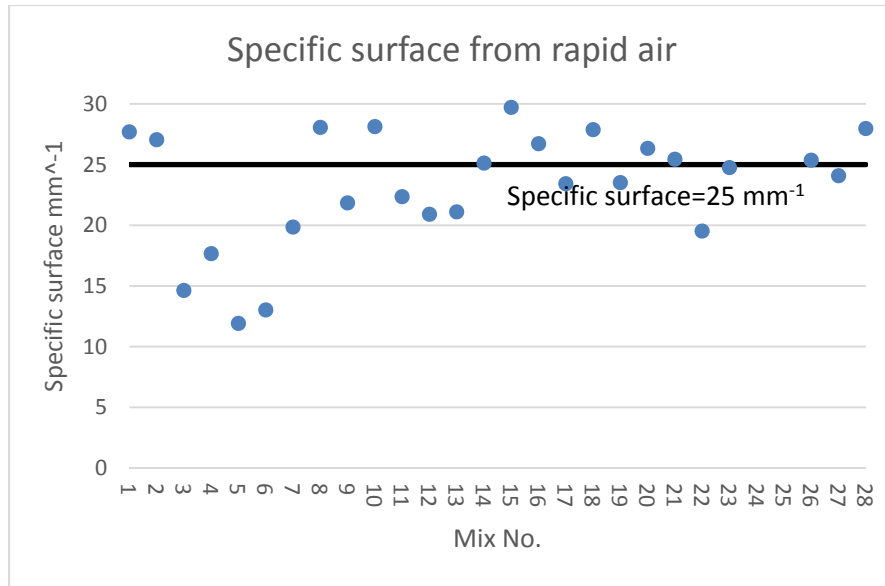
b).

Figure 17. **Specific surface a). AVA; b). Rapid**

Scaling mass loss and air parameters

MTO indicates that a maximum mass loss of 800 g/m^2 is an indication of good scaling

resistance (Hooton and Vassilev 2012). Results from the three test methods are presented in

Figure 18. Using ASTM C 672, only mix 7 failed to pass the limitation, while for new method,

mix 7, mix 8, and mix 21 failed to pass. For accelerated curing method, all of the mixes had

more mass loss than 800 g/m^2.

As discussed above, some mixes have small mass loss (less than 800 g/m^2) but a severe

scaling damage (visual rate of 5). The equivalency chart relating visual rating to mass loss

(Table 11) proposed by Hooton (2012) could be the answer to this dilemma.

Table 11. Visual rating of surface from new method

Category	Approximate Mass Loss Range g/m^2	Characteristics of the scaling surface
0	0 - 50	No significant scaling observed
1	51 - 210	Very slight scaling 3mm (1/8") depth, max, no coarse aggregate visible and no pop-outs present
2	211 - 500	Slight to moderate scaling and/or presence of a few pop-outs
3	501 - 1300	Moderate scaling with some exposed coarse aggregate
4	1301 - 2100	Moderate to severe scaling where the coarse aggregate is clearly exposed and there is scaling of the surface mortar
5	>2100	Severe scaling coarse aggregates are visible over the entire surface
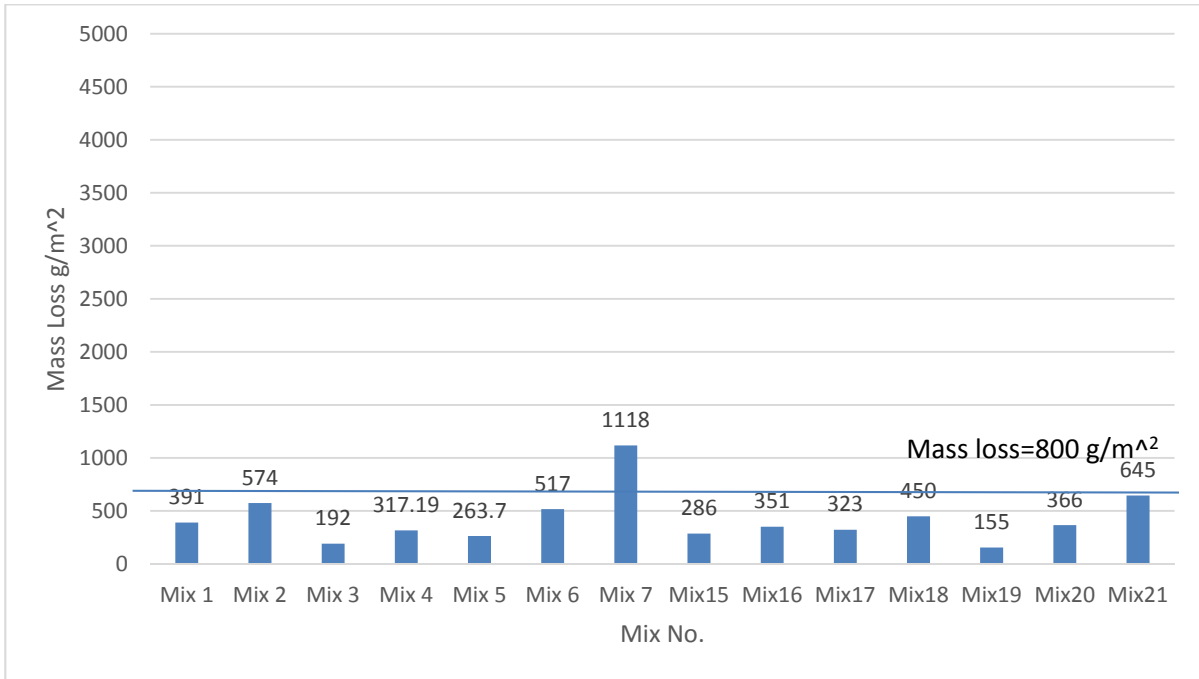
a). ASTM C 672 Mass Loss
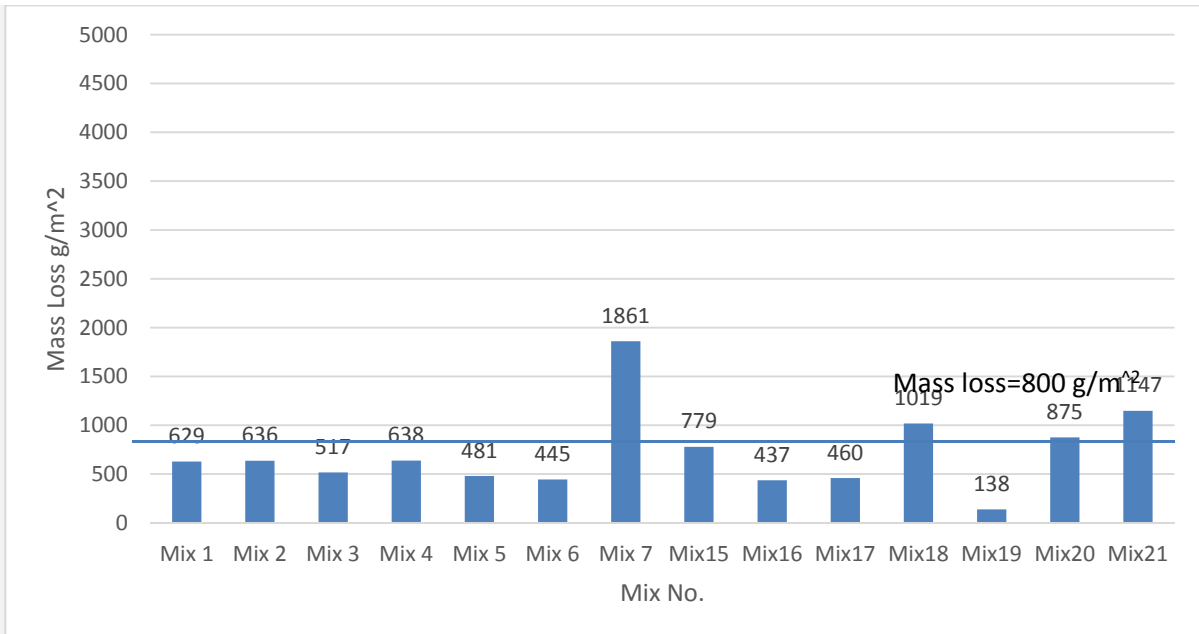
b). New Method (Standard Curing)
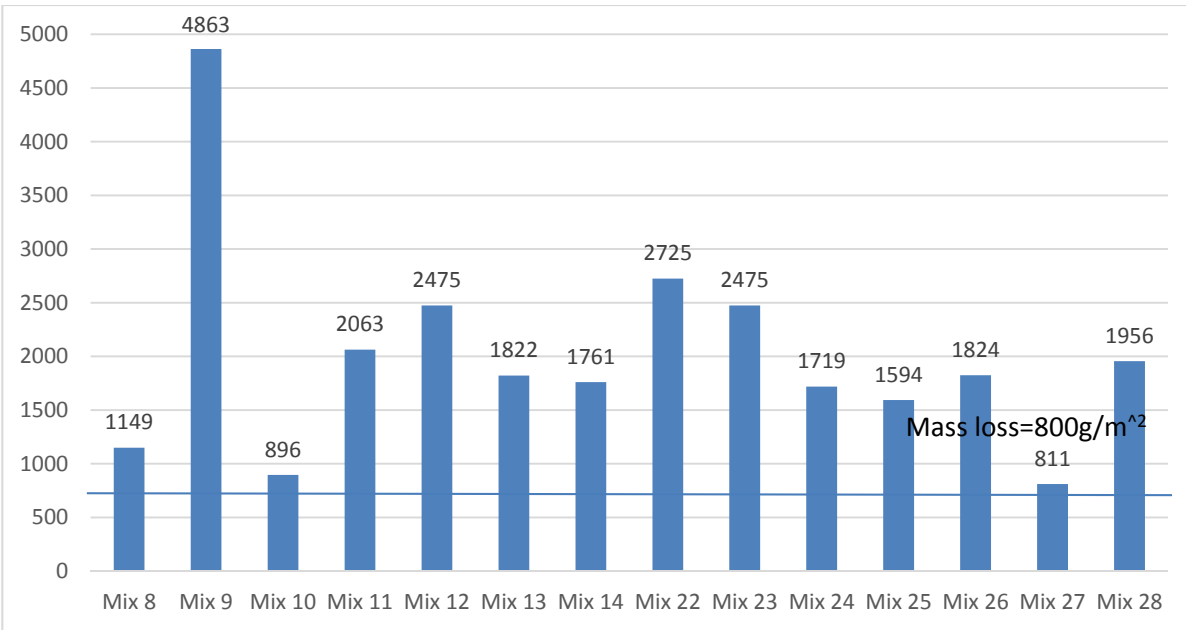
c). New Method (Accelerated Curing)

Figure 18. **Mass loss of each mix a). ASTCM C 672 with standard curing; b). New method with standard curing; c). New Method with accelerated curing**

Table 12 compares the measured air-void system with performance in scaling tests. It can be seen that mixes 1-6 have a bad air system, from both test methods, but actually have a good scaling resistance, even for the new method which appears to be more aggressive. While mix 15 to mix 21 had a good test result from rapid air, but they actually have more mass loss than previous ones with a bad air system. Only mix 8 to mix 13 showed a correlation between air system and scaling resistance.

In general, no direct relationship was found between air parameters (specific surface and spacing factor) and scaling resistance (scaling mass loss). This point of view was proposed by Panesar and Chidiac (2006) saying that no clear correlation between spacing factor and scaling resistance could be found. Possible reason could be that scaling may only occur when large capillaries are saturated, and permeability or the capacity of the surface to resist saturation would control the scaling resistance, instead of spacing factor (Foy and Pigeon 1988)

Table 12. Acceptance of air test and scaling test

		Air tests			Scaling test	
	ITEM	AVA (0.2 mm)	AVA (0.38 mm)	Rapid Air	C672	New Method
Standard Curing	Mix 1	NP	P	P	P	P
	Mix 2	NP	NP	NP	P	P
	Mix 3	NP	P	NP	P	P
	Mix 4	NP	NP	NP	P	P
	Mix 5	NP	P	NP	P	P
	Mix 6	NP	NP	NP	P	P
	Mix 7	NP	NP	NP	NP	NP
	Mix15	NP	NP	P	NP	NP
	Mix16	NP	NP	P	NP	NP
	Mix17	NP	NP	P	P	NP
	Mix18	NP	P	P	NP	NP
	Mix19	NP	NP	P	NP	NP
	Mix20	NP	P	P	NP	NP
	Mix21	NP	NP	P	NP	NP
Rapid Curing	Mix 8	NP	P	P	P	P
	Mix 9	NP	P	P	P	P
	Mix 10	NP	NP	P	P	P
	Mix 11	NP	P	P	P	NP
	Mix 12	NP	P	P	P	P
	Mix 13	NP	P	P	P	P
	Mix 14	NP	NP	P	P	NP
	Mix 22	NP	NP	P	NP	NP
	Mix 23	NP	NP	P	NP	NP

Mix 24	NP	NP	P	NP	NP
Mix 25	NP	NP	P	NP	NP
Mix 26	NP	P	P	NP	NP
Mix 27	NP	NP	P	NP	NP
Mix 28	NP	NP	P	NP	NP

NOT PASS > NP

PASS > P

Conclusions:

- During scaling tests, concrete may experience more damage at early ages compared with later ages.

- When the same replacement level is applied, concrete containing G120 slag had a better scaling resistance than G100.

- Low alkali cement concrete has a better scaling resistance than high alkali concrete.

- Samples tested with ASTM C 672 method showed slightly less damage than those tested with the new method, while when VADOT curing regime was applied, severe damage was found in the corresponding samples.

- No clear relationship was found between spacing factor and scaling resistance.

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CHAPTER 4. EFFECT OF THE INTERFACIAIL TRANSITION ZONE ON JOINT DETERIORATION OF CONCRETE PAVEMENTS

A paper to be submitted to Journal of ASTM Advances in Civil Engineering Materials

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Abstract

In the Midwestern region of the U.S., some concrete suffers from deterioration of sawn joints, generally related to freezing and thawing of saturated concrete. One form of the distress occurs as cracks forming about one inch from, and parallel to, the free surface. These cracks are observed to go around the coarse aggregate and leave little or no paste adhering to it.

It is hypothesized that a mechanism for this observation is that when joints are sawn, the cut exposes the interfacial transition zone (ITZ) around coarse aggregate particles. Water or salt solution subsequently held in the saw-cut can be wicked around the coarse aggregate particles through the ITZ. Subsequent freezing and thawing action can lead to the aggregate being separated from the paste, and a crack propagating to the surface. Once the now-loose piece is removed by traffic loading, the cycle is repeated. The mechanisms behind the separation of aggregate and paste are not clear and may include freezing expansion of water, salt crystallization and dissolution of the ITZ.

This paper describes an experimental program aimed at investigating this hypothesis and to assess what mechanism(s) can be responsible of the observed behavior. It was found that

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chemically induced expansion of the paste likely caused a stress concentration around the non-expanding aggregate, so resulting in a crack in the ITZ.

Keywords: Interfacial transition zone, Magnesium Chloride, Deicer deterioration

Introduction

Farran (1950) first observed and described an interfacial transition zone (ITZ) between large aggregate particles and cement paste. The concept, and effects of an ITZ have since been discussed at length.

The ITZ can have a significant impact on both mechanical properties and potential durability (Tasong et al. 1998). While the effects ITZ of on mechanical properties have been studied extensively, few researchers seem to have investigated the influence of deicing chemicals on the ITZ. Because of the increased permeability, there is, however, a significant potential for the ITZ to be impacted by the ingress and reactions of deicing chemicals.

Most highway agencies still prefer to use chloride based solutions for de-icing and anti-icing activities, despite a range of alternative products being available on the market, largely because of their relative benefits and costs. However, chloride solutions can cause deterioration in concrete both physically (increased saturation) and chemically (formation of calcium oxychloride or freidel's salt). It is likely than that an exposed ITZ may accelerate these distress mechanisms because it is more permeable, and the compounds that comprise the ITZ may be more soluble than calcium silicate hydrate (C-S-H), particularly at low temperature.

In 2013, Zhang and Taylor proposed that the ITZ around coarse aggregate particles exposed by saw-cutting may be damaged under the action of deicing salts in cold weather (Figure 19). This is notable because in general it is difficult to separate aggregate from paste in

mature concrete, yet this was regularly being observed in distressed sections of pavements. The mechanisms that may be responsible for the damage include:

- Freezing and thawing of water in the ITZ leading to localized expansion
- Salt crystallization causing expansive forces
- Dissolution of the ITZ by deicing salts at low temperatures, especially because some calcium compounds are increasingly soluble under reducing temperatures

Valenza and Scherer (2006) discounted the first two alternatives. The first was considered unlikely because water expanding as temperatures dropped would have to be held in the ITZ to cause pressure, and it was considered more likely that the water would simply be expelled back into the saw-cut. In addition, the volume of freezing water in the ITZ would likely be too low to set up significant stresses. The second mechanism was considered unlikely because osmotic pressure caused by freezing salt solution is about 160 psi, and the crystallization pressure is about 374 psi (Correns 1949), while the typical tensile strength of concrete with w/c ratio 0.45 is about 650 psi (Bhanja and Sengupta 2005).

A   B

Figure 19. **Test samples from Zhang and Taylor (2013)**

Images showing aggregates cleanly separated from paste in samples that had been
subjected to freeze thaw cycles in A: water and B: 3% NaCl

In this paper, the authors' objective is to improve understanding of the mechanisms

behind the break-down of the interfacial transition zone of concrete exposed to de-icing salts. An

experiment was conducted by soaking concrete samples in different chloride solutions at a

constant temperature (40°F) and observing the samples under optical and scanning electron

microscopy. The mechanism of ITZ deterioration in deicer is then discussed based on the

observations and those reported by others.

Experimental Work

Materials and mix proportions

   An experimental program was conducted to investigate the mechanisms contributing to

the deterioration of ITZ exposed to salt solutions. The approach was to prepare concrete samples

from a single mixture and partially submerge them in water, NaCl solution, or $MgCl_2$ solution at

40°F for 56 days, followed by examination of the tested samples using microscopy. The low,

constant temperature was selected to remove the effects of freezing, while enhancing potential

dissolution of calcium compounds.

The materials and critical mixture parameters are presented in Table 13.

Table 13. Concrete mixture details

Cement	Type I/II
Fly Ash	Class C, 20%
Binder content	564 pcy
w/cm ratio	0.45
Air Content	6%
1'' Coarse aggregate	Round gravel (Ab%=0.3, SG=2.66) or Crushed limestone (Ab%=0.9, Gs=2.67)
Fine aggregate	River sand

Concrete was mixed in accordance with ASTM C192 and cast into 4 x 3 x 16'' beams. The beams were cured in a fog-room for 28 days before they are cut by diamond saw into ½'' thick slices (Figure 20). The slices were deliberately thin to ensure that some aggregate particles are exposed on both faces of the slice.

The slices were partially immersed, sawn face down, in a ¼'' layer of test liquid comprising either water, 3% NaCl, or 3% $MgCl_2$, at a constant 40°F (Figure 21). For each solution, four samples were tested. After 56 days, slices were cut into two halves to create vertical section so that the effects of the solutions could be observed through the thickness of the samples. Selected samples were examined in a Scanning Electron Microscope (SEM).

Figure 20. **Concrete slices before soaking**

Figure 21. **Slices immersed in salt solution**

Results

Typical photos and SEM images of samples are presented below to illustrate the observed changes in the samples. Limestone and gravel mixtures showed the similar results, so only pictures and images of gravel samples are presented.
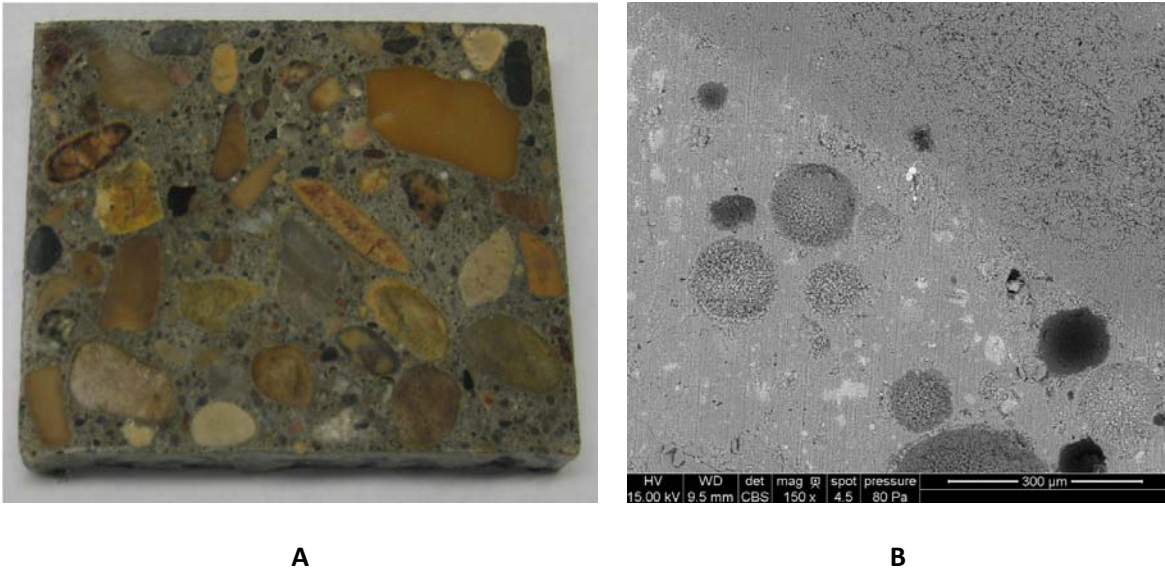
Samples tested in water

<div align="center">A   B</div>

Figure 22. **Typical sample tested in water after 56 days at 40°F**
A: Optical image. B: SEM image

No obvious deterioration is observed in either Figure 22A or 22B.

Samples tested in NaCl
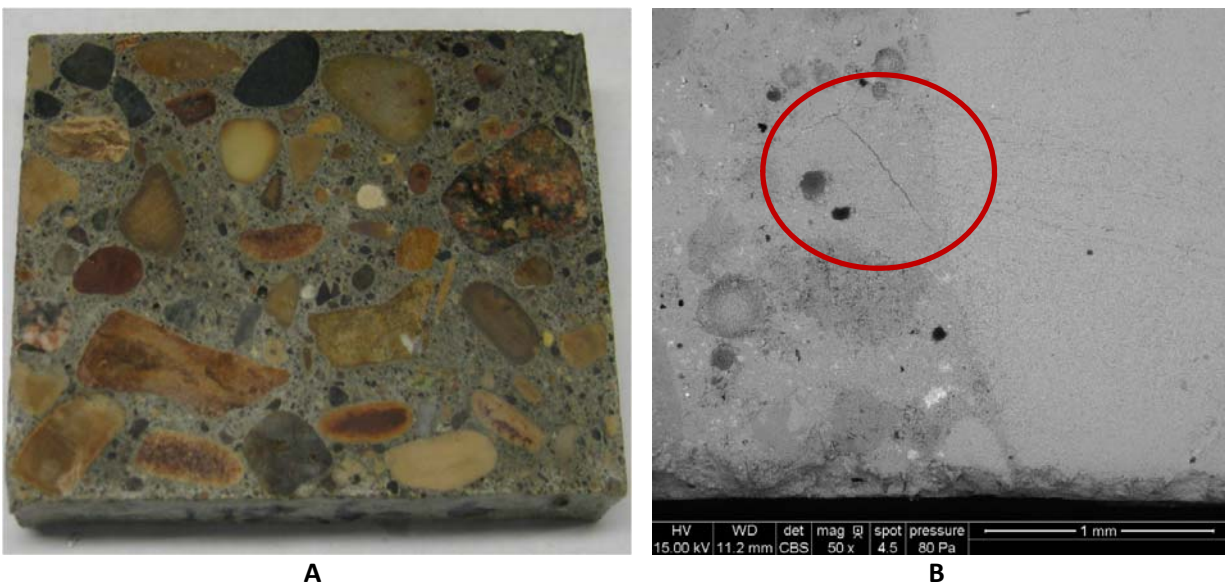

<div align="center">A   B</div>

Figure 23. **Typical sample tested in NaCl after 56 days at 40°F**
A: Optical image. B: SEM image

Similar to the samples soaked in water, little distress was observed in the NaCl soaked specimens under visual examination (Figure 23A). However, in the SEM, some cracks were observed in the paste (Figure 23B). Cracking appeared to be uniform through the full thickness of the sample.

There were no signs of salt crystallization, nor of dissolution of the ITZ. Chemical mapping did not indicate concentrations of chlorides in any location, but rather a uniform spread through the paste.
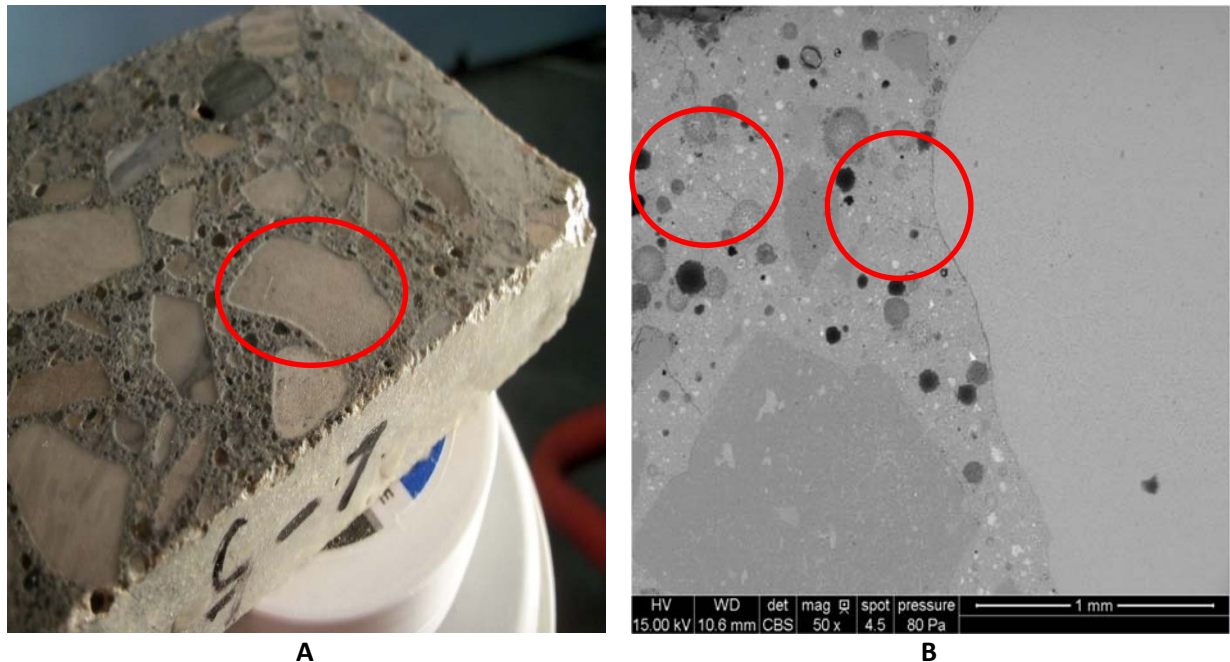
Samples tested in MgCl₂

A   B

Figure 24. **Typical sample tested in MgCl₂ after 56 days at 40°F**
A: Optical image. B: SEM image

In Fig 24A, the photograph of a sample partially immersed in MgCl₂ for 56 days at 40°F clearly shows that the paste has expanded around the aggregate particles. Fig 24B shows the same sample imaged using a SEM. Cracks are observed around the coarse aggregate particles

and inside the paste. This cracking was more prevalent toward the face of the samples that had been exposed to the solution. Similar to the samples soaked in other solutions, there was little sign of salt crystallization or dissolution of the ITZ. There was also little evidence of chloride concentrations in the ITZ.

Discussion

In a previous phase of this project, Zhang and Taylor (2013) proposed a hypothesis that deterioration of interfacial transition zone would play a role in concrete sawn-joint failure under the action of deicing salts in cold regions. The aim of the work discussed in this paper was to investigate the mechanisms behind the hypothesis.

The materials used by Zhang and Taylor were similar to those used here but their samples were subjected to cyclic freezing and thawing for 600 cycles. Samples in this work were stored at a constant 40°F in order to remove the effects of freezing.

Figure 25. **Sample in MgCl2 solution after freezing and thawing (Zhang and Taylor, 2013)**

Samples tested in water

No noticeable deterioration could be found for samples soaked in water for 56 days in 40°F. This result is consistent with Sutter et al. (2008), that damage caused by water without freezing is negligible.

When F-T cycles are applied, examination of Figure 1A, showing a sample after 600 freeze thaw cycles in water (Zhang and Taylor 2013), indicates that paste has been pushed above the aggregate (Figure 20). It is likely that the expansion of water when it freezes within the paste pore structure is the primary mechanism causing this distress. Pure water expands about 9% as it freezes, and if pore structure cannot resist this expansion, resulting in micro cracking and apparent expansion of the paste. It is likely that the samples were at a high degree of saturation by nature of their size and preparation, thus freeze thaw damage would occur through the full thickness.

Samples tested in NaCl

Examination of Fig 23 shows a few cracks throughout the paste. The result is similar to that reported by Sutter and Petersen (2008). These researchers believe that sodium chloride reacts with and dissolves calcium hydroxide (CH) (Sutter and Van Dam 2006, Dirk, Wang and Daniel 2006, Catinaud 2000, Lea 1998). One of the products of this reaction is expansive calcium oxychloride that would lead to expansion and micro-cracking through the paste.

Fig 19B shows a sample subjected to F-T cycling in NaCl (Zhang and Taylor 2013). A split has occurred between aggregate and paste. This supports the hypothesis that the ITZ has been attacked. The ITZ is likely to contain a higher amount of CH than the bulk paste, and as

such would be preferentially attacked by a dissolution reaction, so leaving a smooth aggregate surface (Douglas and Menashi 1994, Maso 1996).

Samples tested in MgCl₂

It is clear from figure 24A that the paste has been pushed above the aggregate, indicating an expansion reaction occurring within the body of the paste. This is similar to findings by Sutter and Petersen (2008) under similar conditions, and is likely to be due to the formation of expansive calcium oxychloride in the paste. The microscopy (Figure 24 B) indicated that there did not appear to be crystal formation nor was dissolution in the ITZ, but there cracking around the aggregates. The mechanism therefore appears to be that differential movement between the paste and the aggregate caused by oxychloride formation, has caused the aggregate to become debonded from the paste. It is possible that CH in the ITZ was preferentially decalcified, but this was not clearly observed. It is notable that this is far more extensive in the MgCl₂ solution than in the NaCl, which is consistent with the findings of Sutter and Petersen.

This mechanisms would be expected to be exacerbated under cyclic freezing conditions, and this is consistent with the findings of Zhang and Taylor (2012).

In summary then, it appears that under constant 40°F conditions, MgCl₂ is likely to cause significant damage, probably due to formation of calcium oxychloride, leading to separation of paste and aggregate. A similar, but less aggressive trend is seen in NaCl, while no effect is seen in water. The addition of freeze thaw cycles appears to compound the chemical reactions with the mechanisms traditionally considered, namely expansion of freezing water and salt scaling effects such as osmosis, making damage possible in all three solutions. Exposure of the ITZ will

likely accelerate all of these mechanisms because it allows faster access of solutions into the body of the paste.

Conclusions

In summary then, it appears that under constant 40°F conditions, $MgCl_2$ is likely to cause significant damage, probably due to formation of calcium oxychloride, leading to separation of paste and aggregate at the ITZ. A similar, but less aggressive trend is seen in NaCl, while no effect is seen in water.

The addition of freeze thaw cycles appears to compound the chemical reactions with the mechanisms traditionally considered, namely expansion of freezing water and salt scaling effects such as osmosis, making damage possible in all three solutions. Exposure of the ITZ will likely accelerate all of these mechanisms because it allows faster access of solutions into the body of the paste.

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CHAPTER 5. GENERAL CONCLUSIONS

Conclusions

The main purpose of this work is to perform a comprehensive study of two different aspects of the deicer deterioration to concrete, scaling of concrete containing slag cement and the effect of ITZ on joint deterioration. To determine the scaling resistance, air system tests were performed for both fresh and hardened concrete samples, and different evaluation methods were also used to determine scaling resistance. Multiple sources of slag and cement were used to determine the impaction of slag and cement type to scaling resistance. To determine impactions from ITZ to joint deterioration, multiple chloride based deicers were used, and SEM was applied to detect the micro-cracks or any other changes happened in concrete.

The main conclusion of the study are as follows:

- During scaling tests, concrete may experience more damage at early ages compared with later ages.

- When the same replacement level is applied, concrete containing G120 slag had a better scaling resistance than G100.

- Low alkali cement concrete has a better scaling resistance than high alkali concrete.

- Samples tested with ASTM C 672 method showed slightly less damage than those tested with the new method, while when VADOT curing regime was applied, severe damage was found in the corresponding samples.

- No clear relationship was found between spacing factor and scaling resistance.

- Under constant 40°F conditions, $MgCl_2$ is likely to cause significant damage, probably due to formation of calcium oxychloride, leading to separation of paste and aggregate at the ITZ. A similar, but less aggressive trend is seen in NaCl, while no effect is seen in water.

- The addition of freeze thaw cycles appears to compound the chemical reactions with the mechanisms traditionally considered, namely expansion of freezing water and salt scaling effects such as osmosis, making damage possible in all three solutions. Exposure of the ITZ will likely accelerate all of these mechanisms because it allows faster access of solutions into the body of the paste.

Recommendations for Future Research

For scaling resistance, a more precise mechanism of scaling should be studied, and the difference between scaling resistance and F-T resistance should studied. At the same time, the scaling depth should be studied in order to find if it is possible to prevent scaling from surface.

For joint deterioration, finding out the chemical mechanism behind NaCl and $MgCl_2$ deterioration to ITZ should be the major objective, and as another chloride deicer, $CaCl_2$ should be added into the matrix. Samples treated with three solutions and water should be tested before

and after merging in solutions, and additional XRD tests around ITZ should be performed to samples to analysis the chemical composition changes during the attacking. Also, compressive strength of samples merged in solutions should be tested as a reference of how much damage do different solutions cause to ITZ.