HyunGu Jeong[1], Mirian Velay-Lizancos[1], Jan Olek[1], Daniel K. Pannell[2], Robert Geiger[2]
[1]Lyles School of Civil Engineering, Purdue University, West Lafayette, IN, 47907, USA,
[2]Compass Minerals, 9900 West 109th St, Overland Park, KS 66210, USA

Influence of Type of Deicers on Scaling Resistance of Plain and Fly Ash Concretes

Salt, Safety and the Environment

Abstract

The weather conditions at many geographic locations throughout the world often require application of deicers to concrete roadways, sidewalks, and driveways in order to keep them available and safe for their intended purpose. Deicing of such concrete structures is most often accomplished with various salts. The deicers prevent the build-up of snow and ice on the exposed concrete surfaces by lowering the freezing point of the brine. However, the brine also increases the degree of moisture saturation of concrete, thus increasing the potential number of freezing and thawing cycles. The combination of these factors can lead to early deterioration of the treated areas of the concrete, which manifests itself as a local flaking of the surface (commonly referred to as scaling). This study evaluated the influence of three different types of deicers ($CaCl_2$, $MgCl_2$, and NaCl) on scaling resistance of four different types of concrete typically used in the construction of driveways and sidewalks. The types of concrete used in the course of this investigation included the following: (a) two plain (i.e. containing only portland cement binder) concretes, each prepared with different air content and different water-to-cement (w/c) ratio, and (b) two concretes in which 30% of the weight of cement was replaced with equivalent weight of Class F fly ash.

The scaling resistance of concretes was evaluated after 50 freezing-thawing cycles using the visual rating scale of the of ASTM C 672 specification. In addition, the scaling resistance was also evaluated by monitoring the mass of the scaled-off material as prescribed in the test procedure of the Ontario Ministry of Transportation (MTO). The scaling of plain concretes was observed to be low to moderate (less than 3 on the ASTM C 672 visual scale), irrespective of the type of deicer used. However, the scaling of the fly ash concrete was found to be strongly depended on the type of the deicer used, with specimens exposed to $MgCl_2$ scaling substantially less than those exposed to $CaCl_2$ and NaCl deicers.

Keywords: deicers, scaling, plain concrete, fly ash, sidewalks, driveways.

 Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

Introduction

The use of deicing salts during inclement weather ensures safe roads conditions for pedestrians and drivers in the cold regions of the world. Deicing operations on the roadways typically involve applications of various salts. The most common chloride-based deicers available on the market include sodium chloride (NaCl), calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$). Of these three deicers, NaCl is the least effective under very cold conditions as its lowest effective working temperature is only about 15°F (-9°C). Thus, other deicers, such as $CaCl_2$ and $MgCl_2$, are often used during the coldest temperatures periods as they can melt ice faster under such conditions due to their lower effective temperature ranges (about -25°F (-32°C) for $CaCl_2$ and about 0°F (-18°C) for $MgCl_2$).

While effective with respect to snow and ice removal, the application of deicers can also accelerate the physical and chemical degradation of concrete by increasing the degree of saturation of the elements and thus making them more prone to freeze/thaw damage [1, 2]; by initiating chemical reactions with calcium hydroxide (Ca(OH)2) and calcium-silicate hydrates (C-S-H) to form expansive and/or non-cementitious hydrates [3-8]; and by contributing to growth of salt crystallization products that can infill air voids/cracks and therefore produce internal stresses [9]. One of the most effective ways of minimizing the potentially negative effects of deicers on the durability of concrete involves replacing part of the portland cement binder with reactive pozzolanic materials, such as fly ash, silica fume or slag cement. When used in concrete mixture, these pozzolanic materials react with calcium hydroxide (the by-product of portland cement hydration) and water to form additional amounts of calcium silicate hydrate (C-SH), which is the main strength-generating component of concrete. In addition to increasing strength and facilitating the removal of deicer reaction-prone calcium hydroxide, these pozzolanic materials also reduce the internal porosity of concrete, thus making it less susceptible to the ingress of surface moisture and deicing salts. However, since the pozzolanic reaction can only commence after sufficient amount of calcium hydroxide becomes available as the result of the hydration reaction of the ordinary portland cement (OPC), the pozzolan-containing concrete will initially have lower strength [10]. In fact, in practice it is often assumed that concretes containing pozzolanic materials (especially ASTM C618 Class F fly ash) will require about 56 days of curing in order to develop the same level of strength as that achieved by plain OPC concrete after just 28 days of curing [11]. As a result, when subjected to deicing chemicals prior to achieving their full maturity, the concrete containing pozzolanic materials may be more susceptible to surface scaling.

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This paper presents the results of a research study that was designed to evaluate the scaling resistance of four, commercial-grade concretes: two plain (i.e. using cement only as a binder) concretes and two fly ash concretes (i.e. concerts in which 30% (by mass) of cement was replaced by ASTM C618 Class F fly ash). The mixtures used in the study were designed to meet the Indiana Department of Transportation (INDOT) specifications for concrete suitable for construction of pavements, driveways, and sidewalks (INDOT, 2016).

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

Materials and test specimens

This study evaluated the scaling resistance of four types of concretes (each with different scaling susceptibility) exposed to three different deicers: $CaCl_2$, $MgCl_2$ and NaCl. De-ionized water was used as reference solution.

Types and composition of concrete mixtures
The following four types of concrete mixtures were selected for the study:

- Concrete A: Plain cement mixture (Type I portland cement - 564 lb/yd^3, w/c=0.42, target air content 6.5±1.0%, target slump 3-5 in.)
- Concrete B: Plain cement mixture (Type I portland cement - 564 lb/yd^3, w/c=0.45, target air content 4.0±1.0%, target slump 3-5 in.)
- Concrete C: Fly ash mixture (Type I portland cement plus 30% of Class F fly ash (by mass of total cementitious materials); mass of total cementitious materials - 564 lb/yd^3, w/cm=0.42, target air content 6.5±1.0%, target slump 3-5 in.)
- Concrete D: Fly ash mixture (Type I portland cement plus 30% of Class F fly ash (by mass of total cementitious materials); mass of total cementitious materials - 564 lb/yd^3, w/cm=0.45, target air content 4.0±1.0%, target slump 3-5 in.)

All four types of concrete were prepared using Indiana Department of Transportation (INDOT) No. 8 (INDOT, 2016) crushed limestone as a coarse aggregate. The maximum size of the coarse aggregate was 1.0 in. (25 mm), its saturated surface dry (SSD) specific gravity was 2.667, and its absorption was 1.98 %. The fine aggregate used was INDOT No. 23 (INDOT, 2016) natural siliceous sand with a specific gravity (SSD) of 2.637 and absorption of 1.5%.

Table 1 summarizes the mixture design parameters for each of the four concretes used in this study. Table 2 shows detailed mixture proportions of each concrete

Table 1. Concrete mixtures design parameters

Type	Concrete	w/cm	% Fly Ash (Class F)	Target air content (%)	Target Slump (in.)/(mm)
Plain	A	0.42	0	6.5	3-5/(76-127)
	B	0.45	0	4.5	3-5/(76-127)
Fly Ash	C	0.42	30	6.5	3-5/(76-127)

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

D	0.45	30	4.5	3-5/(76-127)

Table 2. Mixture proportions (SSD conditions)

Component	Concrete			
	A	B	C	D
Cement (kg/m^3)	335	335	234	234
Fly Ash (kg/m^3)	0	0	100	100
Water (kg/m^3)	141	151	141	151
Fine Aggregate (kg/m^3)	816	816	816	816
Coarse Aggregate (kg/m^3)	1,009	1,009	1,009	1,009
Air Entrainer (mL/m^3)	135	77	174	97
Water reducer (mL/m^3)	812	425	870	329

Number of specimens, casting, fresh concrete properties, and curing.
All concretes were mixed in a standard 4 cu ft. (113 L) steel drum mixer. Three separate batches were required for each concrete in order to produce all specimens needed for the experiments. The fresh concrete was sampled from each batch and tested for air content and slump using ASTM C 231 and ASTM C 143, respectively.

Table 3 provides both, the target an average measured values of slump and air content for all concrete mixtures used in this study.

Table 3. Target and measured values of slump and air content of fresh concretes

Concrete	Slump (in./(mm))		Air content (%)	
	Target	Measured	Target	Measured
A	3 – 5/(76-127)	3.75/(95)	6.5	6.7
B	3 – 5/(76-127)	4.25/(108)	4.0	4.0
C	3 – 5/(76-127)	3.50/(89)	6.5	5.2
D	3 – 5/(76-127)	4.50/(114)	4.0	3.2

The fresh concrete samples were also used to determine the unit weight of concrete. These values were used to crosscheck the values of the measured air content as the research shows that, in general, there is a linear relationship between these two parameters [12]. As seen from the results presented in Figure 1, the relationship between the unit weight and air content of all batches can indeed be considered linear.

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

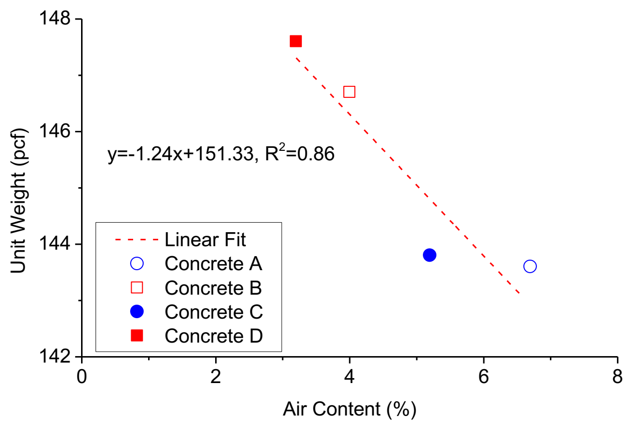

Figure 1. Relationship between unit weight and air content of fresh concretes

Each series of the scaling test specimens consisted of two 3 in. x 8 in. x 11 in. (76 mm x 203 mm x 279 mm) concrete slabs. The surface area of the test specimens was 8 in. x 11 in. = 88 in^2 and thus it exceeded the ASTM C 672 requirements for minimum surface area (72 in^2). Similarly, the selected depth met the minimum depth requirement of 3.0 in. In total, the scaling test involved evaluation of 32 different slabs (2 slabs x 4 deicers x 4 types of concrete).

In addition to scaling test specimens, 17 concrete cylinders (4 in. x 8 in. or 100 mm x 200 mm) were also cast from each of the four concrete mixtures. These cylinders were used for determination of the overall quality of concretes utilized in this study by evaluating the following properties: compressive strength, resistance to chloride penetration (RCP), chloride diffusion coefficients (CDC), and the depth of chloride penetration (after 50 FT cycles). Table 4 summarizes the number of specimens and types of tests used for evaluation of the quality of concrete.

All test specimens were removed from the molds about 20-24 h after casting and placed in the storage tanks filled with water saturated with calcium hydroxide for 14 days of moist curing. Once the period of moist curing was completed, the specimens were placed in the laboratory room maintained at 23°C and 50% relative humidity (RH) for additional 14 days of air curing. After completion of the air curing, the specimens were tested according to the relevant standards.

Deicers.

Three types of deicers were used in this study: $CaCl_2$, $MgCl_2$, and NaCl. All deicers contained 4 grams of anhydrous salt per 100 mL of solution and were prepared as described below:

- 4% $CaCl_2$: 4g of anhydrous $CaCl_2$ pellets were placed in the beaker and a small amount of deionized water was added to dissolve the salt. The beaker was subsequently filled with deionized water to 100 mL line.

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

- 4% $MgCl_2$: 8.54g of $MgCl_2$ hexahydrate crystals were placed in the beaker and a small amount of deionized water was added to dissolve the salt. The beaker was subsequently filled with deionized water to 100 mL line.
- 4% NaCl: 4g of NaCl anhydrous crystals were placed in the beaker and a small amount of deionized water was added to dissolve the salt. The beaker was subsequently filled with deionized water to 100 mL line.

In each case, after the final addition of the deionized water, the beaker was placed on the magnetic stirrer and the solution was stirred for at least 10minutes.

Table 4. Number of specimens and types of tests used for evaluation of the quality of concrete

Concrete	Compressive strength [Test ages: 14, 28 (dry), 28 (wet) and 56 days: 3 samples for each age]	Chloride penetration depth (1 cylinder/solution)	RCP/CDC	TOTAL for each concrete
A	12	3	2 cylinders / 2 slides per cylinder	17
B	12	3	2 cylinders / 2 slides per cylinder	17
C	12	3	2 cylinders / 2 slides per cylinder	17
D	12	3	2 cylinders / 2 slides per cylinder	17
TOTAL	48	12	8 cylinders / 16 slices	68

Methods

Evaluation of the initial quality of the concrete

As already mentioned, the initial quality of each type of concrete was evaluated by determining the values of 28 days compressive strength (ASTM C39), resistance to chloride penetration (ASTM C 1202), and chloride diffusion coefficients (using combination of the NT-Build 492/AASHTO T 357 migration test methods). The compressive strength test was performed on full-length cylinders whereas the chloride ingress-related tests were performed on a 2 in. (50 mm) -thick discs removed from the central portion of the 4 x 8 in. (100 x 200 mm.) cylinders.

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

Evaluation of Scaling Resistance

The scaling resistance test was conducted in accordance with ASTM C 672 specification. As stipulated in this specification, the test specimens were subjected to 50 freezing and thawing (FT) cycles while being ponded with about 0.25 in. thick (~ 6 mm) layer of 4% deicer solutions. The test was conducted in the programmable environmental chamber. One of the test slabs was instrumented with the temperature and humidity sensor (iButton®) to record the internal temperature of concrete specimen during the freezing and thawing cycles. Similar sensor was also installed in the chamber itself. Figure 2 shows the comparison of temperatures recoded by these two sensors.

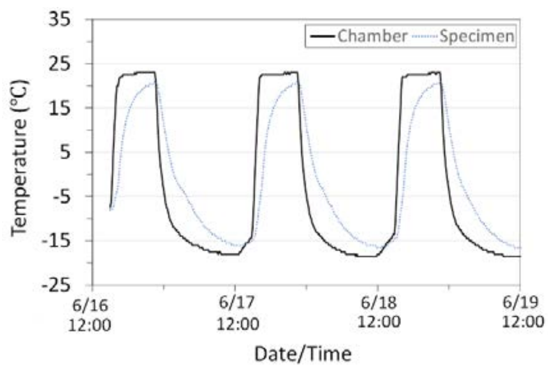

Figure 2. Temperature of the chamber vs. the internal temperature of the slab

At the end of each five of the FT cycles, the surfaces of all specimens were thoroughly flushed with water to remove the deicer and the spalled pieces of concrete. The flushed surfaces were then visually examined and photographed to document the extent of damage. The specimens were rated visually using the scale of 0 (no scaling) to 5 (severe scaling). This rating scale is illustrated in Figure 3 [13] and summarized in Table 5 (ASTM C672). Once the visual examination was completed, the new batch of deicing solution was placed on the surface of each of slabs and the slabs were returned to the environmental chamber for continuation of the FT exposure.

The overall mass loss of the specimens was calculated by comparing the initial mass of the samples (i.e. mass obtained after 14 days of drying at 23°C and 50% RH) with mass of the same specimens determined after completion of 50 FT cycles and after they have been dried to a constant mass (again under the conditions of 23°C and 50% RH).

Depth of chloride penetration

The determination of the depth of chloride penetration resulting from the FT exposure was performed on one 4 in. x 8 in. cylinder selected from each of four types of concrete used in the study. The top portions of these cylinders were outfitted with about 2-in. long plastic collar which was used to contain the deicer ponded on the top surface while the specimens were exposed to

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

the same 50 FT cycles as the scaling slabs. At the end of the FT exposure period, these cylinders were split-opened and the freshly exposed surface was sprayed with 0.1N silver nitrate. After a few minutes of exposure to light, the whitish layer of silver chloride precipitated within the chloride-containing zone of the surface and its depth was measured using digital calipers.

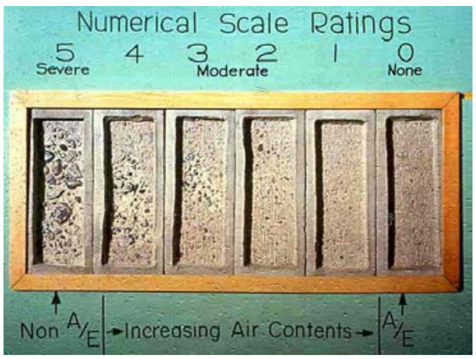

Figure 3. Illustration of the surface rating scale for visual evaluation of scaling [13]

Table 5. ASTM C672 surface scaling rating table

Rating	Condition of Surface
0	No scaling.
1	Very slight scaling (3 mm [1⁄8 in.] depth, max, no coarse aggregate visible).
2	Slight to moderate scaling.
3	Moderate scaling (some coarse aggregate visible).
4	Moderate to severe scaling.
5	Severe scaling (coarse aggregate visible over entire surface).

Results and Discussion

Results of evaluation of the initial quality of the concrete

- Compressive strength

The evolution of the compressive strength for each type of concretes used in the study is shown in Figure 4. As expected, the 28 day compressive strengths of concretes with fly ash (concretes C and D) was somewhat (~12%) lower than that of plain concretes (A and B). Since the fly ash concretes will continue to gain strength upon further exposure to moisture (in fact the 56 days data (not shown here due to space limitation) indicated that concretes C and D were about 15%

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

stronger that concretes A and B) it was assumed that the initial quality (as measured by strength values) of all concretes used in this study was about the same In other words, it is not believed that strength of concretes used in this study significantly affected their scaling resistance.

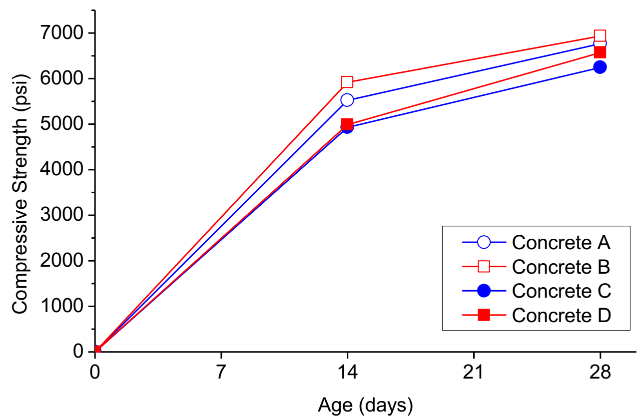

Figure 4. Evolution of compressive strength

- Chloride Diffusion and Depth of Chloride Penetration

Further confirmation of the comparable quality of all concretes prior to their scaling (i.e. FT) exposure can be found by examining test results shown in Figure 5 (chloride diffusion coefficient) and Figure 6 (total charge passed). Examination of Figure 5 reveals that the average values of the chloride diffusion coefficient were quite comparable for all four mixtures used in the study. Similarly, the analysis of total charge passed (electrical indication of concrete's ability to resist chloride ion penetration) also shows that the maximum observed difference was smaller than about 500 coulombs, again indicating a very comparable quality of concretes used in the study.

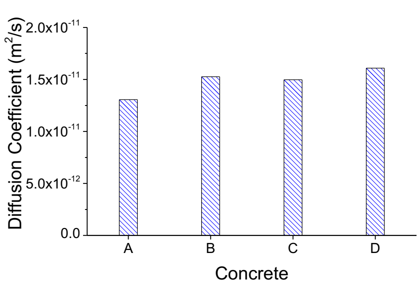

Figure 5. Average values of diffusion coefficient

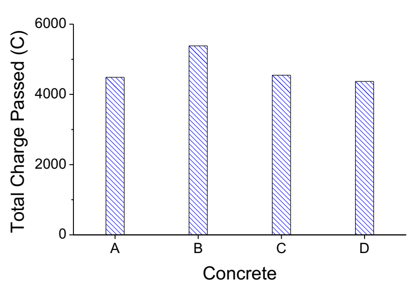

Figure 6. Average values of total charge passed

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

Effects of type of deicer and the FT exposure on the chloride penetration depth

Figure 7 shows the results of the chloride penetration depth measurements for each of four types of concretes, each exposed to three different deicers. Since, as argued in the previous sections, the initial quality of all concretes before the initiation of the FT cycles was about the same (at least in terms of strength and chloride diffusion/resistance based on accelerated electrical tests), the observed differences in the depth of chloride penetration must be the result of other variables (e.g. characteristics of capillary pore system (and associated degree of saturation), characteristics of the air-void system, chemical changes in the microstructure caused by the interaction of the deicers with the various components (C-SH, calcium hydroxide) of the hydrated cement paste, and the viscosity of individual deicers. As it can be from Figure 7, in general, the highest depth of penetration was observed for $CaCl_2$ while the depth of penetration of $MgCl_2$ was the lowest.

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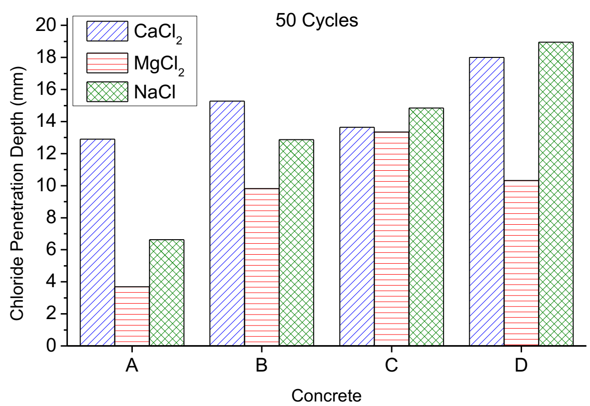

Figure 7. Chloride penetration depth of concretes exposed to 50 FT cycles

Scaling resistance

- Visual evaluation of scaling severity

The previously presented rating scale (Figure 3 and Table 5) was used to qualitatively evaluate the effects of various deicers on the scaling resistance of concreters by visual examination of surfaces of the slabs after completion of 50 FT cycles. The overall appearance of these surfaces (along with the assigned rating values) is summarized in Figure 8. The individual rating values for each of the deicers and concretes used in this study are shown in Figure 9.

Examination of pictures shown in the first column of Figure 8 indicates that exposure to the de-ionized water (i.e. the control solution) caused only slight to moderate scaling (visual rating 2) in the (nominally) most scaling-prone concrete (i.e. concrete D; w/cm=0.45 and air content < 4%). For this reason, data for slabs exposed to de-ionized water were not included in the summary presented in Figure 9.

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

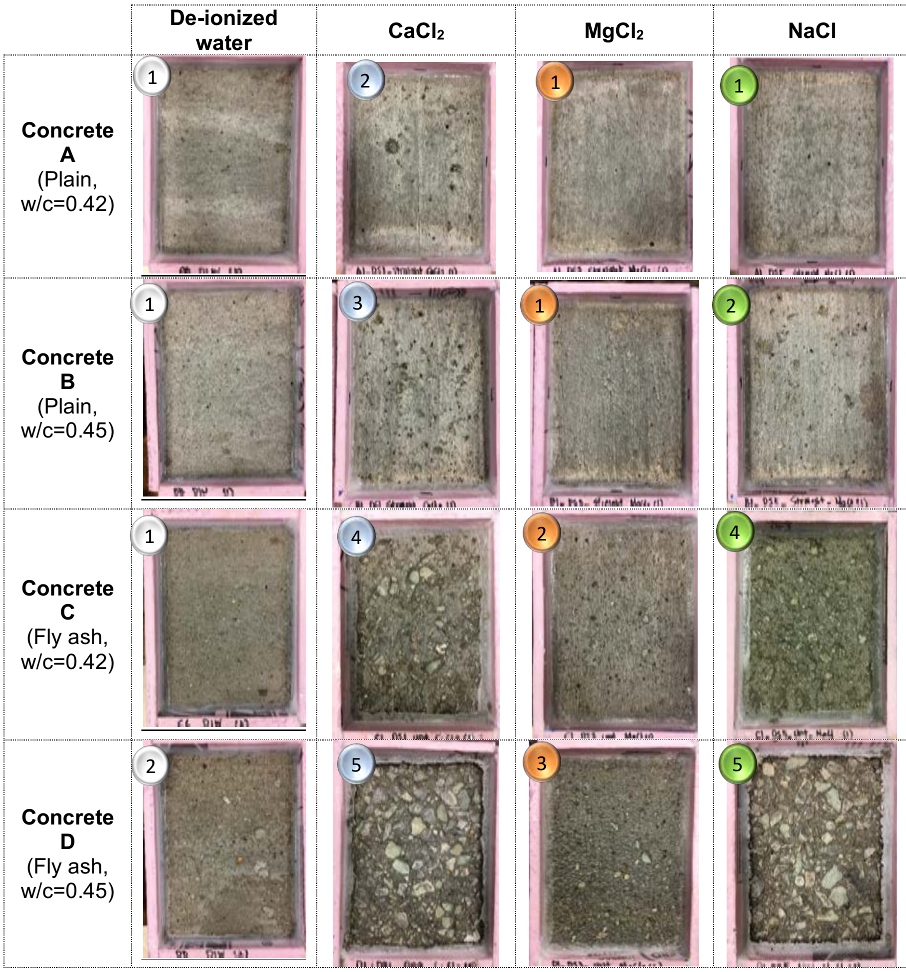

Figure 8. The overall appearance of surfaces of slabs and the assigned visual rating numbers after exposure to 50 FT cycles

The examination of other columns shown in Figure 8 reveals that severity of scaling of plain concrete varied from very slight to moderate (rating 1-3), depending on the type of mixture and the type of deicer used. In the highest quality concrete (i.e. concrete A), only very slight scaling was observed upon exposure to NaCl and $MgCl_2$ deicers. On the other hand, the visual rating of the same concrete exposed to $CaCl_2$ deicer was slight to moderate. As expected, the scaling of

Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

the fly ash concretes was more extensive, but even in that case, the surfaces of concretes exposed to $MgCl_2$ showed only slight to moderate scaling (ranking 2 and 3). In contrast, surfaces exposed to both, $CaCl_2$ and NaCl deicers, developed moderate to severe scaling (ranking 4 and 5). The previously described trends are further emphasized by summation of ranking data shown in Figure 9, which clearly indicates progressive increase in the severity of scaling with the decreasing quality of concrete and the higher severity of exposure to $CaCl_2$ and NaCl deicers compared to $MgCl_2$.

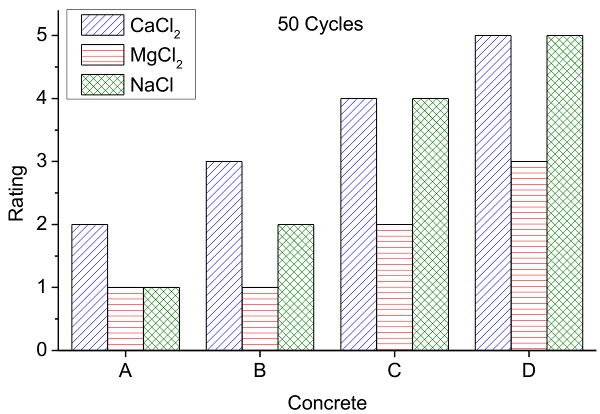

Figure 9. Summary of visual surface scaling ratings after completion of 50 FT cycles

- Mass loss after 50 cycles

Since the visual rating provides only qualitative information regarding the scaling resistance of concrete, the information on the total mass losses after 50 FT cycles was also collected (as described earlier in the "Methods" section of the paper) and used to examine the observed scaling tends in a more quantitative manner. Using the criteria established by the Ontario Ministry of Transportation (MTO), the cumulative mass loss should not be higher than 0.8 kg/m^2 after 50 FT cycles for concrete to be considered as scaling resistant. That criterion is shown as a red dashed line in Figure 10.

Figure 10 presents the results of the cumulative mass loss for each combination of deicers and types of concretes used in this study. Again, the mass losses experienced by slabs exposed to de-ionized water have been excluded as they were very small (less than 0.1 kg/ m^2 in all the concretes). As expected, both of plain concretes (i.e. concrete A and B) show relatively small mass loses compared to fly ash concretes (i.e. concretes C and D). In fact, the cumulative mass losses for all but one (concrete A exposed to NaCl) of these concretes were lower than the critical value of 0.8 kg/m^2. On the other hand, both fly ash concretes exposed to $CaCl_2$ and NaCl experience mass losses higher than 0.8 kg/m^2.

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Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

These mass losses were particularly high for concrete D (about 10 kg/m^2 for $CaCl_2$ deicer and about 15 kg/m^2 for NaCl deicer). The only deicer that did not caused the critical mass losses in the fly ash concretes was $MgCl_2$.

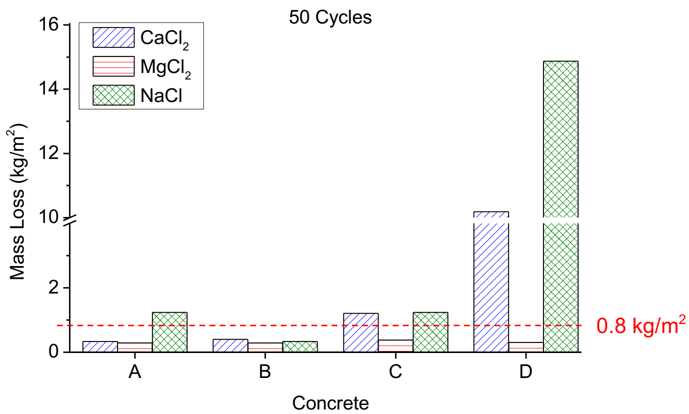

Figure 10. Cumulative mass loss after 50 FT cycles

Conclusions

For all concretes studied in this paper, the highest chloride penetration depths were observed for cases associated with the use of $CaCl_2$, and the lowest chloride penetration depths for cases involving $MgCl_2$.

The effect of deicers on scaling resistance of plain concretes used in this study was relatively similar. In contrast, the scaling resistance of concretes containing fly ash was highly dependent on the type of deicer used. In particular, the use of $CaCl_2$ or NaCl deicers resulted in severe scaling, whereas the use of $MgCl_2$ resulted only in slight to moderate scaling.

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Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu

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Jan Olek Phone: 765-494-5015 Email: olek@purdue.edu