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ORIGINAL ARTICLE

Freeze–thaw damage and chemical change of a portland cement concrete in the presence of diluted deicers

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Abstract The present study experimentally investigates the effect of different diluted deicers on concrete deterioration. Laboratory simulations of environmental freeze/thaw cycling were first conducted on Portland cement concrete specimens in the presence of various deicers (NaCl, K-formate, NaCl-based deicer, K-acetate-based deicer, Na-acetate/Na-formate blend deicer, CMA deicer, or $MgCl_2$ liquid deicer); and SEM/EDX measurements were then conducted for the concrete samples. Under the experimental conditions in this study, the CMA solid deicer and the $MgCl_2$ liquid deicer were benign to the concrete durability, whereas K-formate and the Na-acetate/Na-formate blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer, and the K-acetate-based deicer were the most deleterious to the concrete. In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks. Such physiochemical changes of the cement paste induced by the deicers pose various levels of risks for the concrete durability.

Keywords Deicer · Portland cement concrete · SEM · EDX · Freeze–thaw

1 Introduction

In cold-climate regions, snow and ice control operations are crucial tools to maintain the highways enduring cold and snowy weather. Each year the U.S. and Canada uses approximately 15 million and 4–5 million tons of deicing salts, respectively [1]. The growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment [2–5]. The deleterious effect of chloride-based deicers on reinforcing steel bar (rebar) in concrete structures is well known [6–8]. Deicers may also pose detrimental effects on concrete infrastructure through their reactions with the cement paste and/or aggregates and thus reduce concrete integrity and strength, which in turn may foster the ingress of moisture, oxygen and other aggressive agents onto the rebar surface and promote the rebar corrosion.

In light of existing knowledge base, deicers may pose a risk for the durability of Portland cement concrete (PCC) structures and pavements through

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three main pathways: (1) physical deterioration of the concrete surface by salt scaling; (2) chemical reactions between deicers and concrete; and (3) deicer aggravating aggregate-cement reactions.

First, the scaling of concrete in presence of deicers, referred to as "salt scaling", has been recognized as the main cause for frost-related concrete deterioration, and has been found closely related to concrete quality (e.g., air entrainment level), weather conditions, and the number of freeze/thaw cycles [9–11]. Recently, however, the treatment of PCC with sodium acetate solutions was claimed to be a promising technology to reduce water penetration into concrete and thus extend the service life of concrete [12].

Second, previous research studies have shown that concentrated $MgCl_2$-based deicers cause more severe deterioration to concrete than those based on $CaCl_2$ or NaCl. This is due to the reaction between Mg^{2+} and the hydrated products in cement paste [13–17], which has been reported to be responsible for the degradation of concrete matrix caused by $MgCl_2$ and calcium magnesium acetate (CMA) [18]. It has also been found that concrete exposed to concentrated $CaCl_2$ deteriorated in a similar pattern to those exposed to $MgCl_2$, although at a slower and less severe pace [19].

Finally, both $MgCl_2$ and $CaCl_2$ deicers are known to deteriorate concretes containing reactive dolomite ($CaMg(CO_3)_2$) aggregates by accelerating the alkali-carbonate reaction (ACR) [20, 21]. The long-term use of NaCl can initiate and/or accelerate alkali-silica reaction (ASR) by supplying additional alkalis to concrete [20–26], whereas $CaCl_2$ and $MgCl_2$ do not have as obvious an effect on ASR. Recent research has found that the acetate or formate-based deicers could induce increased levels of expansion in concrete with ASR-susceptible aggregates, and could trigger ASR in concrete that previously did not show ASR susceptibility [27–29].

Previous studies on deicer/concrete interactions generally focused on macroscopic observations and property testing. In this study, we aim to shed more light on the underlying mechanisms responsible for the accelerated deterioration of concrete in the presence of chloride-based or non-chloride deicers, by focusing on physiochemical changes induced by the deicers at the microscopic level of the concrete. In addition, previous studies used mostly concentrated deicer solutions. This study will test diluted deicers (assuming a 100-to-3 dilution ratio for all liquid and solid deicers, which is also the underlying assumption for the deicer corrosivity test method established by the Pacific Northwest Snowfighters Association), since the deicer concentrations experienced by the PCC structures and pavements in the field are often diluted by precipitation and generally low in the long term. We also utilized a laboratory test of freezing-thawing to simulate the temperature cycling in the field in an accelerated manner.

2 Materials and methods

2.1 Materials

The reagent-grade sodium chloride, NaCl (99%, solid) was purchased from ScienceLab.com (Houston, TX). The non-inhibited IceSlicer^{TM} distributed by Enviro-Tech Services (Greeley, CO) was provided by the Colorado Department of Transportation (CDOT) out of its solid stockpile, consisting of naturally occurring complex chlorides (mostly NaCl) and more than 40 trace minerals. The $MgCl_2$-based deicer was provided by the CDOT out of its liquid tank, with active ingredient concentration of 27–29%. The solid CMA deicer was obtained from Cryotech (Fort Madison, IA) with 96% of hydrated calcium magnesium acetate. The reagent-grade potassium formate, KFm (99%, solid), was purchased from Alfa Aesar (Ward Hill, MA). The liquid deicer CF7^{TM} was obtained from Cryotech (Fort Madison, IA) with 50% KAc. The NaAc/NaFm deicer was a blend made from NAAC^{TM} (solid, 97% anhydrous NaAc, from Cryotech, Fort Madison, IA) and Peak SF^{TM} (98% granulated NaFm, from the Blackfoot Company, Toledo, OH) at 50:50 weight ratio. It should be noted that the test solution of CMA, CF7^{TM}, NAAC^{TM} and Peak SF^{TM} deicers contained 18.4, 0.2, 6.6, and 11.4 mM chloride respectively, based on chloride sensor measurements. The deicers and reagent-grade chemicals used in this study are listed in Table 1.

The concrete mix design was specified following the ASTM C 672-91 standard. An ASTM specification C150-07 Type I/II low-alkali Portland cement (ASH Grove Cement Company, Clancy, MT) was used in this study. The chemical composition and physical properties of the cement are available from

Table 1 Deicers or chemicals tested in this study

Deicer abbreviation	Reagent-grade (R)/ commercial deicer (CD)	Liquid (L)/ solid (S)	Source	Active ingredient	Active ingredient concentration
NaCl (r)	R	S	ScienceLab.com	NaCl	99%
KFm (r)	R	S	Alfa Aesar	KCOOH	99%
IceSlicer$^{\text{TM}}$	CD	S	EnviroTech	NaCl	Unknown[a]
CDOT $MgCl_2$	CD	L	Colorado DOT	$MgCl_2$	27–29%[b]
CMA	CD	S	Cryotech	$CaMg(CH_3COO)_2$	96%
CF7 (KAc)	CD	L	Cryotech	$K(CH_3COO)$	50%
NaAc/Fm	CD: NAAC$^{\text{TM}}$	S	Cryotech	$Na(CH_3COO)$	97%
	CD: Peak SF$^{\text{TM}}$	S	Blackfoot Co.	NaCOOH	98%

[a] Mostly NaCl, also containing trace amounts of other chlorides

[b] Provided by the Colorado Department of Transportation out of stockpiles

our previous paper [30]. The fine aggregates used were clean, natural silica sand sifted to allow a maximum aggregate size of 1.18 mm before proportioning and admixing. The coarse aggregates used were crushed limestone with a maximum size of 3/8 in. (0.95 cm). The concrete mix design had a water-to-cement ratio (*w*/*c*) of 0.51, a coarse-aggregate-to-cement ratio of 2.36, and a fine-aggregate-to-cement ratio of 1.75. The coarse aggregates and fine aggregates were prepared to saturated-surface-dry (SSD) condition before mixing, featuring a moisture content of 0.55% and 3.6% respectively. The fine and coarse aggregates were added to the mixing container and mixed until a homogeneous mixture was obtained. Then the cement was added and mixed again until a homogeneous mixture was obtained. Next, water was added from a graduated cylinder and mixed until the concrete is homogeneous and of the desired consistency. The batch was remixed periodically during the casting of the test specimens and the mix container was covered to prevent evaporation. The fresh concrete featured a slump of nearly zero (by the ASTM C 143 method) and air content of 3% (after compaction). Concrete specimens were made in 1½ in. diameter × 1⅞ in. height (3.8 cm × 4.8 cm) poly(vinyl chloride) piping with a volume of 54 cm^3. At least four specimens were made for each deicer solution or control solution. To facilitate de-molding, one saw cut was made through each specimen mold along the × 1⅞ in. length axis. The cut was then covered with duct tape. In the first 24 h of molding, the concrete specimens were placed on a rigid surface and at a relative humidity of about 50% and covered to present excessive evaporation of water. Next, the specimens were de-molded and cured in a moist cure room with relative humidity of 98% for 27 days (which deviates from the curing regime specified by the SHRP method). The 28-day compressive strength of test cylinders was 6,619 psi, well above the recommended 4,000 psi.

2.2 Freeze/thaw test

Laboratory measurements of changes to Portland Cement Concrete (PCC) through freeze/thaw cycling in the presence of deicers were conducted following the SHRP H205.8 test method entitled “Test Method for Rapid Evaluation of Effects of Deicing Chemicals on Concrete” with minor modifications. The SHRP H205.8 test evaluates the effects of chemical deicing formulations and freeze/thaw cycling on the structural integrity of small test specimens of non-air-entrained concrete. The method quantitatively evaluates degradation of the specimen through weight loss measurements. This test method is not intended to be used in determining the durability of aggregates or other ingredients of the concrete.

Once fully-cured the concrete specimens were allowed to dry overnight and weighed. For each deicer, four concrete specimens were placed on a cellulose sponge inside a dish containing 310 ml of deicer solution and then covered with plastic wrap to avoid water evaporation and to slightly compress each test specimen into the sponge. The deicer solutions were made at a 3% by volume for liquids and 3% by weight solution for solids using de-ionized water. One end of each test specimen was in full contact with the sponge. The test specimens (along with the deicer sponge and dish) were placed in the freezer for 16–18 h at −17.8 ± 2.7°C (−0.04°F) and every diluted deicer tested froze at this temperature once it was placed in the freezer for some time. Subsequently, the specimens (along with the deicer sponge and dish) were placed in the laboratory environment at 23 ± 1.7°C (73.4°F) and with a relative humidity ranging from 45 to 55% for 6–8 h, at which temperature every diluted deicer tested thawed once it was taken out of the freezer for some time. This cycle was repeated 10 times. The average heating rate and cooling rate was observed to be 0.4°C/min and 1.2°C/min, respectively. After complete thawing following the tenth cycle, test specimens were carefully removed from the dish, individually rinsed under running tap water, and hand-crumbled to remove any material loosened during the freeze/thaw cycling. The largest intact part of each test specimen was then placed in open air to dry for 24 h at 23 ± 1.7°C (73.4°F) and a relative humidity ranging of 45–55%. After drying, test specimens are weighed and the final weights recorded.

2.3 SEM/EDX measurements

Following the modified SHRP H205.8 freeze–thaw test, the concrete specimens were used for FESEM and EDX testing. For surface analyses, a 0.2 in. (0.5-cm) thick slice sample was cut from the bottom of each remaining concrete specimen, using a concrete saw with a diamond crusted blade that was cooled with de-ionized water. These samples were then washed with de-ionized water to remove debris and desiccated under vacuum for 7 days prior to surface analysis.

The newly cut concrete surface was subjected to field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX), in order to examine its localized morphology and elemental distributions at the microscopic level. We used a Zeiss Supra PGT/HKL system coupled with the energy dispersive X-ray analyzer. Under an accelerating voltage of 1 kV and a pressure of typically 10^{-5} to 10^{-4} torr, the FESEM was used to investigate the effect of deicers on the morphology and chemistry of cement hydrates, by collecting data from at least five randomly selected sites from the cement paste. Care was taken to examine only the cement paste, and the sites were randomly selected to avoid overlapping areas and aggregates. Images detailing morphology were taken using an SE2 detector and at magnifications beginning at 500 times and up to 14000 times. The EDX data were obtained using a micro-analytical unit that featured the ability to detect the small variations in trace element content. For the EDX analysis, an accelerating voltage of 20 kV was used with a scan time of 60 s per sampling area. Areas used for EDX analysis corresponded directly to the FESEM morphological examination at 500× magnification. The area analyzed was approximately 212.5 μm by 143.75 μm. Elements chosen for analysis were based on the known chemical components of the cement paste and deicers.

3 Results and discussion

3.1 Weight loss and macroscopic observations of freeze/thaw specimens

The weight loss of PCC specimens following the modified SHRP H205.8 laboratory test is a good indicator of the freeze/thaw resistance of PCC in the presence of various solutions. Experimental results show that the concrete mix itself had high freeze/thaw resistance in the absence of deleterious deicers. As shown in Fig. 1, the impact of deicers on the structural integrity of PCC fell into three groups. In the first group, the PCC specimens in the presence of de-ionized water, the CMA solid deicer, or the CDOT $MgCl_2$ liquid deicer showed minimal amount of weight loss and little visual deterioration of the concrete. In the second group, the PCC specimens in the presence of KFm or the NaAc/NaFm blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. Finally, the PCC specimens in the presence of NaCl, the NaCl-based deicer (IceSlicer^{TM}), or the KAc-based deicer (CF7^{TM}) showed significant amount of weight loss and marked visual deterioration of the concrete. The differences in the level of concrete deterioration are the joint outcome of physical and chemical mechanisms that merit further investigation: (1) the deicers may have chemically reacted with the cement paste and thus negatively affected its structural integrity

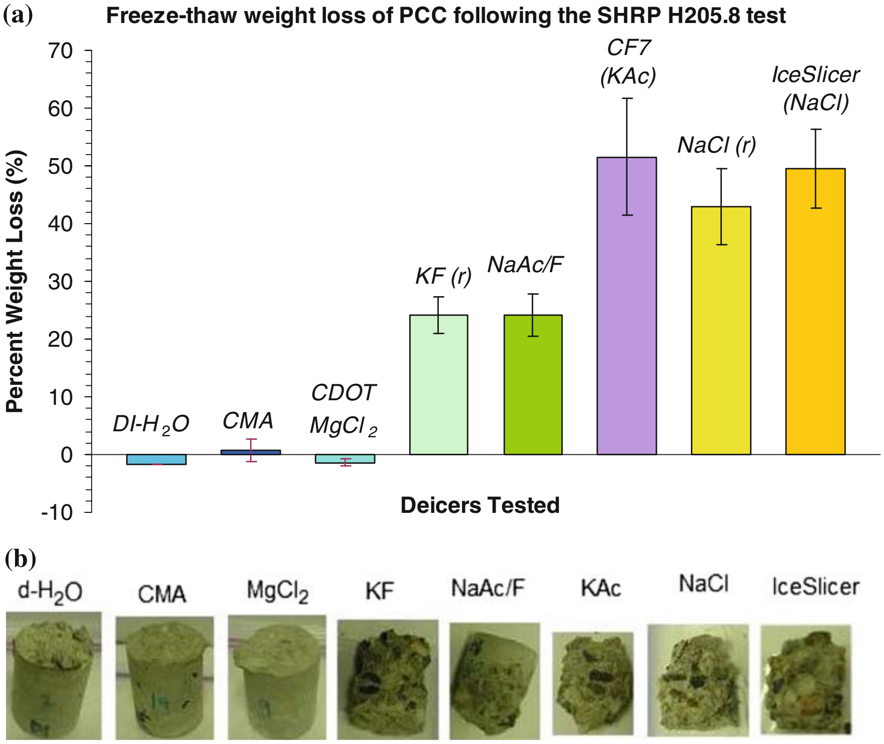

Fig. 1 Weight loss (**a**) and typical digital photo (**b**) of PCC specimen following the SHRP H205.8 freeze–thaw test in the presence of various solutions

(e.g., through the loss of cementitious phases); (2) the diluted deicer may penetrate into the concrete microstructure and affect the chemistry of the concrete pore solution and the ice formation/thawing processes inside the concrete.

It should be cautioned that in the field environment, the deicer impact on the durability of concrete may not follow a similar pattern, as it is further complicated by the concentration and longevity of the deicer and its additives, the chemical composition and microstructure of the concrete, and the temperature regimes experienced by the concrete.

Regarding the relatively negative impact of $MgCl_2$ to NaCl on PCC durability, the modified SHRP H205.8 test results of diluted deicers (~0.85% $MgCl_2$ vs. ~3% NaCl) from this study differed from the ASTM C 666 freeze/thaw test results of concentrated deicers (14% $MgCl_2$ vs. 18% NaCl) reported by Sutter et al. [17]. In their study, concrete prisms of 4 in. diameter × 2 in. height (10 cm × 5 cm) subjected to 300 freezing-thawing cycles in 14% $MgCl_2$ expanded considerably with 0.17% length change and reported 3.5% mass gain and 50% loss in the dynamic modulus of elasticity, whereas those exposed to 18% NaCl did not expand more than 0.04% and reported 0.5% mass gain and approximately 5% loss in the dynamic modulus of elasticity. In contrast, our data indicated much more deleterious impacts by 3% NaCl than 0.85% $MgCl_2$ on PCC durability. Even though the cement chemistry, aggregate properties, concrete permeability, air content, and micro-cracking level of concrete might have played some role in the difference between the two studies, we argue that the key was the difference in the deicer solution concentration. The concentrations we used better simulate the field exposure scenario, where the liquid $MgCl_2$ deicer (27–29%) or the solid NaCl deicer (99%) applied on pavement is dramatically diluted in the long term (a 100-to-3 dilution ratio was assumed in this study). While the concentrated deicers may react with cement paste at a quicker rate than the diluted deicers (and thus weaken the concrete microstructure), they can decrease the freezing-point temperature of the concrete pore solution and thus reduce the number of freezing-thawing cycles actually experienced by the concrete.

At least two mechanisms were at work in how the deicers affected the freeze/thaw resistance of PCC. First, in the case of NaCl, KAc, NaAc/NaFm, and KFm, the presence of deicer significantly altered the chemical composition of the concrete pore solution and thus the freezing-thawing dynamics, which greatly exacerbated the physical distresses in the concrete. We hypothesize that the Na^+ and K^+ cations derived from deicers increased the salinity of the concrete pore solution more than the Mg^{2+} and Ca^{2+} cations derived from deicers, since these smaller cations can easily exchange with the cations in the cement paste and greatly enhance the solubility of cations and anions from cement hydrates including Portlandite ($Ca(OH)_2$), calcium silicate hydrates (C–S–H) and calcium aluminosulfate hydrates. Second, the presence of each deicer altered the chemical composition of the cement paste to varying degrees, as discussed in the following sections. Such chemical changes may lead to altered microstructure of the concrete matrix and buildup of stresses inside. There was a third mechanism suggesting that the NaAc crystal growth inside the pores reduced the water penetration into concrete [12]; such a beneficial role of NaAc observed for the poor-quality concrete ($w/c = 0.65$ and non-air-entrained), however, was not evident in this study.

3.2 Effect of de-ionized water on the surface chemistry of PCC

For the PCC specimens subjected to freeze/thaw cycling in the presence of de-ionized water, the very low calcium contents and high Si/Ca ratios in them (Fig. 2a, b) were caused by the significant leaching of Ca^{2+} from the cement paste to the concrete pore solution and eventually to the de-ionized water featuring an extremely low ionic strength. Based on the box plots of critical elemental ratios (Fig. 2c–e), the high Al/Ca ratios (0.8–1.6) suggest the loss of Ca^{2+} from either calcium aluminate monosulfate hydrates (AFm phases) or calcium aluminate trisulfate hydrates (AFt phases), whereas the very low S/Al ratios (0.01–0.25) and very low S/Ca ratios (0.001–0.02) suggest the loss of SO_4^{2-} from AFm or AFt phases. Compact or honeycombed structures characteristic of type II C–S–H can be seen in Fig. 3a. Despite the dissolution of Ca^{2+} and SO_4^{2-}, the rosette structures characteristic of AFm phases remained, as shown in Fig. 3b. Overall, the examined PCC surfaces were dominated by AFm phases and calcium-rich type II C–S–H, whereas structures of Portlandite, silicate-rich type I C–S–H, or AFt phases were not observed. In the presence of de-ionized water, the residual AFt phases from cement hydration might have further evolved to become AFm phases. It is interesting to note that the chemical changes in the cement paste caused minimal amount of weight loss and little visual deterioration of the concrete (Fig. 1).

3.3 Effect of acetate/formate-based deicers on the surface chemistry of PCC

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% CMA deicer solution, the low calcium contents and relatively high Si/Ca ratios in them (Fig. 2a, b) were caused by the leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the high end of Al/Ca ratios (0.1–1.3) suggests some loss of Ca^{2+} from AFm or AFt phases, whereas the very low S/Al ratios (0.03–0.27) and very low S/Ca ratios (0.008–0.018) suggest the loss of SO_4^{2-} from AFm or AFt phases. Platey structures, likely calcium acetate hydrate crystals as reported in [23], and spherulites characteristic of type I C–S–H can be seen in Fig. 3c. Despite the dissolution of Ca^{2+} and SO_4^{2-}, the rosette structures characteristic of AFm phases remained, as shown in Fig. 3d. Overall, the examined PCC surfaces were dominated by silicate-rich type I C–S–H and AFm phases, whereas structures of AFt phases and calcium-rich type II C–S–H were not observed, likely preferentially dissolved by CMA. As shown in Fig. 1, the chemical changes in the cement paste caused minimal amount of weight loss and little visual deterioration of the concrete. In addition to the short test duration, a likely explanation is that while the detrimental reactions of CMA with cement paste were thermodynamically possible and proven in this study, the kinetics of such reactions was slow due to the low CMA concentration (~3%). Nonetheless, the preferential dissolution of some cement hydrates by CMA explains the observed deterioration of the cement matrix and exposure of the aggregates in another laboratory study [31], where 8 months of continuous exposure of good-quality concrete ($w/c = 0.45$ and air-entrained) to concentrated CMA solutions (25%) caused a significant decrease in load capacity, mass loss and severe visual degradation of the concrete. Cement mortar samples ($w/c = 0.485$) were also reported to lose cohesiveness and disintegrate completely after 30-day exposure to

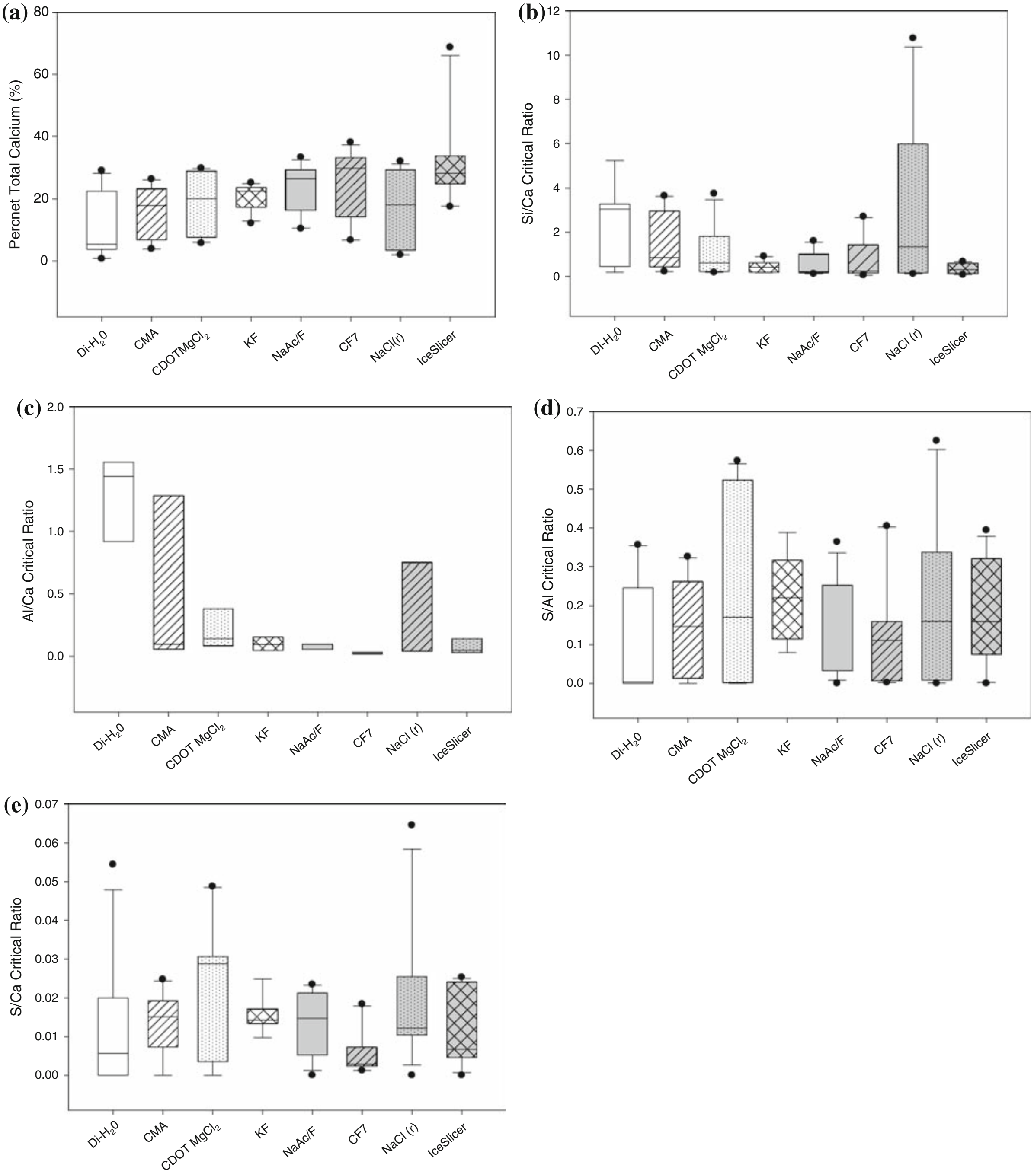

Fig. 2 Chemical composition of PCC samples following the modified SHRP H205.8 freeze–thaw test in the presence of various solutions, with box plots illustrating the EDX data collected from multiple locations on the sample. (**a**) percent total Ca; (**b**) Si/Ca; (**c**) Al/Ca; (**d**) S/Al; (**e**) S/Ca. Note that box plot is a well-established statistical way of graphically illustrating groups of numerical data, in which the top, middle and bottom line of the box itself corresponds to the 75-, 50-, and 25-percentile value ($x_{.75}$, $x_{.5}$, and $x_{.25}$) respectively. The interquartile range (IQR) is defined by subtracting the first quartile from the third quartile ($x_{.75} - x_{.25}$). Also in each box plot, outliers (shown as *dots*) are the values either above the very top line ($x_{.75} + 1.5\text{IQR}$) or below the very bottom line ($x_{.25} - 1.5\text{IQR}$)

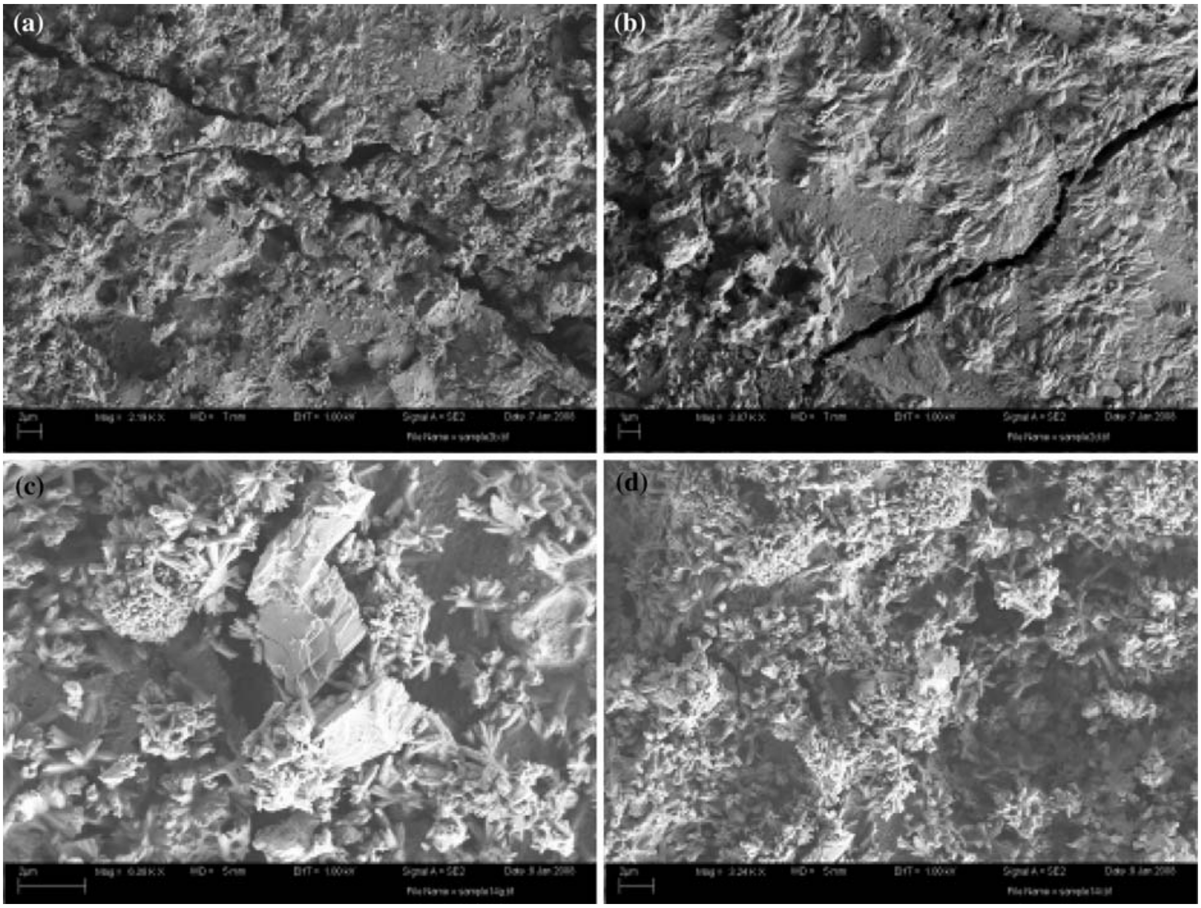

Fig. 3 Representative SEM image of PCC samples following the modified SHRP H205.8 freeze–thaw test in the presence of various solutions. **a** de-ionized water, 2190 times; **b** de-ionized water, 3870 times; **c** CMA, 6380 times; **d** CMA, 3240 times

28% CMA solution at room temperature, and the formation of calcium acetate hydrate phases were confirmed by X-ray diffraction results [17].

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% KFm solution, the moderate calcium contents and low Si/Ca ratios in them (Fig. 2a, b) suggest little leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the relatively low Al/Ca ratios (0.1–0.2) further confirms little leaching of Ca^{2+}, whereas the low S/Al ratios (0.12–0.33) and low S/Ca ratios (0.014–0.016) suggest the loss of SO_4^{2-} from AFm or AFt phases. Rosette structures characteristic of AFm phases can be seen in Fig. 4a, whereas poorly crystalline fibers characteristic of AFt phases and honeycombed structures characteristic of calcium-rich type II C–S–H can be seen in Fig. 4b. Overall, the examined PCC surfaces showed a very high presence of bladed calcium-rich crystals. We hypothesize that the exposure of the cement paste to potassium formate led to the preferential dissolution of silicate-rich type I C–S–H and the releasing of calcium sulfate ($CaSO_4$) from AFm phases and promoted the formation of calcium formate hydrate crystals and AFt phases. The disintegration of the cement paste and the formation of new cement hydrates contributed to the moderate amount of weight loss and noticeable deterioration observed in the freeze/thaw specimens.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% NAAC™ +Peak SF™ (NaAc:NaFm ~ 1:1) deicer solution, the moderate calcium contents and low Si/Ca ratios in them (Fig. 2a, b) suggest little leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the low

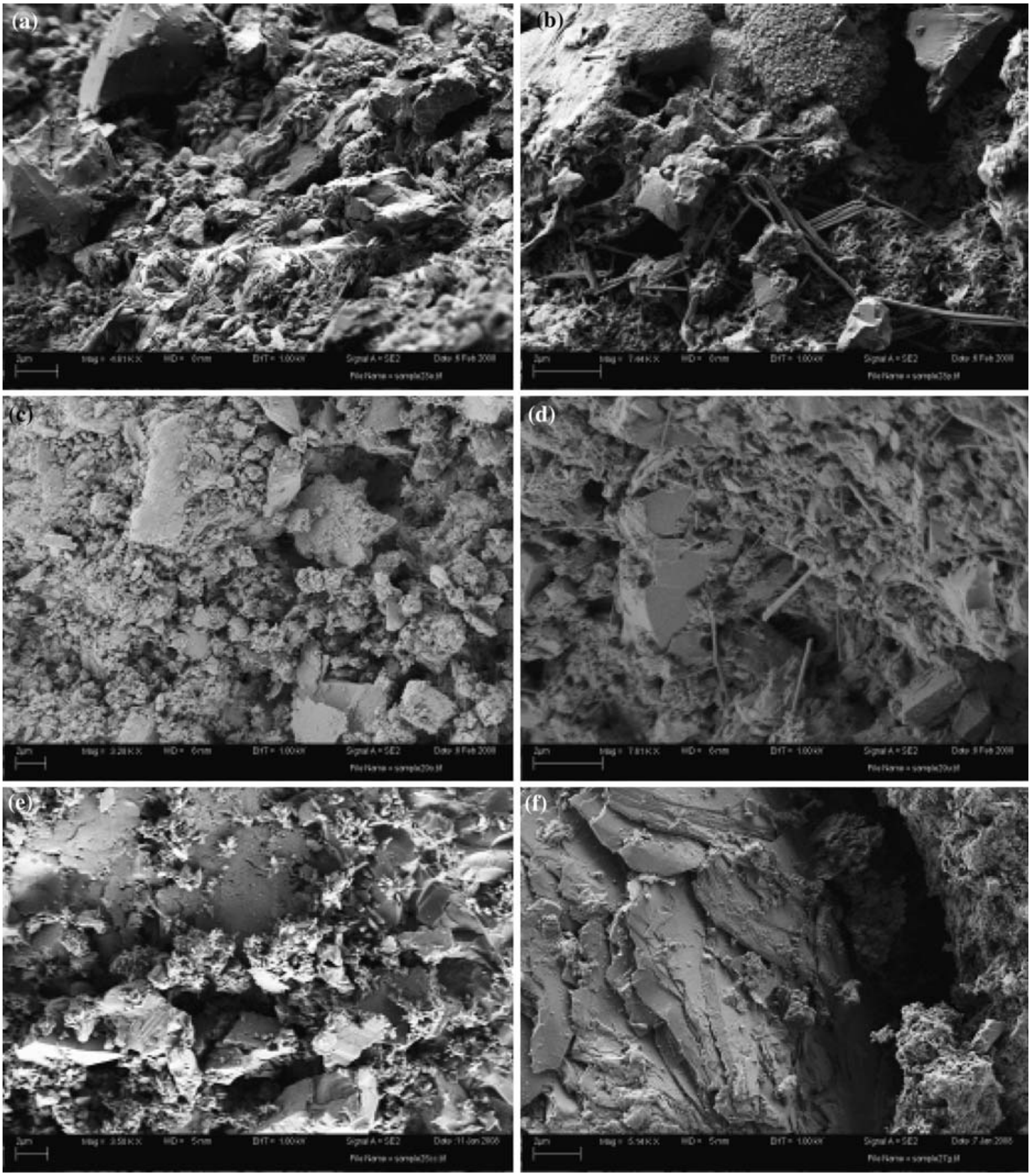

Fig. 4 Representative SEM image of PCC samples following the modified SHRP H205.8 freeze–thaw test in the presence of various solutions. **a** KFm (r), 4610 times; **b** KFm (r), 7440 times; **c** NaAc/NaFm, 3280 times; **d** NaAc/NaFm, 7610 times; **e** KAc, 3500 times; and **f** KAc, 5140 times

Al/Ca ratios (~ 0.1) further confirms little leaching of Ca^{2+}, whereas the low S/Al ratios (0.05–0.25) and low S/Ca ratios (0.006–0.022) suggest the loss of SO_4^{2-} from AFm or AFt phases. Overall, the examined PCC surfaces showed a very high presence of platey or bladed calcium-rich crystals and coarsening of the concrete pores (Fig. 4c, d). Spiky sodium-rich crystals and honeycombed structures characteristic of calcium-rich type II C–S–H were present as well. We hypothesize that the exposure of the cement paste to sodium acetate and sodium formate led to the preferential dissolution of silicate-rich type I C–S–H and the releasing of calcium sulfate ($CaSO_4$) from AFm and AFt phases and promoted the formation of calcium acetate and calcium formate hydrate crystals. The disintegration of the cement paste and the formation of new cement hydrates contributed to the moderate amount of weight loss and noticeable deterioration observed in the freeze/thaw specimens.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~1.5% CF7™ (KAc) deicer solution, the relatively high calcium contents and relatively low Si/Ca ratios in them (Fig. 2a, b) suggest little leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the very low Al/Ca ratios (~0.02) further confirms little leaching of Ca^{2+}, whereas the low S/Al ratios (0.01–0.15) and low S/Ca ratios (0.004–0.008) suggest the loss of ${SO_4}^{2-}$ from AFm or AFt phases. Overall, the examined PCC surfaces showed a high presence of lamella structures (Fig. 4f). In addition, compact structures characteristic of calcium-rich type II C–S–H can be seen in Fig. 4e, along with platey calcium-rich crystals and residual rosette structures attributable to AFm phases deficient in Ca^{2+} and ${SO_4}^{2-}$. We hypothesize that the exposure of the cement paste to potassium acetate led to the preferential dissolution of silicate-rich type I C–S–H and the releasing of calcium sulfate ($CaSO_4$) from AFm and AFt phases and promoted the formation of calcium acetate hydrate crystals and some lamella structures. The disintegration of the cement paste and the formation of new cement hydrates contributed to the significant amount of weight loss and marked visual deterioration observed in the freeze/thaw specimens. In particular, the exfoliation of the lamella crystals might be responsible for expansion and subsequent cracking or spalling of the concrete, as suggested by a previous study [32].

3.4 Effect of chloride-based deicer on the surface chemistry of PCC

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~ 0.85% $MgCl_2$ deicer solution, the relatively low calcium contents in them (Fig. 2a) indicate some leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the low end of S/Al ratios (0.02–0.52) and low S/Ca ratios (0.003–0.03) suggest the loss of ${SO_4}^{2-}$ from AFm or AFt phases, whereas the Al/Ca ratios were in the reasonable range of 0.1–0.4. The high Cl signals on the examined PCC surfaces and the presence of layer structures likely attributable to Friedel's salt (calcium chloroaluminates) suggest partial substitution of the sulfate anion in AFm or AFt phases by the chloride anion (i.e., chloride binding). Overall, the examined PCC surfaces featured a high presence of fibrous crystals (Fig. 5a) and needle-like crystals (Fig. 5b). Some platey calcium-rich crystals were also observed. The fibrous crystals were magnesium chloride hydroxide hydrates formed by the Ca^{2+} substitution for Mg^{2+} and Cl^- substitution for ${SO_4}^{2-}$ in the cement hydrates, with pseudomorphs replacing the AFm and AFt phases observed. The needle-like crystals can be attributed to the formation of some hydrated magnesium oxychlorides similar to $Mg_3(OH)_2Cl{\cdot}4H_2O$ crystals formed in the hardened Sorel cement paste [33]. The presence of platey calcium-rich crystals can be attributed to the formation of hydrated calcium oxychloride phases, as reported previously [34]. The structures of brucite were not observed on the examined PCC surfaces, even though they were observed in the outer layers of the specimens exposed to concentrated $MgCl_2$ [17]. These microscopic observations confirm the following reactions commonly accepted to be responsible for concrete degradation by $MgCl_2$:

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2 \tag{1}$$

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO \cdot CaCl_2 \cdot 15H_2O \tag{2}$$

In addition, previous studies suggest that $MgCl_2$ can also react with the cementitious C–S–H phases and produce non-cementitious magnesium silicate hydrate (M–S–H) and $CaCl_2$ and thus significantly degrade the strength of the concrete. In the case of concentrated $MgCl_2$, the formation of brucite inside the concrete was accompanied with great expansive forces and subsequently aggravated concrete deterioration [13, 14, 16]. As shown in Fig. 1, the chemical changes in the cement paste caused minimal amount

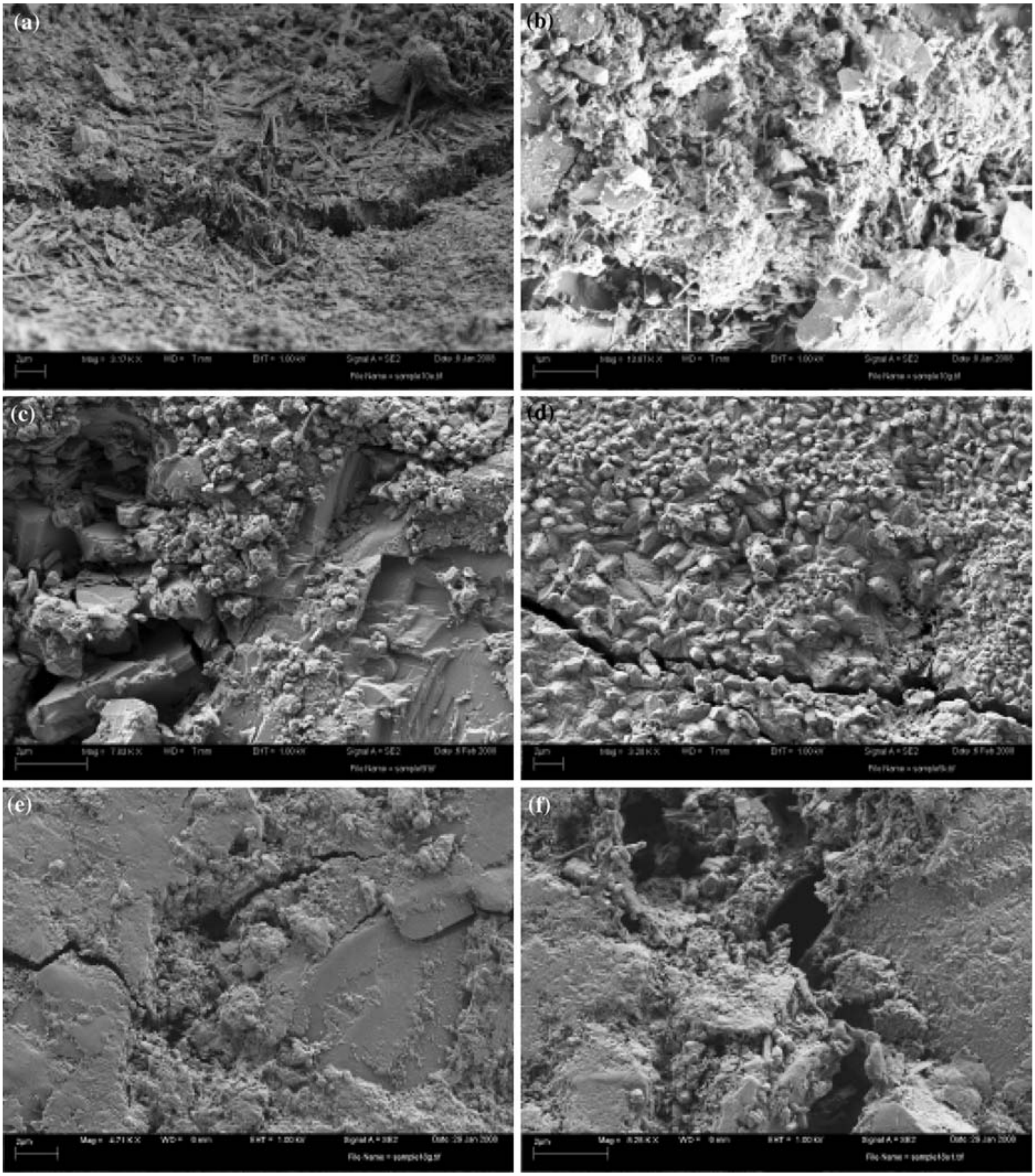

Fig. 5 Representative SEM image of PCC samples following the modified SHRP H205.8 freeze–thaw test in the presence of various solutions. **a** $MgCl_2$, 3170 times; **b** $MgCl_2$, 13870 times; **c** NaCl (r), 7830 times; **d** NaCl (r), 3200 times; **e** IceSlicer, 7290 times; and **f** IceSlicer, 8250 times

of weight loss and little visual deterioration of the concrete. In addition to the short test duration, a likely explanation is that while the detrimental reactions of $MgCl_2$ with cement paste were thermodynamically possible and proven in this study, the kinetics of such reactions was slow due to the low

$MgCl_2$ concentration (~0.85%). Nonetheless, the physiochemical changes in the cement paste induced by $MgCl_2$ explains the findings in another laboratory study [17], where concentrated $MgCl_2$-based deicers chemically attacked mortar and concrete, leading to volume change, loss of compressive strength, and microcracks.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% NaCl deicer solution, the low calcium contents and high Si/Ca ratios in them (Fig. 2a, b) indicate leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the high end of Al/Ca ratios (0.06–0.75) suggests loss of Ca^{2+} from AFm or AFt phases, whereas the low end of S/Al ratios (0.02–0.34) and low S/Ca ratios (0.01–0.025) suggest the loss of SO_4^{2-} from AFm or AFt phases. The Cl signals on the examined PCC surfaces suggest limited level of chloride binding. Compact or honeycombed structures characteristic of type II C–S–H and hexagonal Portlandite crystals can be seen in Fig. 5c. Residual rosette structures can be seen in Fig. 5d, as a result of the dissolution of Ca^{2+} and SO_4^{2-} decomposing AFm phases. Overall, the examined PCC surfaces were dominated by AFm phases and calcium-rich type II C–S–H, whereas structures of AFt phases and silicate-rich type I C–S–H were not observed. We hypothesize that the exposure of the cement paste to sodium chloride led to the preferential dissolution of silicate-rich type I C–S–H and the releasing of calcium sulfate ($CaSO_4$) from AFm and AFt phases. While previous studies suggest that NaCl may react with Portlandite and lead to Portlandite dissolution and pH increase [20, 22–24], this process was found to be quite slow and might be masked by other short-term effects. The preferential dissolution of certain cement hydrates, along with exacerbated physical distresses in the freeze/thaw test, led to the significant amount of weight loss and marked visual deterioration of the concrete. This finding from diluted deicers differed from the study of concentrated deicers [17], where NaCl seemed to be more chemically benign to concrete than $MgCl_2$.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% IceSlicer^{TM} (NaCl and other chlorides) deicer solution, the high calcium contents and low Si/Ca ratios in them (Fig. 2a, b) indicate little leaching of Ca^{2+} from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Fig. 2c–e), the low Al/Ca ratios (0.02–0.15) further confirms little leaching of Ca^{2+}, whereas low S/Al ratios (0.09–0.33) and low S/Ca ratios (0.005–0.024) suggest the loss of SO_4^{2-} from AFm or AFt phases. The Cl signals on the examined PCC surfaces suggest limited level of chloride binding. Overall, the examined PCC surfaces were dominated by compact or honeycombed type II C–S–H phases with few resolvable crystals, whereas structures of AFt phases and silicate-rich type I C–S–H were not observed. Platey Portlandite crystals and spiky sodium-rich crystals can be seen in Fig. 5e and f, respectively. We hypothesize that the exposure of the cement paste to IceSlicer^{TM} led to the preferential dissolution of silicate-rich type I C–S–H and the releasing of SO_4^{2-} from AFm and AFt phases. Similar to the reagent-grade NaCl, the diluted IceSlicer^{TM} led to significant amount of weight loss and marked visual deterioration of the concrete.

4 Conclusions

- This work investigated the effect of diluted deicers on the durability of a Portland cement concrete. Based on the gravimetric and macroscopic observations of freeze/thaw specimens following the modified SHRP H205.8 laboratory test, de-ionized water, the CMA solid deicer, and the CDOT $MgCl_2$ liquid deicer were benign to the PCC durability, whereas KFm and the NaAc/NaFm blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer (IceSlicer^{TM}), and the KAc-based deicer (CF7^{TM}) were the most deleterious to the concrete.
- The SEM/EDX measurements revealed that each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks. Such physiochemical changes of the cement paste induced by the deicers pose various levels of risks for the concrete durability.
- This work provides new insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. With the improved

knowledge, more research should also be conducted on countermeasures designed to minimize the deicer impact on concrete durability.

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References

1. Salt Institute Deicing salt and corrosion, http://www.saltinstitute.org/th2020s.html. Accessed in July 2007
2. Buckler DR, Granato GE (1999) Assessing biological effects from highway runoff constituents, U.S. Department of the Interior and U.S. Geol Surv Open-File Rep (US): 99–240
3. Federal Highway Administration (2002) Corrosion costs and preventative strategies in the United States, Publication No. FHWA-RD-01-156
4. Johnson JT (2007) Corrosion costs of motor vehicles, http://www.corrosioncost.com/pdf/transportation.pdf. Accessed in July 2007
5. Amrhein C, Strong JE, Mosher PA (1992) Effect of deicing salts on metal and organic matter mobilization in roadside soils. Environ Sci Technol 26(4):703–709. doi:10.1021/es00028a006
6. Cook HK, McCoy WJ (1977) Chloride corrosion of steel in concrete, ASTM STP 629. In: Tonini DE, Dean SW (eds) ASTM, Philadelphia, pp 20–29
7. Mangat PS, Molloy BT (1992) Factors influencing chloride-induced corrosion of reinforcement in concrete. Mater Struct 25(151):404–411. doi:10.1007/BF02472256
8. Neville A (1995) Chloride attack of reinforced concrete: an overview. Mater Struct 28(176):63–70. doi:10.1007/BF02473172
9. Marchand J, Sellevod EJ, Pigeon M (1994) The deicer salt scaling deterioration of concrete—an overview. In: Malhotra VM (ed) Proceedings of Third CANMET/ACI International Conference on Durability of Concrete, ACI SP-145, American Concrete Institute, Detroit, pp 1–46
10. Pigeon M, Pleau R (1995) Durability of concrete in cold climates. E & FN Spon, New York
11. Mussato BT, Gepraegs OK, Farnden G (2004) Relative effects of sodium chloride and magnesium chloride on reinforced concrete: the state of art. Transp Res Rec 1886(8):59–66. doi:10.3141/1866-08
12. Al-Otoom A, Al-Khlaifa A, Shawaqfeh A (2007) Crystallization technology for reducing water permeability into concrete. Ind Eng Chem Res 46(16):5463–5467. doi:10.1021/ie070527l
13. Cody RD, Cody AM, Spry PG, Gan G (1996) Experimental deterioration of highway concrete by chloride deicing salts. Environ Eng Geosci 2(4):575–588
14. Lee H, Cody RD, Cody AM (2000) Spry PG Effects of various deicing chemicals on pavement concrete deterioration. In: Center for Transportation Research and Education (ed) Mid-continent transportation symposium proceedings, Iowa State University, Ames, U.S.A., pp 151–155
15. Deja J, Loj G (1999) Effect of cations occuring in the chloride solutions on the corrosion resistance of slag cementitious materials. In: Swamy RN (ed) Infrastructure regeneration and rehabilitation improving the quality of life through better construction—a vision for the next millennium international conference, Sheffield, ROYAUME-UNI, pp 603–620
16. Cody RD, Spry PG, Cody AM, Gan G (1994) The role of magnesium in concrete deterioration, The Iowa Highway Research Board, Final Report-Iowa DOT HR-355
17. Sutter L, Peterson K, Julio-Betancourt G, Hooton D, Vam Dam T, Smith K (2008) The deleterious chemical effects of concentrated deicing solutions on Portland cement concrete. Final report for the South Dakota Department of Transportation
18. Levelton Consultants Ltd (2008) Guidelines for the selection of snow and ice control materials to mitigate environmental impacts, NCHRP REPORT 577, National Cooperative Highway Research Program, Transportation research board of the national academies, Washington, D.C, http://onlinepubs.trb.org/onlinepubs/nchrp/nchrp_rpt_577.pdf. Accessed in July 2008
19. Monosi S, Collepardi M (1990) Research on $3CaO \cdot CaCl_2 \cdot 15H_2O$ identified in concretes damaged by $CaCl_2$ attack. Cimento 87:3–8
20. Chatterji S, Thaulow N, Jensen AD (1987) Studies of alkali-silica reaction. Part 4. Effect of different alkali salt solutions on expansion. Cem Concr Res 17(5):777–783. doi:10.1016/0008-8846(87)90040-8
21. Nixon PJ, Page CL, Canham I, Bollinghaus R (1988) Influence of sodium chloride on the alkali-silica reaction. Adv Cem Res 1(2):99–106
22. Kawamura M, Takemoto K (1989) Ichise M Influences of the alkali-silica reaction on the corrosion of steel reinforcement in concrete. In: Okana SN, Kawamura M (eds) Proceedings of 8th international conference on alkali-aggregate reaction in concrete. Elsevier, Kyoto, Japan, pp 115–120
23. Kawamura M, Takeuchi K, Sugiyama A (1994) Mechanisms of expansion of mortars containing reactive aggregate in NaCl solution. Cem Concr Res 24(4):621–632. doi:10.1016/0008-8846(94)90186-4
24. Kawamura M, Takeuchi K (1996) Alkali-silica and pore solution composition in mortars in sea water. Cem Concr Res 26(12):1809–1819. doi:10.1016/S0008-8846(96)00178-0
25. Sibbick RG (1993) The susceptibility of various UK aggregates to alkali-silica reaction, Ph.D. Dissertation, Aston University, Birmingham, UK
26. Sibbick RG, Page CL (1996) Effects of sodium chloride in the alkali-silica reaction in hardened concrete. In: Shayan A (ed) Proceedings of 10th International Conference

on Alkali-Aggregate Reaction in Concrete, CSIRO, Melbourne, Australia, pp 822–829

27. Rangaraju PR, Sompura KR, Olek J, Diamond S, Lovell J (2005) Potential for development of alkali-silica reaction in the presence of airfield deicing chemicals. In: International Society for Concrete Pavements (ed) Proceedings of the 8th International Conference on Concrete Pavements, Colorado Springs, USA, pp 1269–1289
28. Rangaraju PR, Sompura KR, Olek J (2007) Modified ASTM C 1293 test method to investigate potential of potassium acetate deicer solution to cause alkali-silica reaction. Transp Res Rec 2020(1):50–60. doi:10.3141/2020-07
29. Rangaraju PR, Desai J (2006) Effectiveness of Selected SCMs in Mitigating ASR in Presence of Potassium Acetate Deicer Solution. In: Transportation Research Board (ed) Proceedings (CD-ROM) of the 85th Annual Meeting of Transportation Research Board, Paper No. 06-3010, Washington, DC
30. Shi X, Yang Z, Nguyen TA, Suo Z, Avci R, Song S (2009) An electrochemical and microstructural characterization of steel-mortar admixed with corrosion inhibitors. Sci China Ser E 52(1):52–66. doi:10.1007/s11431-008-0276-5
31. Santagata MC, Collepardi M (2000) The effect of CMA deicers on concrete properties. Cem Concr Res 30(9):1389–1394. doi:10.1016/S0008-8846(00)00334-3
32. Beaudoin JJ, Ramachandran VS (2001) Handbook of analytical techniques in concrete science and technology: Principles, techniques, and applications. William Andrew Pub, Norwich, NY
33. Tooper B, Cartz L (1966) Structure and formation of magnesium oxychloride sorel cements. Nature 211(5040):64–66. doi:10.1038/211064a0
34. Sutter L, Peterson K, Touton S, Van Dam T, Johnston D (2006) Petrographic evidence of calcium oxychloride formation in mortars exposed to magnesium chloride solution. Cem Concr Res 36(8):1533–1541. doi:10.1016/j.cemconres.2006.05.022