

# Physico-chemical Changes in Plain and Fly Ash Modified Concretes Exposed to Different Deicing Chemicals

<sup>1</sup>Jain J, <sup>1</sup>Janusz A, <sup>1</sup>Olek J\*

<sup>1</sup>Purdue University, School of Civil Engineering, West Lafayette, IN, USA

<sup>2</sup>Jozwiak-Niedzwiedzka D

<sup>2</sup>Institute of Fundamental Technological Research (IFTR),  
Polish Academy of Sciences, Pawlinskiego 5B, 02-106, Warsaw, Poland.

## Abstract

The deicing/anti-icing chemicals are routinely used on pavement surfaces during cold weather to ensure safe driving conditions. Traditionally, solid rock salt (NaCl) or NaCl brines have been used for these purposes but their efficiency is reduced at lower temperatures. In order to provide a more reliable means of ice and snow control, chemicals with lower freezing points, such as CaCl<sub>2</sub> or MgCl<sub>2</sub> (or sometimes rock salt pretreated with CaCl<sub>2</sub> or MgCl<sub>2</sub> brines,) are increasingly being applied to the pavements. The extent and magnitude of chemical reactions of these “new-generation” deicers with pavement concrete is still somewhat unclear. This paper presents the results of investigation of the physicochemical changes in pavement concretes exposed to different deicers and subjected to both wetting/drying (W/D) and freezing/thawing (F/T) regimes.

Plain concretes (PC) and concretes with 20% of mass of cement replaced by Class C fly (FA20) were exposed to three different types of deicing solutions (NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>), with total ion molality of, respectively, 10.5 for W/D and 5.5 for F/T regimes. For comparison purposes, additional set of specimens was kept in deionized water (DIW) under similar exposure regimes. The companion set of control specimens was kept in saturated limewater at 23°C. The physical alterations taking place in the prismatic (76x76x292 mm) specimens were evaluated weekly by measuring changes in mass and in the relative dynamic modulus of elasticity (RDME) of the specimens. After 154 W/D cycles prismatic specimens exposed to 28% CaCl<sub>2</sub> solution exhibited considerable visual distress, reduction in mass, and reduction in RDME. The same deicer also caused reduction in mass and in RDME after only 35 F/T cycles. The performance of fly ash modified concretes was better than that of PC in all deicing solutions under both W/D and F/T regimes.

To ensure a unidirectional penetration of deicers, several 76 mm diameter concrete cylinders were ponded with the same deicing solutions as the prismatic beams while being exposed to W/D cycles. These cylinders were used to prepare the SEM analysis samples.

## Originality

The durability of PC and fly ash pavement concretes exposed to several different deicers was evaluated by monitoring physico-chemical changes in the specimens subjected to W/D, and F/T regimes. The selected W/D regime consisted of storing specimens for 16 hrs in the liquid deicer at 4°C followed by 8 hrs of air drying at 23°C. In addition to being reasonably realistic with respect to the actual field exposure conditions, the adopted W/D regime was also designed to verify the hypothesis that regularly alternating wetting and drying cycles will prevent the build-up of expansive oxychloride phases which were shown (in an unrelated study involving up to 84 days of continuous exposure at 4.4°C) to be capable of completely destroying the test specimens.

## Chief contributions

Three different deicing solutions were used for evaluating the physico-chemical alterations in plain and fly ash concretes during W/D and F/T cycles. These alterations were monitored in terms of dynamic modulus of elasticity and mass changes in the prismatic specimens. The results collected after 154 W/D cycles indicated no deterioration for the specimens exposed to MgCl<sub>2</sub> solution, contrary to the results reported in previous studies. The F/T test showed 10% reduction in relative dynamic modulus of elasticity (RDME) for specimens kept in 17% CaCl<sub>2</sub> solutions after 90 cycles while specimens kept in 15% MgCl<sub>2</sub> showed similar reduction only after 200 cycles. The microscopic examination was carried out to analyze the causes for this kind of behavior.

Keywords: Deicer, Durability, Physico-chemical, Microstructure

\*Corresponding author: Email [olek@purdue.edu](mailto:olek@purdue.edu) Tel +17654945015, Fax +17654940395

## 1.0 INTRODUCTION

For a number of years sodium chloride (NaCl), commonly known as rock salt, has been used as the deicer to control ice and snow build-up on pavement surfaces. However, since the ice melting efficiency of NaCl diminishes rapidly below  $-8^{\circ}\text{C}$ , deicers with an increased ability to melt ice at lower temperatures (such as calcium chloride ( $\text{CaCl}_2$ ) and magnesium chloride ( $\text{MgCl}_2$ )) are being increasingly used in winter maintenance operations of pavements. While these deicers offer a very effective means of snow and ice control, their impact on the durability of concrete infrastructure is still a subject of debate, mostly due to strong dependence of the test results on the exposure conditions and concentrations of the salt solutions used.

The results of several of the past studies (Cody et al., 1996; Darwin et al., 2008; Kozikowski et al., 2007; Lee et al., 2000; Monosi and Collepardi, 1990; Sutter et al., 2006; Wang et al., 2006) on the effects of deicers on concrete vary greatly, depending on such factors as the exposure conditions, concentrations of the deicers, and the test temperature. In some cases, chemical reactions of deicers with the matrix leading to formation of such products as calcium hydroxide, calcium oxychloride and magnesium silicate hydrate were indicated as the main reasons for concrete deterioration. In other cases, the observed damage was attributed to the combined effects of physical interactions (crystallization of complex salts leading to expansion and cracking) and chemical reactions.

## 2.0 MATERIALS, MIXTURE PROPORTIONS AND EXPERIMENTAL PROGRAM

The study described in this paper was performed on two types of concrete: plain concrete (PC) prepared with ASTM C 150 Type I cement and fly ash (FA20) concrete in which 20% (by mass) of cement was replaced by the ASTM C 618 Class C fly ash ( $\sim 18.8\%$  CaO). The local crushed limestone with nominal maximum size of 25 mm, specific gravity of 2.74 and absorption of 0.8 %, was used as coarse aggregate. The natural siliceous sand, with specific gravity of 2.66 and absorption of 1.5% was used as fine aggregate.

The total amount of cementitious materials used in both types of concrete was  $348 \text{ kg per m}^3$  and the water-to-cementitious material ratio was 0.42. The synthetic air entraining admixture and the mid-range water reducer were used to obtain, respectively, a target air content of 6.5% and the slump of about 75 mm. The test specimens used in the study included  $76 \times 76 \times 292$  mm prisms and two sizes of cylinders:  $100 \times 200$  mm and  $76 \times 152$  mm. All specimens were demolded one day after casting and placed in the moist room (100% relative humidity) for 28 days of curing. At the end of this curing period the specimens were removed from the moist room and allowed to air-dry at for 3 days at a temperature of  $23^{\circ}\text{C}$  and a relative humidity (RH) of 50% before being subjected to various exposure regimes.

The test procedures for prismatic specimens involved exposing them to two different environmental conditions: wetting/drying (W/D) cycles and freezing/thawing (F/T) cycles. One W/D cycle consisted of submerging specimens for 16 hours in the deicing solutions (or deionized water) at a temperature of  $4^{\circ}\text{C}$  and drying them for 8 hours at the temperature of  $23^{\circ}\text{C}$  and 50% RH. The duration of each of the F/T cycles was 24 hours. During this time, the specimens were subjected to 9 hours of cooling (from  $22^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ ), 5 hrs of constant low ( $-20^{\circ}\text{C}$ ) temperature, 6 hours of heating (from  $-20^{\circ}\text{C}$  to  $22^{\circ}\text{C}$ ) and 4 hours of constant room ( $22^{\circ}\text{C}$ ) temperature. The total (anions + cations) ion molalities of deicing solutions were kept constant at 10.5 for W/D cycles and 5.5 for F/T cycles (Table 1).

For comparison purposes, additional set of specimens was kept in deionized water (DIW) under the same W/D exposure regime as that used for the deicers. Finally, a set of control specimens was also prepared and kept in saturated limewater at  $23^{\circ}\text{C}$ . The physical changes taking place in the prisms were monitored by measuring (at 2 weeks intervals) changes in their mass, length and stiffness (relative dynamic modulus of elasticity (RDME)). The testing of prisms was discontinued either when their surfaces showed signs of considerable damage or when their RDME reduced to below 80%, whichever occurred first.

Table 1: Concentrations of different deicing solutions used in this study

Deicing solution	Salt Concentration (mass percent)		Total ions molality	
	W/D	F/T	W/D	F/T
Sodium Chloride (NaCl)	23%	14%	10.5	5.5
Magnesium Chloride (MgCl <sub>2</sub> )	25%	15%	10.5	5.5
Calcium Chloride (CaCl <sub>2</sub> )	28%	17%	10.5	5.5

The cylindrical specimens were subjected to the same deicers and the same W/D regime as the prisms. However, unlike prisms (which were submerged in the solutions during the wetting cycles) the cylinders were ponded with the deicers (by placing the plastic dam and the top of the cylinder and filling the resulting reservoir with the solution). After the termination of the test, which happened at the same time as the termination of the test for prisms) the small samples were extracted from the most affected cylinders (those exposed to either 28% CaCl<sub>2</sub> or 25% MgCl<sub>2</sub> solutions) and examined under the scanning electron microscope (SEM) to determine the changes in the microstructure as the function of the deicer type and the distance from the ponded surface.

### 3.0 MASS CHANGES

The positive values of the mass change indicate mass gain due to ingress of moisture and deicers into the specimen while the negative values indicate mass loss due to surface degradation, particularly along the edges of the specimens.

#### 3.1 MASS CHANGES OF SPECIMENS EXPOSED TO WETTING/DRYING (W/D) REGIME

Figure 1 shows the average mass changes in PC and FA 20 specimens at the end of the W/D test. The total duration of the test was 350 cycles for all specimens except for those exposed 28% CaCl<sub>2</sub> solution. For these specimens, the test was terminated after 154 W/D cycles due to severe cracking and deterioration which was accompanied by a mass loss of about 1.8%. After 350 W/D cycles the PC specimens exposed to 25% MgCl<sub>2</sub> and 23% NaCl solutions experienced comparable (~0.7%) mass gain while the mass gain of the same specimens exposed to DIW was lower (~0.5%). All of the FA concrete specimens also experienced mass gain which ranged from ~0.4% for specimens exposed to MgCl<sub>2</sub> to ~0.9% for those exposed to CaCl<sub>2</sub>.

#### 3.2 MASS CHANGES FOR SPECIMENS EXPOSED TO FREEZING/THAWING (F/T) REGIME

The average mass changes for specimens undergoing F/T exposure in different deicing solutions are shown in Figures 2(a) for the PC and 2(b) for FA20 concretes. The PC specimens exposed to 17% CaCl<sub>2</sub> solution started losing mass after ~50 cycles and lost about 1.5% of the original mass by 240 cycles. That mass loss was accompanied by significant surface deterioration which was visible as early as after 166 F/T cycles (Figure 3(a)). The specimens exposed to 15% MgCl<sub>2</sub> solution experienced some surface cracking (see Fig. 3(a)) and gained about 2 % of mass by 240 cycles. PC specimens stored in DIW and 23% NaCl solution did not show such visible distress and gained 0.5% and 0.8% mass respectively.

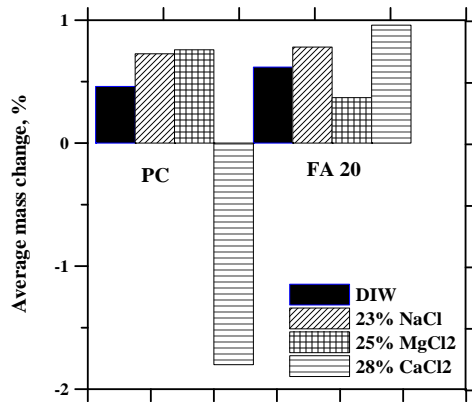


Figure 1: Total mass change in specimens subjected to W/D regime in different deicing solution

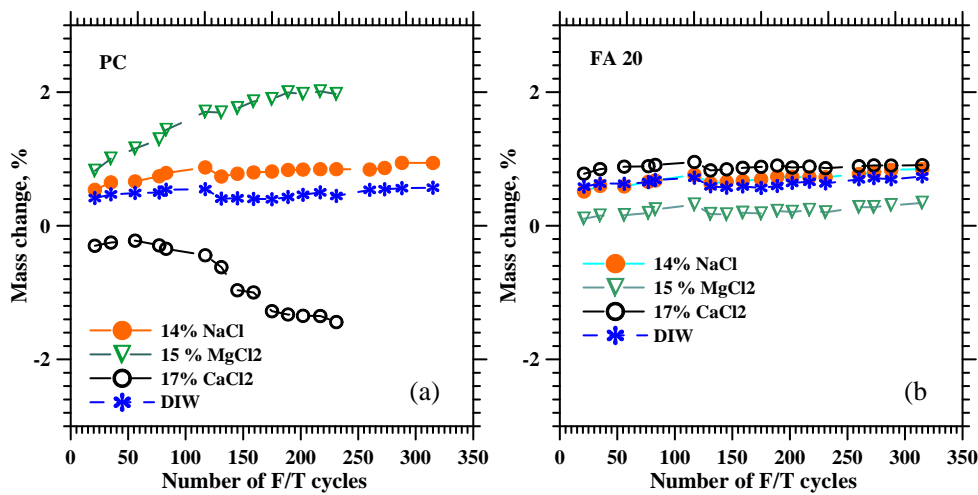


Figure 2: Mass changes for the PC (a) and FA 20 (b) specimens exposed F/T regime in different deicers

When examined after undergoing 166 F/T cycles, none of the FA20 specimens exhibited any surface cracking or deterioration (Figure 3(b)). This indicates a better deicer resistance of the FA concretes.

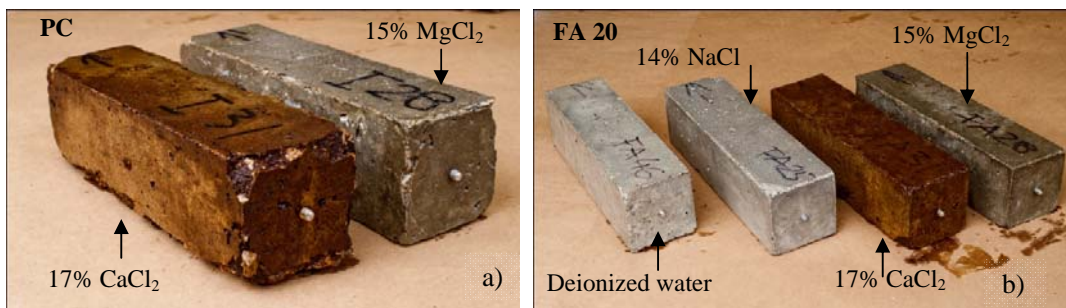


Figure 3: a) Plain concrete (PC) Specimens and b) Fly ash concrete (FA20) specimens after 166 F/T cycles in different deicing solutions

#### 4.0 RELATIVE DYNAMIC MODULUS OF ELASTICITY (RDME)

The relative dynamic modulus of elasticity was calculated by measuring resonance frequency of the prisms according to the ASTM E 1876.

#### 4.1 RDME FOR SPECIMENS EXPOSED TO WETTING/DRYING (W/D) REGIMES

Figures 4 (a) and 4 (b) show changes in the relative dynamic modulus of elasticity (RDME) values for PC and FA 20 specimens exposed to W/D regimes. The RDME increased continuously for both types of specimens (PC and FA20) exposed to DIW or 23% NaCl solution. However, the PC specimens exposed to 28% CaCl<sub>2</sub> solution started experiencing the decrease of the RDME after only 25 cycles. The RDME for these specimens dropped to below 85% of the initial value and the test had to be terminated after just 154 W/D cycles due to development of severe surface deteriorations which prevented accurate determination of the resonance frequencies.

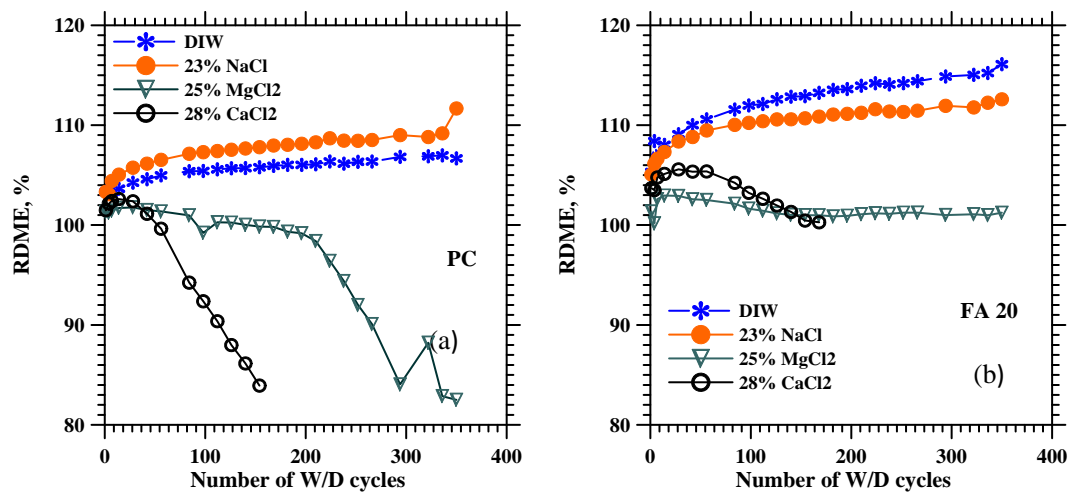


Figure 4: The relative dynamic modulus of elasticity (RDME) of (a) PC and (b) FA20 specimens subjected to W/D regimes

The PC specimens stored in 25% MgCl<sub>2</sub> solution did not show significant reduction in RDME values until about 200 cycles and reached to RDME value of 85% by 300 cycles. The fly ash modified concretes performed better than the plain concrete as indicated by the RDME values of 100% for specimens exposed to 350 W/D cycles in the 25% MgCl<sub>2</sub> solution and those exposed ~200 W/D cycles in the 28% CaCl<sub>2</sub> solution. The FA20 specimens exposed to DIW and 23% NaCl solutions exhibited continuous increase in the RDME. This can be attributed to microstructure densification due to secondary hydration for these concretes in presence of moisture.

#### 4.2 RDME FOR SPECIMENS EXPOSED TO FREEZING/THAWING (F/T) REGIMES

The RDME values for PC and FA20 specimens exposed to F/T regime are shown, respectively, in Figures 5(a) and 5(b). After 240 F/T cycles the RDME values of PC specimens in 17% CaCl<sub>2</sub> and 15% MgCl<sub>2</sub> were reduced by about 20% whereas the RDME for specimens in DIW and 14% NaCl solutions increased by about 5%. This obviously indicates damaging potential of these deicers. In case of the FA20 concretes only the specimens exposed to 17% CaCl<sub>2</sub> experienced about 5% reduction in the RDME after about 280 F/T cycles. This can be attributed to microstructure

densification due to secondary hydration and additional chloride binding due to presence of more aluminates in fly ash as compared to the cement.

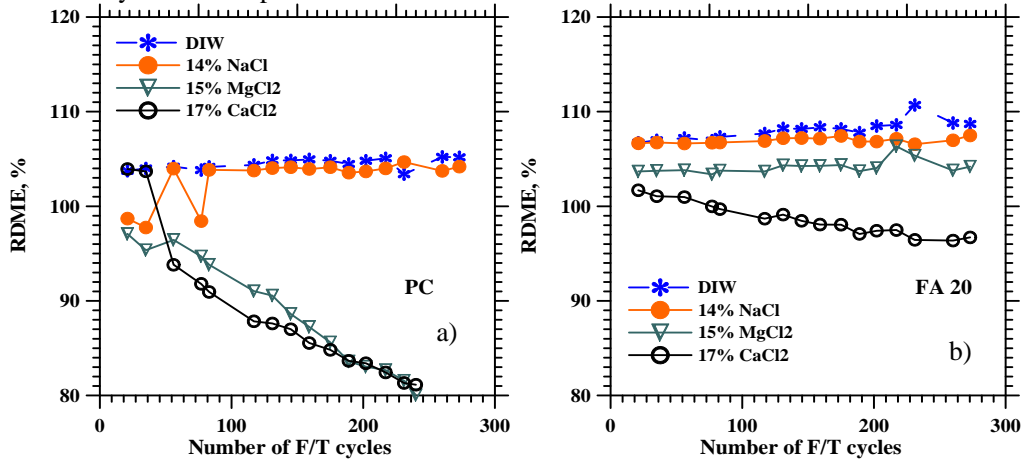


Figure 5: The RDME for PC (a) and FA 20 (b) specimens subjected to F/T regime

### 5.0 MICROSTRUCTURAL CHANGES IN THE CONCRETE MATRIX

The microstructural changes due to the interactions of deicers with the hydrated cementitious matrix during W/D regime were evaluated by SEM analysis. Figure 6(a) shows calcium oxychloride ( $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ ) in the microstructure of PC specimens exposed to 28%  $\text{CaCl}_2$  solution. This is in line with previous study by Sutter and his co-workers (Sutter et al., 2006) which concluded that this reaction is occurring most efficiently in concrete exposed to freezing and thawing cycles. These authors further report that the formation of the calcium oxychloride is damaging to the concrete matrix as it generates disruptive hydraulic pressure. This was confirmed in this study in terms of lower RDME values observed for specimens exposed to 28%  $\text{CaCl}_2$  solution.

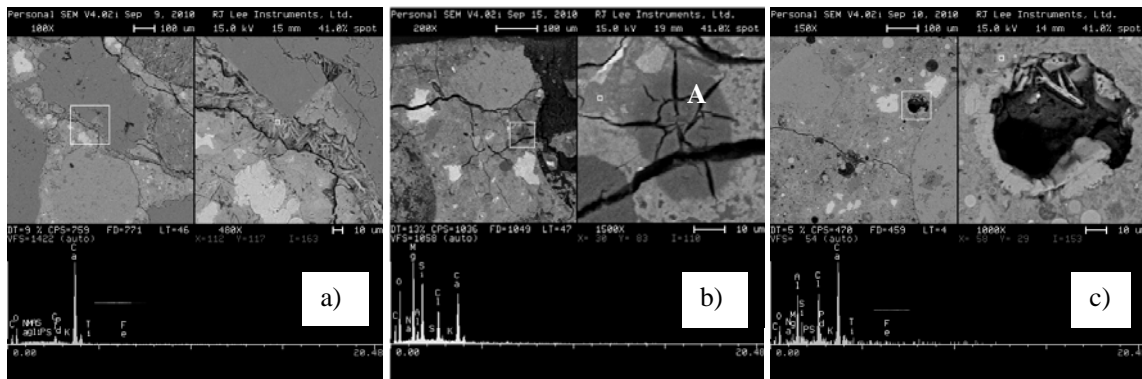


Figure 6: Scanning Electron Micrograph for specimens exposed to 28%  $\text{CaCl}_2$  (a) and 25%  $\text{MgCl}_2$  (b and c) solutions under W/D regime

The  $\text{MgCl}_2$  has been reported (Sutter et al., 2006) to react with C-S-H gel and form non-cementitious M-S-H gel as illustrated by Equation 1. The formation of such product is shown in Figure 6 (b).



Another reaction identified as reportedly taking place in pastes exposed to  $\text{MgCl}_2$  (Sutter et al., 2006) is the depletion of  $\text{Ca}(\text{OH})_2$  and formation of  $\text{CaCl}_2$  and  $\text{Mg}(\text{OH})_2$  as illustrated by equation 2.



The dark deposit (marked as “A” in Figure 6(b)) consists mainly of magnesium, chlorine and oxygen and is completely devoid of calcium and silicon. Additional microstructural changes for FA20 specimens were observed in terms of formation of Friedel’s salt (Figure 6(c)) in the top and middle (~2.2cm from the surface) regions of the specimens exposed to these salts.

## 6.0 SUMMARY

The present study investigated the effects of exposure of plain and fly ash concretes to different deicing solutions while being subjected to wetting/drying (W/D) and freezing/thawing (F/T) regimes. The main observations from the study can be summarized as follows:

- 1) PC specimens subjected to 28%  $\text{CaCl}_2$  solution and W/D regime developed very visible surface deterioration and 15% reduction in relative dynamic modulus of elasticity (RDME) after only 154 W/D cycles. By comparison, similar reduction of RDME in specimens subjected to 25%  $\text{MgCl}_2$  was observed only after about 300 W/D cycles.
- 2) After the 240 F/T cycles the reduction in the RDME was similar (about 20%) for PC specimens exposed to 15%  $\text{MgCl}_2$  and 17%  $\text{CaCl}_2$  solutions. However, the reduction of RDME happened much earlier for specimens exposed to  $\text{CaCl}_2$  solution. These specimens lost 10% of the initial value of the RDME after about 90 F/T cycles whereas specimens exposed to  $\text{MgCl}_2$  solution showed similar loss only after about 200 F/T cycles.
- 3) The SEM-EDX analysis indicated formation of calcium oxychlorides in specimens exposed to 28%  $\text{CaCl}_2$  solution under W/D regime. The changes in the matrix of specimens exposed to 25%  $\text{MgCl}_2$  solution involved formation of M-S-H gel and  $\text{MgCl}_2$  and  $\text{Mg}(\text{OH})_2$  deposits.
- 4) The fly ash modified concretes displayed better performance (in terms of lower mass loss and lower reduction in RDME) than plain concretes during the reported period of test in both exposure regimes. This can be attributed to formation of secondary hydration products and increased chloride ion binding (due to formation of Friedel’s salt) in fly ash concretes.

## 7.0 REFERENCES

- ASTM C1876, 2009. Standard Test Method for Dynamic Young’s Modulus, Shear Modulus, and Poisson’s Ratio by Impulse Excitation of Vibration, ASTM International, West Conshohocken, PA, USA
- Cody, R.D., Cody, A.M., Spry, P.G., Gan, G.L., 1996. Concrete Deterioration by Deicing Salts: An Experimental Study. *Semisequicentennial Transportation Conference Proceedings*, Ames, Iowa, May 1996, 6.
- Darwin, D., Browning, J., Gong, L., Hughes, S. R., 2008. Effects of Deicers on Concrete Deterioration. *ACI Materials Journal*, December 2008, 622-627.
- Kozikowski, R.L., Taylor, P.C., Pyc, W.A., 2007. Evaluation of Potential Concrete Deterioration Related to Magnesium Chloride ( $\text{MgCl}_2$ ) Deicing Salts”, *Research & Development Information, PCA R&D Serial No. 2770*, Portland Cement Association, Skokie, IL, 2007, 30.
- Lee, H., Cody, R.D., Cody, A.M., Spry, P.G., 2000. Effects of Various Deicing Chemicals on Pavement Concrete Deterioration”, *Proceedings, Mid-continent Transportation Symposium*, Ames, Iowa, 2000, 151-155.
- Monosi, S., Collepari, M., 1990. Research on  $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$  Identified in Concrete Damaged by  $\text{CaCl}_2$  Attack”, *Il Cemento*, Vol. 87, 3-8,.
- Sutter, L., Van Dam, T., Peterson, K. R., and Johnston, D. P., 2006. Long-Term Effects of Magnesium Chloride and Other Concentrated Salt Solutions on Pavement and Structural Portland Cement Concrete. *Transportation Research Record*, No. 1979, 60-68
- Wang, K., Nelson, D.E., Nixon, W.A., 2006. Damaging Effects of Deicing Chemicals on Concrete Materials. *Cement & Concrete Composites*, Vol. 28, Issue 2, 173-188.