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Investigation of Anti-Icing Chemicals and Their Interactions with Pavement Concretes



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16. Abstract <p>The interactions of concrete specimens (both plain and with fly ash addition) with six different deicers was investigated by exposing them to solutions of sodium chloride (NaCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), and the combinations of: sodium chloride with magnesium chloride (NaCl + MgCl₂), sodium chloride with calcium chloride (NaCl + CaCl₂), sodium chloride with agricultural by product – Ice Ban® (NaCl + Ice Ban®). In addition, control group of specimens was exposed to the deionized water. The exposures consisted of wet/dry (W/D) and freeze/thaw (F/T) cycles as well as a continuous storage in lime water at 23°C.</p> <p>The effects of various exposure conditions were evaluated based on the changes in the following: relative dynamic modulus of elasticity (RDME), ultrasonic pulse velocity (UPV), mass of specimens, length of specimens, mass of scaled material and compressive strength. In addition, absorption and chloride penetration measurements were performed for specimens exposed to various deicers at room temperature of 23°C. Finally, the qualitative visual evaluation of the appearance of the samples was also performed along with documentation of microstructural changes using the scanning electron microscopy (SEM).</p> <p>Among the deicer/anti-icers tested, calcium chloride and magnesium chloride solutions caused comparatively higher degree of deterioration than other solutions. Although the ultimate extent of visual degradation of the specimens exposed to both of these deicers was very comparable, the onset of the degradation process in specimens exposed to magnesium chloride was significantly delayed when compared to the onset of deterioration of specimens exposed to calcium chloride.</p> <p>The best performance (least amount of damage) was observed for specimens exposed to sodium chloride solutions followed by the specimens exposed to the combination of sodium chloride with magnesium chloride and sodium chloride with calcium chloride.</p> <p>The test results indicate that F/T exposure conditions are much more severe than W/D regimes, even though the concentrations of deicers/anti-icers used for F/T cycles were about 50% lower than those used for W/D cycles. Moreover, the addition of fly ash has a positive influence on performance of the concrete regardless of the type of the exposure regime.</p>			
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EXECUTIVE SUMMARY

INVESTIGATION OF ANTI-ICING CHEMICALS AND THEIR INTERACTIONS WITH PAVEMENT CONCRETES

Introduction

The increasing costs of deicing chemicals, environmental concerns, and user demands for ice-free pavements all dictate changes in the pavement maintenance strategies used by the Departments of Transportation (DOTs) in the United States of America. As an example, during the last several years, in addition to traditional deicing operations the DOTs also introduced such treatments as anti-icing of pavements and pre-wetting of salt and sand before spreading them on the pavements.

The deicing process involves applying snow and ice control materials directly on the top of already accumulated snow (or ice) layers in order to destroy their bond with pavement surface and thus facilitate easier removal of these materials from the roads.

The anti-icing treatment is defined as a snow and ice control method in which deicing chemicals are applied to the bare pavement surface hours before the expected precipitation to prevent bonding of ice and snow.

The pre-wetting involves application of salt solutions directly on the particles of dry salt (or sand) to increase their initial surface moisture in order to improve their adherence to the pavement and thus ensure reduction in bounce, scatter, and tracking of these materials. The main economic advantages of using the last two methods are reductions in application rates of the snow and ice control chemicals, the decrease in the cost of labor (or materials) during surface treatment operations, and overall lower snow control costs. In addition, there are safety factors which need to be considered, including better adhesion of snow and ice control materials to the road surface and lower accident rates.

For many years, sodium chloride (NaCl), commonly known as rock salt, has been used as an ice and snow control deicing agent with satisfying results. However, due to diminishing salt effectiveness in temperatures below 21°F, other chemicals, such as calcium chloride (CaCl₂) and magnesium chloride (MgCl₂), were introduced as alternative deicers. These two chemicals have freezing points which are lower than the freezing point of brine made with the rock salt, and thus are more effective at lower temperatures. However, the effect of these alternative chemicals on the long-term durability of concrete surfaces is still not well known and subject to controversy.

The primary objective of this study was to investigate the effects of deicing/anti-icing chemicals commonly used by the Indiana Department of Transportation (INDOT) on the durability of pavement concretes. The chemicals evaluated in this study included: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and Ice Ban[®].

In order to find a solution to the previously stated problem, the scope of the work included the following four tasks: literature review, selection and testing of deicing chemicals, preparation and testing of laboratory concrete specimens, and data analysis.

Findings

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. Overall, the best performance (in terms of reducing the negative impact on concrete) was associated with the use of sodium chloride solutions, followed by the combined solution of sodium chloride with magnesium chloride and sodium chloride with calcium chloride.
2. PC specimens subjected to 28% CaCl₂ 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% MgCl₂ was observed only after about 300 W/D cycles.
3. The SEM-EDX analysis indicated formation of calcium oxychlorides in specimens exposed to 28% CaCl₂ solution under W/D regime. The changes in the matrix of specimens exposed to 25% MgCl₂ solution involved formation of M-S-H gel and MgCl₂ and Mg(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 test period in both exposure regimes.
5. The only concrete property that was negatively impacted (although rather mildly) was scaling resistance. Since the rate of scaling can be strongly influenced by w/c values, air-void system parameter, and the concentration of deicers, careful control of these parameters should allow for safe usage of fly ash in concrete subjected to deicers.
6. Freeze/thaw exposure conditions typically resulted in more severe distress than W/D regimes, even though the concentrations of deicers used for F/T tests were about 50% lower than those used during W/D tests.

Implementation

This study provided INDOT with in-depth evaluation of the effects of various deicers on the properties of both plain and fly ash concretes of the composition suitable for usage as a pavement material in the state of Indiana.

Considering the findings from this study, the following implementation actions can be suggested:

1. Sodium chloride immersed specimens showed the best performance under exposure conditions used in the study; hence it is recommended that this deicer should be preferentially used for winter maintenance operation unless the expected temperatures are below 21°F. At the temperature below this limit the effectiveness of this solution will be reduced.
2. The test results indicate that there may be a potential for improving the low temperature effectiveness of NaCl deicer without severely impacting the durability of concrete by pre-treating it with carefully selected amounts of low concentration MgCl₂ or CaCl₂ solutions.
3. In cases when low temperatures dictate the use of deicers with a lower freezing point than sodium chloride, the application of MgCl₂ is likely to be less damaging (in terms of reducing the rate of deterioration) than the application of CaCl₂.
4. INDOT should consider using the results of this study to develop a best deicing practices manual which will help the winter maintenance personnel to select the least detrimental method of treatment for the purposes of snow and ice removal.

5. Whenever practical, INDOT should encourage the use of fly ash in all pavement concretes as mixtures containing this material offered higher resistance to degradation processes induced by the use of deicers than mixtures containing plain portland cement.

The benefits of this research include:

- Assemblage of detailed information on the effects of various deicing chemicals on several properties of pavement-type mixtures. This information would be useful to INDOT winter maintenance personnel in the process of selecting the most suitable ice and snow removal applications.

- Generation of fundamental information regarding the potential mechanism and the extent of deterioration resulting from the use of deicing chemicals.
- Increased level of awareness among INDOT's pavement engineers and winter maintenance personnel about how deicers can potentially contribute to damage of concrete pavements.

The implementation of findings from this study will help INDOT to reduce the cost of pavement and bridge deck repairs by improving snow and ice removal practices through increased awareness of potentially detrimental effects of certain deicers.

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1. INTRODUCTION

The increasing costs of deicing chemicals, environmental concerns and user demands for ice-free pavements all dictate changes in the pavement maintenance strategies used by the Departments of Transportation (DOTs) in the United States of America. As an example, during the last several years, in addition to traditional deicing operations the DOTs also introduced such treatments as anti-icing of pavements and pre-wetting of salt and sand before spreading them on the pavements.

The deicing process involves applying snow and ice control materials directly on the top of already accumulated snow (or ice) layers in order to destroy their bond with pavement surface and thus facilitate easier removal of these materials from the roads. The anti-icing treatment is defined as a snow and ice control method in which deicing chemicals are applied to the bare pavement surface hours before the expected precipitation to prevent bonding of ice and snow. The pre-wetting involves application of salt solutions directly on the particles of dry salt (or sand) to increase their initial surface moisture in order to ensure better attachment of these materials to the pavement and thus ensuring reduction in bounce, scatter and tracking of the material. The main economic advantages of using the last two methods (i.e., anti-icing and pre-wetting) are reductions in application rates of the snow and ice control chemicals, the decrease in the cost of labor (or materials) during surface treatment operations, and overall lower snow control costs. In addition, there are safety factors which need to be considered, including

better adhesion of snow and ice control materials to the road surface and lower accident rates.

For many years sodium chloride (NaCl), commonly known as rock salt, has been used as an ice and snow control deicing agent with satisfying results. However, due to diminishing effectiveness of salt in temperatures below 21°F (-6°C), other chemicals, such as calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) were introduced as alternative deicers. These two chemicals have freezing points (i.e., lowest temperature at which they can melt ice in a laboratory (the eutectic point)) which are lower than the freezing point of brine made with the rock salt, so they are more effective at lower temperatures (Figure 1.1 and Table 1.1). Although it could be expected that lowering the freezing point may result in lengthening of the wet exposure period the general effects of these alternative chemicals on the long-term durability of concrete surfaces is still not well known.

1.1 Research Objective and Scope

The primary objective of this study was to investigate the effects of deicing/anti-icing chemicals commonly used by the Indiana Department of Transportation (INDOT) on the durability of pavement concretes. The chemicals evaluated in this study included: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and the Ice Ban[®].

The scope of the work described in this report included the following four tasks: literature review, selection and testing of deicing chemicals, preparation and testing of laboratory concrete specimens and data analysis.

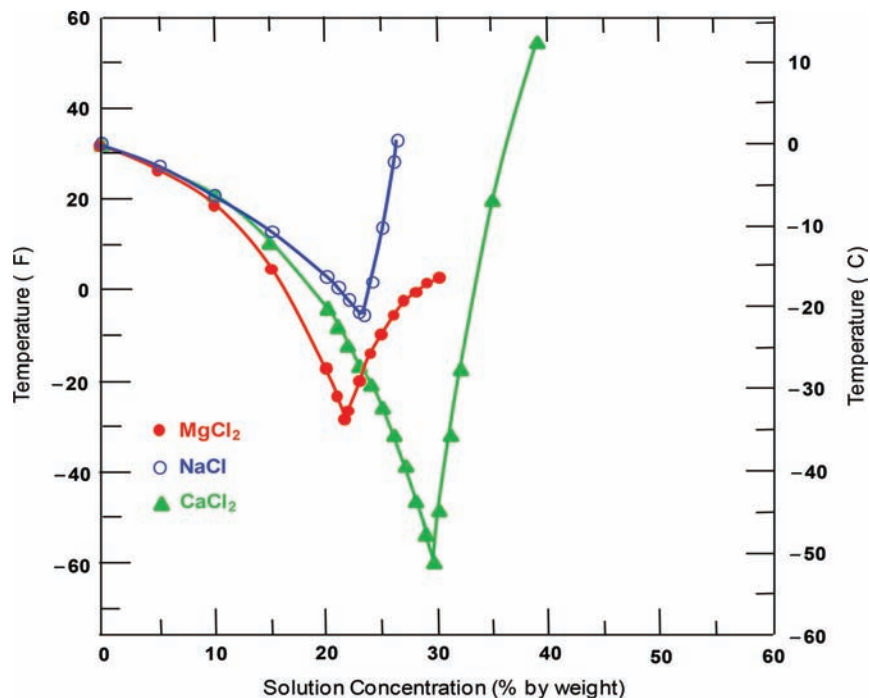


Figure 1.1 Phase diagrams of deicer solutions.

TABLE 1.1
Comparison of Different Deicers

Chemical	Eutectic Temperature°F (°C)	Eutectic Concentration%	Lowest Practical Melting Temperature°F (°C)
sodium chloride (NaCl)	-6 (-21)	23.3	21 (-6)
calcium chloride (CaCl ₂)	-60 (-51)	29.8	-25 (-32)
magnesium chloride (MgCl ₂)	-28 (-33)	21.6	5 (-15)

1.2 Structure of the Report

This report starts with an introduction presented in Chapter 1, which is followed by comprehensive literature review presented in Chapter 2. The experimental program along with a description of the materials and experimental methods used are presented in Chapter 3. Chapter 4 contains results (and related discussion) of all tests performed on concrete specimens with and without addition of Class C fly ash. Chapter 5 contains the conclusions, while the recommendations developed in the course of this research are listed in Chapter 6.

2. LITERATURE REVIEW

2.1 Introduction

The focus of the literature review presented in this report is on the comparison of the effects of different deicing/anti-icing chemicals on concrete pavement deterioration. Moreover, the properties of different deicing/anti-icing materials, their application rates and their snow/ice control effectiveness are also included. Finally, laboratory testing techniques used by various researches to study the effects of deicers on concrete are also critically reviewed.

One of the oldest snow and ice control methods that has been used on roads during the winter is the direct application of sand to the pavement surface. Using this technique, a higher friction can be obtained, even though the actual melting of snow and ice does not take place. This method is still one of the most popular methods used on unpaved or lower volume roads and in places where deicing chemicals can't be applied (1-3). However, the Indiana Department of Transportation (INDOT) no longer uses sand as a traction control agent because of the rapid dispersion of this material by vehicles and problems with drains clogging (4).

Currently, the most widely used snow and ice control agents include: rock salt -sodium chloride (NaCl), calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) (5-10). Among these, the most popular has been rock salt (sodium chloride). The preference towards using of sodium chloride as a deicer can be explained by its relatively low cost and relatively high effectiveness, especially at temperatures above 20°F. Calcium and magnesium chlorides are more expensive snow and ice control chemicals. However, both of these deicers are effective at much lower temperatures (see Table 1.1) than sodium chloride.

In recent years, as a response to the higher costs of deicing chemicals and public pressure to maintain snow and ice-free pavements, the use of preventive measures, such as anti-icing and pre-wetting also become more common (11). The main economic advantages of using these preventive measures include reductions in the application rates of the deicing/anti-icing chemicals, a decrease in labor intensive operations, and the overall lower snow control costs. In addition, these types of treatments improve adhesion of the deicing chemicals to the road surface, resulting in faster rates of snow melting and thereby lower accident rates (7,12).

The biggest difference between deicing and anti-icing operation is in the time when these chemicals are applied to the road surface. By definition, deicing involves application of deicing chemicals directly on the top of snow and/or ice which has accumulated on the pavement in order to break the bond between these accumulated layers and the surface of the pavement and thus facilitate easier removal of the former. In comparison, anti-icing is the method in which deicing chemicals (either in the form of pre-wetted solids or in the form of liquid brine) are applied hours before the expected precipitation to prevent the accumulation of ice and snow at the surface of the pavement (4,6,7,13,14). The pre-wetting is a process in which deicing/anti-icing chemicals are applied to dry solid materials such as salt and sand before or during their application to the pavement. Because the dry salt will not melt the snow, pre-wetting jump-starts the melting process by supplying moisture before the deicer is applied to the pavement (4,11).

Using deicing and anti-icing chemicals on the roads improves traffic safety under winter conditions and results in lower congestion. At the same time, however, the application of deicing chemicals has a destructive effect not only on highway infrastructure, but also on motor vehicles (corrosion) and roadside vegetation. Thus, even though the benefits from using deicers outweigh their damaging effects on concrete pavements, it is very important to evaluate the economical and safety impact of deicers/anti-icing on pavements (15).

2.2 Selection of Deicing and Anti-icing Materials and Their Application Rate

When choosing materials for snow and ice treatment several factors need to be considered. High mobility and time constraints in the business, education,

transportation and manufacturing sectors have always been big issues. To address this problem, appropriate application rates of snow and ice control chemicals were developed, along with the strategies for their most economical applications (2,13,16).

In order to describe the factors which should be considered when selecting the deicing/anti-icing chemicals, the term “dilution potential” needs to be defined. According to Blackburn et al., (2) the “dilution potential” is a term that relates precipitation dilution potential, surface pavement temperature, degree of snow/ice packing in the wheel path after plowing, treatment cycle time and the amount of traffic, and operational conditions to the choice of snow and ice control material and application rate that will generally produce a ‘successful’ result” (2).

According to Blackburn et al., (2) the “precipitation dilution potential is the contribution to overall dilution potential caused by the type and rate of precipitation of a winter weather event in progress. The higher the moisture content of the event per unit time, the higher the precipitation dilution potential” (2). The pavement surface temperature will also influence influences the effectiveness of snow and ice control chemicals. In fact, temperature is one of the most important factors because (as already mentioned) efficiency of the deicers decreases with the drop in the temperature. In addition to the temperature, the surface condition of the pavement (i.e., any accumulation of snow (or ice) and ice that remains on the pavement after plowing also needs to be considered. This accumulation (besides the precipitation) will contribute to the dilution of the applied chemicals. The most critical situation is created by bonding of ice to the pavement. Such situation requires the usage of higher load of chemicals to achieve an unbonded condition. Finally, operational conditions need to be taken into consideration. This factor deals with treatment cycles, traffic volume and speed. The rate of application and the amount of materials to be removed affect the frequency of the treatment. For longer cycles and in cases of critical situations such as bonded ice, more chemicals are needed.

2.3 Commonly Used Deicers/Anti-icers

Although there are many snow and ice control chemicals available on the market; the most popular ones (and most widely used by the State Highway Agencies (SHA)) include sodium chloride, calcium chloride and magnesium chloride (18).

2.3.1 Characteristic of Deicing/Anti-icing Materials

For over 60 years, one of the most widely used deicers has been sodium chloride (NaCl) (19). This snow and ice control material that can work as both a deicer and as an anti-icer chemical is still one of the best solutions for the road during the winter. Popularity of rock salt is primary due to its high deicing efficiency

and low cost. The rock salt can be used as an anti-icing agent to prevent the bonding of ice to the surface if it is applied before heavy accumulation occurs. However, as with any chloride-based deicer, the use of salt needs to be carefully controlled in order to avoid potential side effects (i.e., concrete scaling, corrosion of vehicles or damage to soil and roadside vegetation). Moreover, even though rock salt is a very effective deicer at relatively mild temperatures, its effectiveness quickly diminishes at temperature below about 21°F. As a result, different types of deicing materials such as magnesium chloride (MgCl₂) and calcium chloride (CaCl₂) have also been used by various State Highway Agencies.

Calcium chloride and magnesium chloride melt ice better at lower temperature, but they are more expensive. For this reason, they are often mixed with rock salt to obtain a more cost-effective deicing mixture (5).

2.3.2 Comparison of Effectiveness, Application Rate and Cost of Different Snow and Ice Control Chemicals

There are different comparisons between the various snow and ice control chemicals found in the literature. One of these is a comparison of application rates. Table 2.1 shows the appropriate application rate for sodium chloride (NaCl) (17).

It is easy to observe that application rates for solid, pre-wetted solid and liquid sodium chloride vary with different pavement temperature, adjusted dilution potential, and assessment if ice is bonded (or not) to the pavement. In general, it is not recommended to apply liquid sodium chloride when ice is bonded to the pavement. Additionally, the lower pavement temperature and the higher adjusted dilution potential the higher amounts of chemicals are needed. More sodium chloride should also be used in case of bonded ice. However, when temperature drops below 20 °F application of sodium chloride is not recommended. In such cases, other chemicals shown in Table 2.2 will be more useful (17).

Table 2.2 provides normalized (with respect to sodium chloride) application rate data for calcium chloride, magnesium chloride, potassium acetate (KAc), and calcium magnesium acetate (CMA) as a function of various pavement temperature ranges and application rates. The equivalent application rates shown in Table 2.2 are based on the total amount of ice melted per unit of each of the five chemicals (17).

Comparison of rock salt and pre-wetted salt effectiveness in terms of snow cover thickness is discussed by Fu et al. (20). Pre-wetting has been used as effective method to improve the deicing capability of rock salt. In the pre-wetting process, sodium chloride receives initial moisture from pre-wetting agents and thus, it is able to start the melting process faster than in cases where no pre-wetting agent is being used. The rock salt can be pre-wetted by different chemicals including sodium chloride brine (NaCl), calcium chloride brine (CaCl₂) and magnesium chloride brine (MgCl₂).

TABLE 2.1
Application Rates for Solid, Pre-wetted Solid, and Liquid NaCl (17)

Pavement temperature (°F)	Adjusted dilution potential	Ice pavement bond	Application rate	
			Solid (1) lb/L-M	Liquid (2) gal/L-M
Over 32	Low	No	90 (3)	40 (3)
		Yes	200	NR (4)
	Medium	No	100 (3)	44 (3)
		Yes	225	NR (4)
	High	No	110 (3)	48 (3)
		Yes	250	NR (4)
30 to 32	Low	No	130	57
		Yes	275	NR (4)
	Medium	No	150	66
		Yes	300	NR (4)
	High	No	160	70
		Yes	325	NR (4)
25 to 30	Low	No	170	74
		Yes	350	NR (4)
	Medium	No	180	79
		Yes	375	NR (4)
	High	No	190	83
		Yes	400	NR (4)
20 to 25	Low	No	200	87
		Yes	425	NR (4)
	Medium	No	210	92
		Yes	450	NR (4)
	High	No	220	96
		Yes	475	NR
15 to 20	Low	No	230	NR
		Yes	500	NR
	Medium	No	240	NR
		Yes	525	NR
	High	No	250	NR
		Yes	550	NR
10 to 15	Low	No	260	NR
		Yes	575	NR
	Medium	No	270	NR
		Yes	600	NR
	High	No	280	NR
		Yes	625	NR
Below 10	A. If unbonded, try mechanical removal without chemical. B. If bonded, apply chemical at 700 lb/L-M. Plow when slushy. Repeat as necessary. C. Apply abrasives as necessary.			

NR = Not recommended.

Specific Notes:

1. Values for “solid” also apply to pre-wet solid and include the equivalent dry chemical weight in pre-wetting solutions.
2. Liquid values are shown for the 23% concentration solution.
3. In unbonded, try mechanical removal without applying chemicals. If pretreating, use this application rate.
4. If very thin ice, liquids may be applied at the unbonded rates.

General Notes:

1. These application rates are starting points. Local experience should refine these recommendations.
2. Pre-wetting chemicals should allow application rates to be reduced by up to about 20%, depending on such primary factors as spread pattern and spreading speed.
3. Application rates for chemical other than sodium chloride will need to be adjusted using the information provided in Table 2.2.
4. Before applying any ice control chemicals, the surface should be cleared of as much snow and ice as possible.

TABLE 2.2
Equivalent Application Rates for Five Ice Control Chemicals (17)

Temperature (°F)	NaCl		CaCl ₂		MgCl ₂	
	100% Solid	23% Liquid	90–92% Solid	32% Liquid	50% Solid	27% Liquid
	2	gal/LM	2	gal/LM	2	gal/LM
31.5	100	45	109	32	90	31
31	100	46	111	32	91	32
30.5	100	47	111	33	91	32
30	100	48	107	33	94	33
29	100	49	109	34	91	33
28	100	52	109	34	91	33
27	100	54	109	35	90	34
26	100	56	104	34	96	36
25	100	57	102	34	99	35
24	100	61	108	38	102	41
23	100	62	112	41	102	41
22	100	65	110	41	102	42
21	100	68	107	40	101	42
20	100	70	108	42	98	42
15	100	90	103	44	96	44
10	100	120	101	49	95	47
5	100	165	104	57	96	51

However, performance of each of those pre-wetting agents can be different. In fact, CaCl₂ in the liquid form (32% of concentration) seems to be the most effective in lowering melting temperature.

Calcium chloride as a pre-wetting agent starts the melting process faster than magnesium chloride. Furthermore, in terms of snow cover reduction, calcium chloride was reported (20) to outperform both magnesium chloride and sodium chloride. Comparison of various deicers in terms of working temperature and several other properties has been assembled by Alleman et al. (4) and is shown in Table 2.3.

2.3.3 New Generation Deicing/Anti-icing Chemicals

New generation of deicers/anti-icers that includes such materials as: urea, Calcium Magnesium Acetate (CMA), K-acetate, Ice Ban® and Caliber M 1000 were introduced on the market as alternative to solely chloride based deicing/anti-icing chemicals. Although they are more expensive than commonly used chloride-based deicers; many researches consider these materials to be less harmful to steel and presenting a viable alternative for snow and its removal (9,14,18,21–23).

Since they are not considered to be harmful to metallic components of the aircrafts such deicers/anti-icers as: urea, CMA and K-acetate are widely used at the airfield facilities (9,18), even though they have been reported to cause damage to concrete pavements (22,23).

Ice Ban® and Caliber M 1000 are organic based deicing agents that are reported to have been used by INDOT in LaPorte and Seymour districts (4) to keep road free of ice and snow. It was reported (14) that Ice Ban® has little or no effect on steel and concrete, and

that it reduces the corrosion of equipment and damage to the infrastructure. In addition, this agricultural by-product is less stressful to roadside vegetation than any other chemical (14,24).

2.3.4 The Effect of Deicers/Ant-icers on Durability of Concrete

During winter, concrete pavement subjected to repeated freezing/thawing cycles in the presence of deicing/anti-icing chemicals suffers from two types of deterioration. The first one is physical deterioration (subjecting concrete pavement to expansion and internal stresses). Physical deterioration includes several mechanisms which may explain possible causes of deterioration observed in concrete structures. Among others, these mechanisms include: hydraulic pressure theory, osmotic pressure theory and thermal shock. In addition, layer-by-layer freezing deterioration, salt crystallization and super-cooling mechanisms are also discussed.

The second mechanism of the damage is related to damage resulting from chemical reactions between chloride ions (present in anti-icing solutions) and components of hardened concrete (13). In general, it is accepted that higher permeability and higher porosity of concrete contributes to chemical deterioration which is often a result of calcium hydroxide Ca(OH)₂ dissolution from the concrete matrix. Although significant progress was made in understanding the freezing phenomena in porous materials subjected to the deicing/anti-icing chemicals, it is still unclear and more investigation should be done to clarify the deleterious effects of deicer/anti-icers.

It is commonly known that deterioration caused by deicing/anti-icing chemicals is more physical in nature

TABLE 2.3
Summary of Effectiveness and Costs of Deicers/Anti-icers (4)

	Sodium chloride (rock salt) NaCl	Calcium chloride CaCl ₂ of DowFlakes (77–80% CaCl ₂ with corrosion inhibitor)	Magnesium chloride MgCl ₂	Ice Ban M50 (50% Ice Ban and 50% MgCl ₂ brine)	Caliber M-1000
Eutectic Temp. (°F)	–5.8	–60	–28	Performance of Ice Ban M50 varies from batch to batch and over time	–85
Concentration (%)	23.30	29.80	21.60		30 solids + 30 MgCl ₂
Working Temp. (°F)	15 to 20	–20	5		
Effectiveness	Very effective	Liberates heat when goes into solution: aiding in melting	Similar to CaCl ₂ , slightly less melting capability	Varies	Effective in anti-icing
Surface effects	Dries completely, leaving a white residue	Leaves moist film on road which reduces friction slightly	Residual effect on pavement without slippery film	No impact on effect of NaCl on concrete scaling or metal corrosion	No impact
Use	Wetted CaCl ₂ plain wetted with NaCl brine	Mixed with salt pre-wet salt straight/alone or in solution	Sprayed directly on sand pre-wet salt	Liquid mixed with salt or sand liquid alone	Liquid for anti-icing liquid for deicing liquid for pre-wetting

than chemical (9,25,26). However, the growing evidence of the role of a chemical mechanism cannot be ignored. In fact, the deterioration caused by freeze/thaw phenomena combined with the application of deicers/anti-icers can be more severe than the sum of these separately (13,18).

Moreover, the concentration of deicers/anti-icers in the concrete plays an important role in the development of pressures created during freezing and thawing action (25). Relatively low concentration (in the 2 to 5% range) of deicing/anti-icing chemicals causes more deterioration than a higher concentration (or pure water) regardless of the type of the deicers/anti-icers (27,28).

2.3.5 Physical Deterioration of Concrete

The process of physical deterioration of concrete initiates when saturated concrete freezes and, as a result, is subjected to internal stress and volumetric expansions. The repeated freezing and thawing cycles can subject concrete to two types of deterioration: scaling and internal microcracking (9,27).

Published literature represents several physical deterioration mechanisms of concrete, especially with respect to the development of the pressure within the pore system during freezing and thawing cycles. The mechanisms are briefly summarized below.

2.3.5.1 Hydraulic Pressure Theory. One of physical mechanism of deterioration is the well-known hydraulic pressure theory. This is the first theory connected to the freezing/thawing deterioration of concrete and as reported by Marchand et al. (27), it has been first proposed by Powers in 1949. According to this theory,

as soon as the temperature drops below 0°C, ice crystals begin to form in larger capillaries of a saturated cement paste. In fact, ice crystals expand by 9% in volume in comparison to water, thus, forcing the unfrozen pore water to escape from the larger capillaries into the surrounding paste. If the air void system in hardened cement paste is effective, the created pressure will find relief in the air voids and no damage will occur. However, in the case of excessive internal stress, a concrete matrix can suffer in freeze/thaw damage (8,13,27,29).

2.3.5.2 Osmotic Pressure Theory. Unfortunately, hydraulic pressure theory does not answer all the questions related to concrete deterioration due to freezing/thawing cycles. Therefore, a new theory, called osmotic pressure theory was proposed. This theory partially explains the deleterious effects of deicing/anti-icing chemicals on concrete pavement. Osmotic pressure is also considered a primary cause of paste freeze/thaw damage. The freezing point of the water in the pore system is lowered by surface forces and the alkalinity of deicing/anti-icing salts. According to this theory, only pure water freezes in the larger capillaries, with a more concentrated solution remaining in the smaller pores. In order to maintain a thermodynamic equilibrium, unfrozen water from the smaller pores migrates to the larger pores causing growth of crystals and increasing pressure in the pore structure (8,29,30).

It has also been suggested by Fagerlund, as reported by Marchand et al. (27), that the combined mechanisms of hydraulic and osmotic pressure theories could be the cause of concrete pavement deterioration. Hydraulic pressure is generated as a result of ice formation (first in

large pores) due to cooling. This could trigger the osmotic pressure. The amount of salt dissolved in the pore solution influences the sum of the hydraulic and osmotic pressures. Salt concentration is in inverse proportion to hydraulic pressure and in proportion to osmotic pressure. In fact, when hydraulic pressure decreases, less ice is formed and salt concentration increases. On the other hand, when osmotic pressure decreases, salt concentration also decreases (27). Osmotic pressure theory explains the fact that air-entrained concrete contracts (rather than expands) at a temperature below 0°C (27).

2.3.5.3 Thermal Shock. Thermal shock theory was first introduced by Harnik et al. (31) postulates creation of thermal shock as a result of application of dry deicing chemicals to a frozen concrete surface. According to this theory, heat required for the melting of ice and snow is extracted mostly from the concrete when thawing takes place. Because of the great loss of heat, the temperature of the concrete (usually only a few millimeters below the surface) rapidly decreases causing thermal shock (31,32). This temperature shock is characteristic only of pavement subjected to de-icing/anti-icing chemicals.

2.3.5.4 Layer by Layer Deterioration. Another physical deterioration phenomenon described in the literature is layer-by-layer freezing deterioration. This is caused by stress created as a result of a different concentration of salt solutions between layers. The concentration of deicers/anti-icers in the layer underneath is much higher and achieves its maximum depth around 10 mm. In this layer, freezing practically does not occur. A different situation can exist in the outer layer, which contains a low concentration of deicing/anti-icing salts. This is due to washing out of the salts caused by events such as rain or melting of the snow. In fact, as the temperature of the concrete pavement surface drops below 0°C, ice crystals can form on the outer layer. Variable deformations of the different layers cause stress, which leads to the concrete cracking (27,30).

2.3.5.5 Growth of the Salt Crystals. Another phenomenon, one which is reported to contribute to surface scaling, is the growth of salt crystals within the pores of concrete. It is commonly known that application of salts increases the degree of concrete saturation. The formation of salt crystals starts in the largest pores when the solution reaches supersaturation (30). As a result, salt molecules are drawn out of the smaller pores into the larger pores leading to the growth of crystallization pressure. The corresponding growth of ice crystals is probably a very minor contributor to damage and it is most prominent in surface scaling failure.

2.3.5.6 Supercooling. Harnik et al. (31) reported on the phenomenon of super cooling which is the result combination of freeze/thaw cycles in the presence of

deicers. Specifically, the presence of deicer reduces the freezing point of water in concrete pores. Thus, at a temperature near 0°C, water does not freeze, resulting in a decrease in the hydraulic pressure. However, when water finally starts freezing, the rate of freezing is much higher than that observed during normal (salt-free) freezing. As a result, the magnitude of hydraulic pressure increases and that leads to destructive effects. In addition, a higher osmotic pressure was reported to occur during and after freezing when sodium chloride was present in the pore solution (11,31).

2.3.6 Chemical Deterioration of Concrete

Chemical attack is caused by reactions with cement hydrates and results in the deterioration of the matrix (33).

For many years, chemical interaction between the deicing/anti-icing salts and the cement paste hydration product was ignored by researchers because of their conviction that the influence of deicers/anti-icers on concrete pavement was mostly physical in nature rather than chemical. Nowadays, however, this phenomenon is taken into consideration more often and it is not assumed any more that a chemical mechanism is as benign as previously believed (27). It has also been suggested that repetition of the application of deicing/anti-icing chemicals combined with freezing/thawing cycles is more damaging to concrete pavement structure than any of these actions separately (8,18). The process of chemical deterioration is further complicated by the fact that, often more than one mechanism may be at work (13).

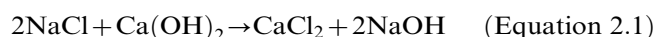
According to Marchand et al. (27), both, an increase in the porosity of exposed surfaces, and increase in permeability lead to an increase in the amount of water available and thus increased probability of ice formation. Very often, increased permeability may be a result of dissolution of calcium hydroxide (Ca(OH)₂). Other research confirms that increasing the permeability and reducing the alkalinity of the concrete pavement in the vicinity of cracks and joints is caused among other things by depletion of Ca(OH)₂. The Michigan Department of Transportation (MDOT) observed significant signs of leaching of calcium hydroxide in the concrete cores located near the transverse cracks in Jointed Reinforced Concrete Pavements (JRCP). The phenomenon of increase in permeability and reduction in alkalinity as a result of leaching of calcium hydroxide was also confirmed by laboratory studies (13).

Sutter (13) also reports on the work by Munoz regarding the mechanisms of joint deterioration included in the report of the Ohio Department of Transportation (ODOT). That study found that weaker concrete with higher porosity (and permeability) contributed to a chemical deterioration and that increase in porosity may be due to the presence of the dowel basket which interferes with the proper consolidation of concrete. It was further suggested that the primary cause of a chemical attack observed during this

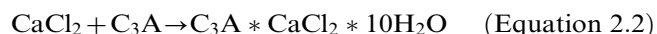
investigation was the dissolution of the concrete paste. Two factors in the dissolution mechanism were presented: the presence of dissolved salt and the velocity of solvent flow through the concrete. According to this research, high permeability and high solvent velocity characterized the concrete at the joints.

The effects of four different deicing/anti-icing chemicals: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and Calcium Magnesium Acetate (CMA) on concrete properties and potential chemical deterioration occurring in hydrated cement paste are described below.

2.3.6.1 Effects of Sodium Chloride (NaCl). Sodium chloride, also known as rock salt has a long history of usage as a deicer. Its effects on concrete were for a long time, considered to be negligible. As an example, Chatterji (34) reports that sodium chloride is not harmful to plain concrete unless reactive aggregate is present. Nowadays, however, it is commonly known that long-term application of NaCl results in the dissolution of calcium hydroxide according to the reaction shown in below Equation 2.1:

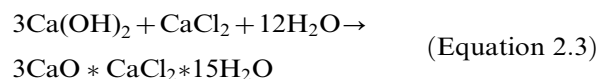


The result of this reaction is the dissolution of Ca(OH)₂, which leads to an increase in porosity near the exposed surface. In addition, an increase in permeability and enhancement of the amount of ice formed near 0°C can be observed (27). Moreover, the product of this reaction, calcium chloride, can interact with the aluminate phases C₃A in the cement paste and form chloroaluminate crystals. This reaction is shown below as Equation 2.2:



Formation of these crystals can affect the long-term frost durability of concrete surfaces in service under field exposure concentrations (27).

2.3.6.2 Effects of Calcium Chloride (CaCl₂). Calcium chloride reacts with calcium hydroxide to form hydrated calcium oxychloride (3CaO.CaCl₂.15H₂O) (26) as per Equation 2.3. Concrete deterioration caused by penetration of calcium chloride occurs most efficiently at low temperatures such as 5–10°C, which is higher than the freezing temperature and therefore this effect should not be confused with the deterioration of concrete due to freezing and thawing action (26,34).

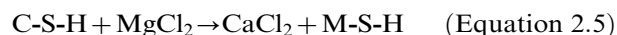
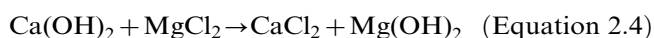


Formation of the calcium oxychloride, can generate hydraulic pressure that can lead to deterioration of the hydrated cement paste. According to Sutter et al., (11) mixes containing dolomite coarse aggregate were found to be especially susceptible to the deterioration caused by CaCl₂. Furthermore, during the interaction of

calcium chloride with hydrated cement paste, decreasing of the pH values and dissolution of Ca(OH)₂ have also been reported (35). It has also been suggested (26) that the scale of this phenomenon is masked by the corrosion of reinforced steel and the freeze/thaw deterioration of the paste. The same authors also reported that the non-air entrained concrete subjected to calcium chloride suffers from severe deterioration, even if it does not contain steel.

Finally, according to Collepari et al. (26), one should keep in mind that oxychloride attack is based on expansive physical action although the product is generated through a chemical process.

2.3.6.3 Effects of Magnesium Chloride (MgCl₂). Equation 2.4 and Equation 2.5 show reactions taking place in the presence of magnesium chloride.



As shown by those equations, Brucite and non-cementitious Magnesium-Silicate-Hydrate (M-S-H) are formed during chemical reactions (37). According to Cody et al., (38) Mg(OH)₂ simply replaces the gel phase, calcium-silicate-hydrate (C-S-H). This new product causes deterioration of the concrete by exerting growth from the pressure and initiating micro-fracturing. Moreover, calcium chloride (CaCl₂), which formed according to Equation 2.4 and Equation 2.5, can contribute to formation of the calcium oxychloride phase. Because Mg²⁺ and Cl⁻ interact with cement hydration products by depleting calcium hydroxide and decalcinating C-S-H, the cement paste structure becomes more porous, with a net result being lowers strengths and higher porosity. Concretes with M-S-H tend to develop shrinkage cracks, which leads to the crumbling of the hydrated cement paste (36).

2.3.6.4 Effects of Calcium Magnesium Acetate (CMA) on Concrete Properties. The CMA was introduced as a less corrosive alternative to sodium chloride. However, most recent studies (10) show that the solutions of CMA can lead to significant deterioration of concrete, including decalcification of paste and loss of mass. The attack was more aggressive at 20°C than at 5°C (10).

2.4 Selection of Concentration of Salt Solutions and Exposure Conditions Used

In order to select relative concentration of deicers and the exposure conditions for the laboratory study the authors reviewed over 100 papers dealing with the effects of deicing salts on concrete. The major facts found from this literature review are given in Appendix A in a summarized form.

Based on information presented in these tables, the concentrations of deicers used as well as details of the

exposure vary widely among individual research works. Some researchers (i.e., Wang et al. (18) or Santagata and Collepari (23)) used directly the concentrations provided by the suppliers of the deicers. This approach was based on the assumption that users, in general, will apply the chemicals received from the suppliers directly to the concrete pavement. According to that approach the concentrations of sodium chloride and calcium chloride were, 26.5% and 37.9%, respectively. While this approach is potentially most severe with respect to concrete durability, it does not, however, take into consideration the fact that the deicer/anti-icer will be diluted upon melting of the snow. To address this issue, some researchers (i.e., Sutter et al. (39)) advocated that the solution selected for laboratory testing should have the same concentration of chloride ions to better facilitate the comparison of the effect of different deicers. In particular, Sutter selected 15% solution of $MgCl_2$ as a basis for comparison in his study, assuming that this concentration represented the dilution that occurs when salt solutions are applied to a road surface. Concentration of sodium chloride and calcium chloride solutions were then selected to have the same molal concentration of chloride ions. These were, respectively 17.8% for NaCl and 17% for $CaCl_2$.

Another approach for selection of solution concentration was used by Darwin et al. (40,41), who assumed that all ions (both anions and cations) influence the durability of concrete. These researchers used two different concentrations of solutions (6.04 and 1.06 molal) which are equivalent in ion concentration to a 15% and 3% solution of NaCl (see Table A.1).

In some cases researches (i.e., Kozikowski et al. (37)) used concentrations in the range 2–4% as this concentration was found to maintain deterioration due to scaling.

Various approaches were also used when it comes to deicing parameters for the exposure condition. The most frequently used were wet/dry (W/D), freeze/thaw (F/T) and an exposure constant low temperature (typically around 40°F) (34,35,39). In addition, an elevated temperature of about 100°F (38°C) was used in some cases.

In terms of the duration of the cycles, one W/D cycle that was used by Wang et al. (18) took 24 hours (15 hours in frozen state and 9 hours in thawed state) while Darwin et al. (40) used 7 day long cycles (4 days of wetting at room temperature and 3 days of drying at elevated temperature of 38°C) (see Table A.1). Wet/dry exposure at elevated temperatures was also used by Lee et al. (21) and Cody et al. (38) (see Table A.1). With respect to F/T exposure; most experiments used the conditions suggested by ASTM C 666. However, Wang et al. (18), Lee et al. (21) and Cody et al. (38) perform their test using 1 day long cycles (see Table A.1 and Table A.4).

Based on the information summarized in Table A.1 through A.5, it is clear that one of the results of reaction between concrete materials and chloride based

deicers/anti-icers is the dissolution of calcium hydroxide dissolution (18,21,27,32,34,35,38,39,42).

Among all presented deicers/anti-icers, sodium chloride solution was recognized as the least harmful with respect to concrete durability (21,38,42). This deicing/anti-icing chemical has small negative impact on concrete properties at low concentration (except scaling test) and greater but still small impact at the higher concentration (40,41).

Higher levels of deterioration were observed in concrete materials that were exposed to magnesium chloride and calcium chloride solutions. According to researchers such as Cody et al. (38), Lee et al. (21) (Table A.4) among the deicers involved in their study the $MgCl_2$ solution was found to cause highest damage. Significant damage caused by this solution was also reported in many other studies (11,39,40,42). In addition, Brucite formation and alteration of C-S-H was observed by Sutter et al. (39,42) and Kozikowski et al. (37).

However, these studies (18,26,38,42) indicated that $CaCl_2$ deicer can also cause deterioration of concrete. Besides calcium chloride formation, which is common for all types of chloride based deicers/anti-icers, chloroaluminate and calcium oxychloride formation was also reported (21,35,38,39). More detailed information about interaction of various deicing/anti-icing chemicals and concrete materials can be found in Sections: 2.3.6.

2.5 Exposure Condition in Indiana

The annual number of freeze thaw cycles is an important factor that is related to the freeze thaw deterioration of concrete. A contour map was developed in (43) for the annual number of freeze thaw cycles in Indiana. In that project, researchers have used the number of annual freeze thaw cycles data from engineering weather data (44). It should be noted here that the engineering weather data counts a freeze thaw cycle when the air temperature drops below freezing (31°F (−0.5°C) or colder) and then rises above freezing (33°F (0.5°C) or warmer). Figure 2.1 shows the freeze thaw cycle contour map. From this figure it can be observed that, the number of annual freeze-thaw cycles in Indiana is within the range of 48 to 58.

Barde et al. (43) has also prepared a map representing cumulative duration of wetting events that lasted more than 6 hours in Indiana (Figure 2.2). According to this contour map the wetting duration varies by approximately 100 hours across state of Indiana. However, if it is assumed that the average wetting period is around 6 hours, and then according to this map the number of wetting and dry cycle should be around 63 to 70 annually in Indiana.

2.6 Summary

This chapter focused on the review of previous researches regarding different deicing agent and their

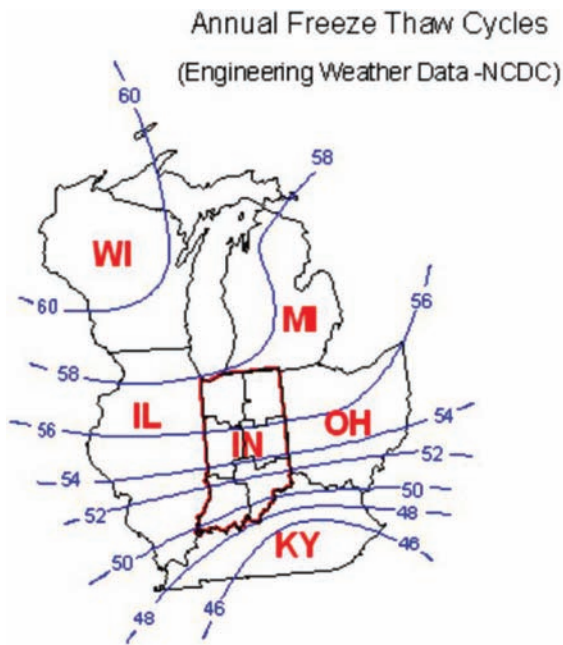


Figure 2.1 Annual freeze-thaw cycles (43)

possible interaction with concrete. From this literature review it has found that sodium chloride, magnesium chloride and calcium chloride are the most common types of conventional deicers. Effects and utility of some new generation deicers such as: Ice Ban[®], Caliber M 1000, Calcium Magnesium Acetate (CMA) are also discussed in this chapter. Based on this review, sodium chloride, magnesium chloride, calcium chloride, Ice Ban[®] and their combinations (details are given in sections 3.1.4 and 3.3) are selected for further investigation in this project. The commonly used concentrations

Cumulative wetting events (Hrs) > 6 Hrs (Yearly)
(Based on the CONCTEMP model for concrete bridge decks)

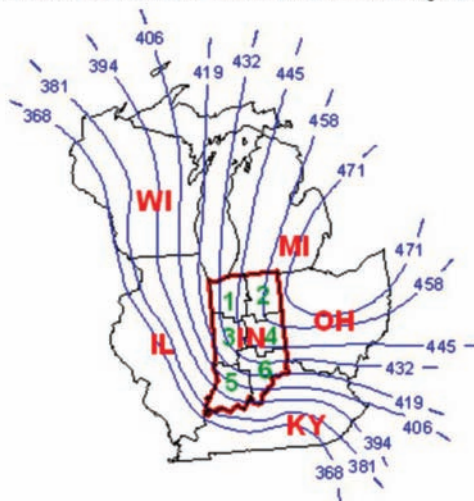


Figure 2.2 Cumulative duration of wetting greater than 6 hours considered over a year.

of these deicers in various projects are also quoted in this literature review which has been further utilized in the following chapter to select the concentration of deicing solution for this current study.

3. EXPERIMENTAL PROGRAM

3.1 Introduction

This chapter briefly describes the materials used in the preparation of test specimens and also, different test methods that were employed in this project. The ingredients of concrete mixture and the process of sample preparations are described in section 3.1 and section 3.2, respectively. Exposure conditions, selection of deicer solution and their concentrations are also explained in the following sections.

3.2 Materials

This section discusses different types of materials that were used in this project including cement, fly ash, aggregate and deicers. All materials used in this project were obtained from the local sources which were approved by the Indiana Department of Transportation (INDOT).

3.2.1 Cement

All samples were prepared using the ASTM C 150. Type I cement supplied by the Buzzi Unicem USA (Greencastle, IN). The chemical and physical data for the cement were obtained from mill certificate are shown in Table 3.1.

3.2.2 Fly Ash

Class C fly ash (collected from the Rockport, IN plant) source was used in this study. This material satisfied the requirements of American Standard Test Method ASTM C 618-03 and American Association of State Highway and Transportation Officials AASHTO M 295-05. Physical and chemical test results provided by the supplier are presented in Table 3.2.

3.2.3 Aggregates

Locally available crushed limestone was used as coarse aggregate in this project. The nominal maximum size of the aggregate sample was 25 mm (1 in.). The specific gravity and absorption of coarse aggregate were 2.74 and 0.8%, respectively. The #23 natural siliceous sand was used as the fine aggregates. The specific gravity and absorption of the fine aggregate was, respectively, 2.66 and 1.5%.

The coarse and fine aggregates were combined to yield gradation used in the actual mixture composition (sec 3.2.1) and this combined material was used to determine the aggregate correction factor (ACF)

TABLE 3.1
Cement Mill Test Report for Type I Cement

Parameter	Test Method	Result
Physical Properties		
1. Air Entrained (%)	ASTM C 185	9.2
2. Fineness (cm ² /gm)	ASTM C 204	3700
3. Autoclave Expansion (%)	ASTM C 151	0.054
4. Compressive Strength, psi	ASTM C 109	
1-Day		2610
3-Day		4350
7-Day		5430
5. Setting Time	ASTM C 191	
Initial, Min.		97
Final, Min.		191
Chemical Properties		
1. Silicon Dioxide (SiO ₂)	ASTM C 114	20.04
2. Aluminum Oxide (Al ₂ O ₃)		6.00
3. Ferric Oxide (Fe ₂ O ₃)		2.27
4. Calcium Oxide (CaO)		64.56
5. Magnesium Oxide (MgO)		1.22
6. Sulfur Trioxide (SO ₃)		2.83
7. Loss on Ignition		1.10
8. Sodium Oxide		0.09
9. Potassium Oxide		1.00
10. Insoluble Residue		0.28
11. Total Alkali as Na ₂ O		0.75
12. POTENTIAL COMPOUND COMPOSITION		
• Tricalcium Silicate (C ₃ S)		59
• Dicalcium Silicate (C ₂ S)		13
• Tricalcium Aluminate (C ₃ A)		12
• Tricalcium Aluminoferrite (C ₄ AF)		7

following the procedure described in ASTM C 231. The ACF was determined to be 0.4%.

3.2.4 Deicers

Five different deicers and their combinations were used in this study. These deicers were selected based on literature review as discussed in section 2.3.1 and section

2.3.3. These products included: sodium chloride (NaCl) – rock salt, sodium chloride brine (NaCl), magnesium chloride brine (MgCl₂), calcium chloride (CaCl₂) brine, and Ice Ban® Performance Plus. Details of these deicer solutions are presented in following sections.

3.2.4.1 Sodium Chloride (NaCl). Two forms of sodium chloride (NaCl) were used in this study: solid

TABLE 3.2
Chemical and Physical Analysis Data for Class C Fly Ash

Chemical Analysis		Physical Analysis	
Silicon dioxide (SiO ₂), %	43.27	Fineness (cm ² /gm), amount retained on #325 sieve, %	20.4
Aluminum oxide (Al ₂ O ₃), %	20.78		
Ferric oxide (Fe ₂ O ₃), %	5.77	Density, mg/m ³	2.57
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , %	69.80	Variation from average, %	-1.9
Calcium oxide (CaO), %	18.76	Strength activity index with Portland Cement at 7 days, % of cement control	90
Magnesium oxide (MgO), %	4.23		
Sulfur trioxide (SO ₃), %	0.64		
Moisture content, %	0.08	Water requirement % of cement control	96
Loss on ignition, %	1.22		
Sodium oxide (Na ₂ O), %	1.44	Soundness, autoclave expansion or contraction, %	0.01
Potassium oxide (K ₂ O)	0.84		

form (rock salt) and liquid form (Sodium Chloride Brine). The solid sodium chloride rock salt was used to prepare the sodium chloride solution which was then combined with magnesium chloride or calcium chloride solution to reflect the field practice of pre-wetting of the rock salt with either calcium or magnesium chloride.

The liquid sodium chloride solution was supplied by INDOT and (based on the information provided by the supplier) it was prepared by mixing rock salt with water to achieve a target concentration of about 23.3%. Based on the independent measurements performed in the laboratory (using ion chromatography, refractive index and oven drying methods) the actual average concentration was about 26%. Since the concentration of a fully saturated solution of NaCl is about 26.3% it appeared that the liquid was indeed a fully saturated brine. In order to bring this brine to the INDOT's target value of 23.3% it was diluted with deionized water. That diluted brine was either used above (as a primary soak solution) or it was mixed with the Ice Ban® (in a weight ratio of 1:9).

3.2.4.2 Magnesium Chloride (MgCl₂). Liquid magnesium chloride deicer was used in this study as either sole deicing solution or as a pre-wetting agent (by being mixed with rock salt in the proportion of 9 gallons of MgCl₂ to 1 ton of solid NaCl). The as supplied concentration of MgCl₂ solutions was 30.5%.

3.2.4.3 Calcium Chloride (CaCl₂). Liquid calcium chloride deicer was used in this study as either sole deicing solution or as a pre-wetting agent (by being mixed with rock salt in the proportion of 9 gallons of CaCl₂ to 1 ton of solid NaCl). The as supplied concentration of CaCl₂ solutions was 40.8%.

3.2.4.4 Ice Ban® Performance Plus (IBPP). Ice Ban® Performance Plus solution (later referred to as Ice Ban®) was the only deicer used in this study that contained agricultural by-products. Ice Ban® is registered trade of the group of biodegradable by-products from breweries and grain processing operations which have been patented for the use as deicing/anti-icing agents. Since, when used alone, these liquids become rather viscous below 0°C (14), they are typically mixed with other chemicals (to reduce viscosity) and marketed under various Ice Ban® names. Although the exact composition of the product used in the current research (IBPP) could not be obtained, the available literature (43) indicates that it was most likely a mixture composed from about 84% of MgCl₂ solution (30% concentration) and about 16% Ice Ban® concentrate. As used in the current study this deicer was mixed with liquid sodium chloride in the ratio of 1:9.

3.3 Specimen Preparation

This section presents information regarding the concrete mixture proportioning and mixing procedures. In addition it also describes the types, dimensions, curing and preconditioning of the test specimens used.

3.3.1 Mixture Compositions

Two types of concretes were produced: (a) the plain concrete, which only contained Type I portland cement (from now on referred to as "Type I" concrete) and (b) fly ash concrete in which 20% (by mass) of cement was replaced by class C fly ash (from now on referred to as "FA20"). The composition of both of these mixtures was based on the actual field mixture used by the Indiana Department of Transportation (INDOT) on one of the paving projects. The composition and fresh properties of these concrete mixtures are given in Table 3.3.

From Table 3.3 it can be observed that for both of these mixtures, paste volume was 25.5%. Thus in this project, the effects of difference deicers on concrete pavement were evaluated based on this paste volume. However, Rudy et al. (44) investigated the influence of paste volume on concrete pavements and found that lowering the paste volume reduces the shrinkage but it also increases the mass loss due to scaling effect. Moreover, in that research the durability factor for concrete mixes containing (23 to 25%) paste volume found to be higher than lower paste content (21 to 22%).

3.3.2 Mixing Procedure

The same mixing procedure was used to prepare all concrete specimens used in this study. The coarse and fine aggregate was presoaked by placing the aggregate in a plastic container with perforated bottom and spraying it with water in order to obtain moisture condition. The fine aggregate was placed in a separate plastic container and mixed with variable amount of water until it appears to be slightly above the saturated surface dry (SSD) condition. The container was then covered with plastic sheet to avoid evaporation and stored at room temperature for about 16–18 hours. The following day (around 2 hrs before mixing) about 1 lb samples of coarse and fine aggregate were obtained, weighed and placed in separate pans on hot plates for drying. The drying continued for about 1.5 hrs and the

TABLE 3.3
Composition and Fresh Properties of Concretes Mixtures Used

Materials	Type of concrete	
	Type I	FA 20
Cement (lbs/yd ³)	586	469
Fly ash (lbs/yd ³)	—	117
Water (lbs/yd ³)	246	246
Fine Aggregates (lbs/yd ³)	1303	1303
Coarse Aggregates (lbs/yd ³)	1780	1780
Water to cementitious materials ratio	0.42	0.42
Air Entraining Agent (fl. oz. per cwt)	1.1	1.5
Water reducing admixture (fl. oz. per cwt)	6.0	3.3
Slump (inches)	2.5	3.0
Air content (percent)	6.8	5.8

weight loss during this period was used to determine the actual moisture content of the aggregates. The actual moisture content was then used to adjust the water content in the batch.

The mixing procedure started by placing both coarse and fine aggregate in the pan mixer and mixing for 30 s. Next, half of the mixing water with Air Entrained Admixture (AEA) was added and mixed for 30 seconds. After 1 minute of total mixing, cementitious materials were added and mixed for additional 40 seconds. Then, Water reducing admixture diluted with the rest of mixing water was added. Total mixing time was 3 minutes. When the mixture was prepared the slump and air content of freshly prepared concrete were determined.

3.3.3 Preparation of Test Specimen

Depending on the test requirements, different types of concrete specimens were prepared. The 3 × 3 × 11.5 in. concrete prisms were cast for the length change, mass change and resonant frequency measurements (to determine the value of the dynamic modulus of elasticity). Compressive strength testing was performed on 4 × 8 in. cylinders. The disc-type specimens (4 × 2 in.) cut from 4 × 8 in. cylinders were used in absorption and chloride penetration tests. Scaling test was performed on 7.2 × 10 × 3 in. slabs. Total number and dimensions of the specimens used in the study are shown in Table 3.4.

3.3.4 Curing and Preconditioning of Test Specimens

All test specimens were removed from molds 24 hours after casting and placed in lime water for 28 days of curing at the temperature of 23°C and then preconditioned in air for 3 days at 23 ± 2°C and in 45 to 55% relative humidity.

3.4 Exposure Regimes and Concentrations of Deicer Solutions

This section describes the selected exposure conditions and deicer solution concentrations that were used in this project.

3.4.1 Exposure Conditions

The exposure conditions for use with deicing/anti-icing chemicals in the current study were selected based on analysis of the previous investigators as discussed in sections 2.4. The exposure conditions used in previous studies along with those selected for current study are summarized in Table 3.5. As seen from Table 3.5, the most common used exposure conditions were wet/dry (W/D) and freeze/thaw (F/T) cycles. In addition, soaking at constant temperature was also reported by several researchers.

Based on previous studies, four different deicer exposure conditions were selected for the current study. These included: wet/dry (W/D), freeze/thaw (F/T), scaling and the room temperature exposures (see Table 3.5). For comparison purposes, additional set of specimens was kept in deionized water (DIW) under both the W/D and the F/T exposure regimes. In addition, a set of control specimens was kept in saturated limewater (SLW) at 23°C (73.4°F) until the completion of the test. Also various temperatures were selected for constant soaking or ponding the concrete specimens such as low temperature of around 4°C, room temperature of 23°C and elevated temperature of 38°C.

3.4.2 Concentrations of Deicing Solutions

Depending on the exposure conditions the concentrations of the deicing (soak) solutions varied (see Table 3.6). The concentrations of deicers used for W/D and F/T concentrations were based on the principle that the total (anions plus cations) ion molalities of MgCl₂ and CaCl₂ deicing solutions will be the same as the molalities of the 21.3% of NaCl solution (for W/D exposure) and 14% solution of NaCl (for F/T exposure). The reason for the 50% reduction in concentrations (molalities) of F/T solutions compared to the W/D solutions was to ensure that the solution can actually freeze during the test. The deionized water was added to the originally supplied deicers to obtain a target concentration of the solution. In order to achieve these target molality the concentration of the originally supplied deicers was dilute (as needed) with the

TABLE 3.4
Inventory and Dimensions of Specimens Used in the Study

Type of specimen	Tests	No. of specimens	
		Type I	FA20
3 × 3 × 11.5 in. prism	Length Changes Mass Changes Dynamic Modulus of Elasticity	45	45
4 × 8 in. cylinder	Compressive Strength	45	45
4 × 2 in. disc	Absorption Chloride Penetration	44	44
7.2 × 10 × 3 in. slab	Scaling	8	8

TABLE 3.5
Summary of Exposure Conditions Used in Previous Deicing/Anti-icing Studies

Exposure condition	Investigator	Temperatures	Duration of the cycle
W/D	Wang et al. (18)	wetting at 4°C for 15 hrs drying at 23°C for 9 hrs	24 hrs
	Darwin et al. (40)	wetting at 23°C for 4 days drying at 38°C for 3 days	1 week
	Lee et al. (21)	wetting at 58°C for 132 hrs drying at 58°C for 24 hrs	1 week
	Cody et al. (38)	wetting at 60°C for 132 hrs drying at 60°C or 90°C	1 week
F/T	Wang et al. (18)	freezing at -20°C for 15 hrs thawing in warm water 9 hrs	24 hrs
	Kozikowski et al. (37)	freezing at -18°C for 16-18 hrs thawing at 23°C for 6-8 hrs	24 hrs
	Lee et al. (21)	freezing at -4°C for 24 hrs thawing at 58°C for 132 hrs	1 week
	Cody et al. (38)	freezing at 0°C or -70°C thawing at 25°C	1 week
Constant	Cody et al. (38)	soaking at 60°C	N/A
	Collepari et al. (26)	submersion at 5°C	N/A
	Kozikowski et al. (37)	submersion at 23°C or 4°C	N/A
	Sutter et al. (11)	submersion at 4.4°C	N/A
W/D	Current study	wetting at 4°C for 16±1 hrs drying at 23°C and 50% RH for 8±1 hrs	24 hrs
F/T	Current study	9 hours of cooling from 22°C to -20°C, 5 hrs of constant -20°C 6 hours of heating from -20°C to 22°C and 4 hours of constant room 22°C.	24 hrs
Constant	Current study	soaking at -4°C soaking at 23°C soaking at 38°C	

deionized water. For example, 15% magnesium chloride (MgCl₂) was prepared by mixing 100 grams of 30.5% liquid Magnesium Chloride with 103 grams deionized water which was then used in FT cycles. Table 3.6 also includes information about concentrations of the solutions used for scaling and abrasion tests.

3.5 Test Methods

3.5.1 Visual Evaluation

Roughly at 2 weeks interval throughout the exposure period the specimens were removed from their soak

TABLE 3.6
Summary of the Concentrations of the Various Deicers/Anti-icers for Different Tests and Regimes

	W/D *[%]	F/T *[%]	Scaling [%]	Absorpt. [%]	Total Molar Ion Conctr. (WD)/(FT)
NaCl	21.3%	12.8%	4%	21.3%	10.20/5.48
MgCl ₂	25%	15%	N/A	25%	10.50/5.56
CaCl ₂	28%	17%	N/A	28%	10.51/5.54
NaCl + MgCl ₂	23%+0.3%	13.4%+1.3%	4%+0.1%	N/A	
NaCl + CaCl ₂	23%+0.4%	13.4%+1.8%	4%+0.1%	N/A	
NaCl + Ice Ban®	19.5%+10%	12%+6.2%	3.7%+1.6%	N/A	

*The specimens subjected to W/D and F/T cycles also tested for length and mass changes.

solutions, placed on a clean sheet of paper and visually examined (with a naked eye) for signs of deterioration.

3.5.2 Modulus of Elasticity

Dynamic modulus of elasticity was determined by measuring resonance frequency of the specimens according to the ASTM E 1876 “Standard Test Method for Dynamic Young’s Modulus, Shear Modulus, and Poisson’s Ratio by Impulse Excitation of Vibration”. Tests were performed on the same specimens that were used for length change determinations.

After collecting all the data the modulus of elasticity was calculated using Equation 3.1 shown below:

$$E = 0.9465 * (m * f_r^2 / b) * (L^3 / t^3) * T_1 \quad (\text{Equation 3.1})$$

Where:

E – Young’s Modulus, Pa

m – Mass of the specimen, g

b – Width of the specimen, mm

L – Length of the specimen, mm

t – Thickness of the specimen, mm

f_r – Fundamental resonant frequency of the specimen in flexure, Hz

T_1 – Correction factor for fundamental flexural mode to account for finite thickness of specimen and the Poisson’s ratio (μ) (see Equation 3.2).

$$T_1 = 1 + 6.585 * (1 + 0.0752 * \mu + 0.8109 * \mu^2) * (t/L)^2 - 0.868 * (t/L)^4 - \frac{8.340 * (1 + .2023 * \mu + 2.173 * \mu^2) * (t/L)^4}{1.000 + 6.338 * (1 + 0.1408 * \mu + 1.536 * \mu^2) * (t/L)^2} \quad (\text{Equation 3.2})$$

Changes in concrete properties were evaluated by calculating the value of the relative dynamic modulus of elasticity (RDME). The RDME was calculated as the ratio of the dynamic elastic modulus at the given number of cycles to the dynamic modulus of elasticity at the initiation of the W/D or F/T cycles according to the Equation 3.3.

$$P_c = (DME_t / DME_0) * 100 \quad (\text{Equation 3.3})$$

Where:

P_c – Relative Dynamic Modulus of Elasticity [%]

DME_t – Dynamic Modulus of Elasticity at time t [GPa]

DME_0 – Dynamic Modulus of Elasticity at time zero [GPa]

3.5.3 Scaling

The scaling experiment was performed according to the ASTM C 672 “Standard Test Method for Scaling Resistance of Concrete Surface Exposed to Deicing Chemicals”.

3.5.4 Absorption

The absorption experiment was performed using the modified ASTM C 1585 “Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concrete”. The modification involved exposing the specimens not just to water (as specified in the standard) but also to various deicing/anti-icing solutions. Eight 4×8 in. cylinders were prepared and cut into 4×2 in. discs. In total, 32 different specimens were prepared (16 plain concrete and 16 FA mixtures). Half (8) of the specimens (in each series of 16) were preconditioned according to the ASTM C 1585. The other half of the specimens was pre-conditioned for 3 days at a temperature of 23 °C and a relative humidity RH of 50% after curing for 28 days in lime water.

Before starting the absorption tests the masses of the specimens and the diameters of the surfaces that were exposed to solutions of all specimens were recorded to the nearest 0.01 g and 0.1 mm, respectively. Next, the side surfaces of the specimens were sealed with duct tape, to ensure the unidirectional absorption. After preparation of the specimens, their sealed masses were recorded. All discs were placed on wooden supports in containers with various solutions. The level of the solutions was kept at 2 ± 1 mm above the supports. The test setup used for absorption test is shown in Figure 3.1. Once the specimens were placed in the solutions, the masses of the discs were recorded at time intervals shown in Table 3.7

After collecting of all data, the absorption was calculated using Equation 3.4 shown below:

$$I = \frac{m_t}{a * d} \quad (\text{Equation 3.4})$$

Where:

I – The absorption, [mm]

m_t – The change in specimen mass at the time t, [g]

a – The exposed area of the specimen, [mm²]

d – The density of the solutions, [g/mm³]

The densities of salt solutions were calculated from known masses and volume (using 50 ml pipette and



Figure 3.1 Picture of absorption test setup.

TABLE 3.7
Mass Measuring Intervals

Time	60 s ± 2 s	5 min ± 10 s	10 min ± 2 min	20 min ± 2 min	30 min ± 2 min	60 min ± 2 min	Every hour up to 6 hrs ± 5 min	Once a day up to 7 days ± 2 hrs
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analytical balance with an accuracy of 0.0001 g). These densities were: 0.00115 g/mm³ for 23% sodium chloride (NaCl), 0.00120 g/mm³ for 25% magnesium chloride (MgCl₂), and 0.00122 g/mm³ for 28% calcium chloride. The density of water was assumed to be 0.001 g/mm³ (as recommended by ASTM 1585 specification).

3.5.5 Length Changes

The measurements of the length changes of the specimens were performed according to AASHTO T 160 (ASTM C 157) “Length Changes of Hardened Hydraulic Cement Mortar and Concrete”. The length change measurements were performed periodically with the first measurement being performed after 28 days curing in lime water. Tests were also performed after 3 days of preconditioning and 1, 4, 7 days of exposure. After that, the specimens were measured every 2 weeks for up to 14 weeks.

After the collection of all data, the length changes were calculated using Equation 3.5 shown below:

$$L_x = \frac{\text{CRD} - \text{initialCRD}}{G} \times 100 \quad (\text{Equation 3.5})$$

Where:

ΔL_x – Length change of specimen at any age, percent

CRD – Difference between the comparator reading of the specimen and the reference bar at any age [in.]; and

G – The gauge length [10 in.]

3.5.6 Mass Changes

Mass changes tests were performed on the same specimens that were used for length change measurements. After collecting all the mass data, the mass changes were calculated using Equation 3.6 shown below:

$$M_x = \frac{M - \text{initialM}}{\text{initialM}} \times 100 \quad (\text{Equation 3.6})$$

Where:

ΔM_x – Mass change of specimen at any age, percent

M – Mass of the specimen at any age [g]; and

initial M – Initial mass of the specimen [g]

3.5.7 Deicer Penetration

The depth of penetration of deicers was determined according to AASHTO TP 64 for 23% of sodium chloride (NaCl), 25% of magnesium chloride (MgCl₂) and 28% of calcium chloride (CaCl₂) on disc specimens

(4 × 2 in.), previously subjected to the absorption test (Section 3.4.4) for 7 days. At the end of absorption period the test specimens were removed from the containers and split longitudinally into halves and sprayed by 0.1 silver nitrite solutions. Then, the depth of penetration of deicers was measured by using a ruler at the intervals of 10 mm, starting with 10 mm from the edge. Five valid measurements were obtained for each specimen.

3.5.8 Compressive Strength

The compressive strength determinations were performed according to the ASTM C 39 “Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens”. Three 4 × 8 in. cylinders were tested for each type of concrete and all age. Compressive strength of the specimens is rounded to the nearest 10 psi (0.1 MPa).

3.5.9 Microstructural Analysis

SEM samples were prepared from concrete cylinders that were used for deicer penetration test. Since the information collected from literature seems to indicate that microstructure changes are only viable to occur in case of exposure to the MgCl₂ and CaCl₂ deicers only these series of specimens were used for SEM examination.

4. TEST RESULTS

In this project, the test samples were investigated using ten different laboratory experiments. This chapter presents the summary of the results from these tests. When needed the test results are provided in both tabular and graphical formats to allow for easy relative comparison of the effects of various deicing solutions on concrete specimens.

4.1 Visual Inspection

Figure 4.1 and Figure 4.2, respectively, show the appearances of prism specimens subjected to 168 W/D and F/T cycles, while being immersed in different deicing solutions and (for control purposes) in the deionized water (DIW). Based on visual inspection of surfaces of various specimens it appears that samples immersed in deionized water (DIW), NaCl solution, NaCl + MgCl₂ solution, NaCl+ CaCl₂ solution and NaCl + Ice Ban[®] solution exhibited none or only negligible surface deterioration. The plain concrete specimens exposed to MgCl₂ showed minor deterioration



Figure 4.1 Appearance of test specimens subjected to 168 F/T cycles in the presence of three different deicing solutions and the deionized water (DIW).

in a form of corner cracking. No such distress was observed in the fly ash concrete specimens exposed to the same solutions (Figure 4.2 (a)). However, samples immersed in CaCl_2 solution displayed considerable amount of surface deterioration after both F/T and W/D cycles. Furthermore, it can also be observed that the extent of surface deterioration for CaCl_2 exposed samples prepared with Type I cement is higher than that of the samples prepared with fly ashes (FA20). Moreover, the extent of surface spalling (if any) of concrete samples subjected to F/T cycles is higher than that exposed to W/D cycles which are due to the fact that F/T cycles represent more severe exposure conditions than W/D cycles.

To provide a more direct comparison of the effects of MgCl_2 and CaCl_2 deicers, Figure 4.3 (a) shows Type I specimens exposed to 28% CaCl_2 (168 WD cycles) and 25% MgCl_2 (275 WD cycles) solutions, respectively. It can be seen that specimens exposed to 28% CaCl_2 solution developed extensive scaling along all edges after 168 cycles. In contrast, only edge cracking was observed in the specimens exposed to MgCl_2 , even though in this case the cumulative number of WD

cycles was about 64% higher (275 vs. 168). Only when the number of WD cycles (350 cycles) was more than double (in comparison to the CaCl_2 exposure), the specimen subjected to MgCl_2 solution developed comparable erosion at the edges (Figure 4.3 (b)).

4.2 Relative Dynamic Modulus of Elasticity (RDME)

4.2.1 Changes in the RDME due to exposure to deicers under WD regime

Figure 4.4 (a) and (b) show the RDME values for Type I and FA 20 specimens exposed to WD regime. It is also relevant to mention that the approximate number of W/D cycles in Indiana is in the range of 63 to 70 (section 2.5). From these figures, it can be observed that the RDME values increased consistently for both types of specimens exposed to deionized water and 23% NaCl solution during the entire test period (350 cycles). However, the plain concrete (Type I) specimens exposed to 28% CaCl_2 solution started showing decrease in RDME values right after 50 W/D cycles and reduced by 15% (of the initial value) after



Figure 4.2 Appearance of test specimens subjected to 168 W/D cycles in the presence of different deicers or the deionized water (DIW).

just 154 W/D cycles. After 168 W/D cycles, the extent of surface deterioration of the samples was extensive enough that the WD exposure was discontinued for CaCl_2 solution. This decrease in the RDME was accompanied by visible surface deterioration of both prismatic and cylindrical specimens.

Type I specimens exposed to 25% MgCl_2 solution did not show significant reduction in RDME values until after about 200 WD cycles and dropped down to RDME value of 85% after about 300 W/D cycles. The

fly ash modified concretes (FA20) performed better than the plain concretes as indicated by the RDME values of 100% for specimens exposed to 350 W/D cycles in the 25% MgCl_2 solution and those exposed ~200 W/D cycles in the 28% CaCl_2 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.



Figure 4.3 Type I specimens subjected to (a) 275 and 168 WD cycles in 25% MgCl₂ and 28% CaCl₂ solutions, and (b) Type I specimens subjected to 350 WD cycles in 25% MgCl₂.

4.2.2 Changes in the RDME of Prismatic Specimens due to FT exposure

The RDME values for Type I and FA20 specimens exposed to FT regime are shown, respectively, in Figure 4.5 (a) and (b). After 240 FT cycles, the RDME values of Type I specimens in 17% CaCl₂ and 15% MgCl₂ were reduced by about 20% whereas the RDME for specimens in DIW and 14% NaCl solutions increased by about 5%.

In case of the FA20 concretes only the specimens exposed to 17% CaCl₂ experienced about 5% reduction in the RDME after about 280 FT cycles.

4.2.3 Role of Exposure Regimes on Performance of Different Deicing Salt Solutions

The effects of deicing salt solutions can be different under various temperature and moisture level as these

parameters affect the absorption behavior and reaction mechanisms of deicers. Thus, in this study, two different exposure conditions are expected to affect differently due to significant differences in their temperature and moisture levels. Moreover, the salt concentrations of the solutions were different for these two exposures which are also very critical for the reaction mechanism. To analyze these effects, the RDME values for two exposure conditions are compared for exposure to different deicing solutions.

Figure 4.6 (a) and (b) show the RDME values for Type I and FA20 concretes after the completion of the test for both exposure conditions. It can be seen from Figure 4.4 and Figure 4.5 that the Type I specimens exposed to DIW do not exhibit any reduction in RDME values even after more than 350 WD cycles. Whereas, in case of FT exposure, the RDME values of Type I specimens exposed to DIW reduces by about 5% after 350 FT cycles and thus not very different behavior

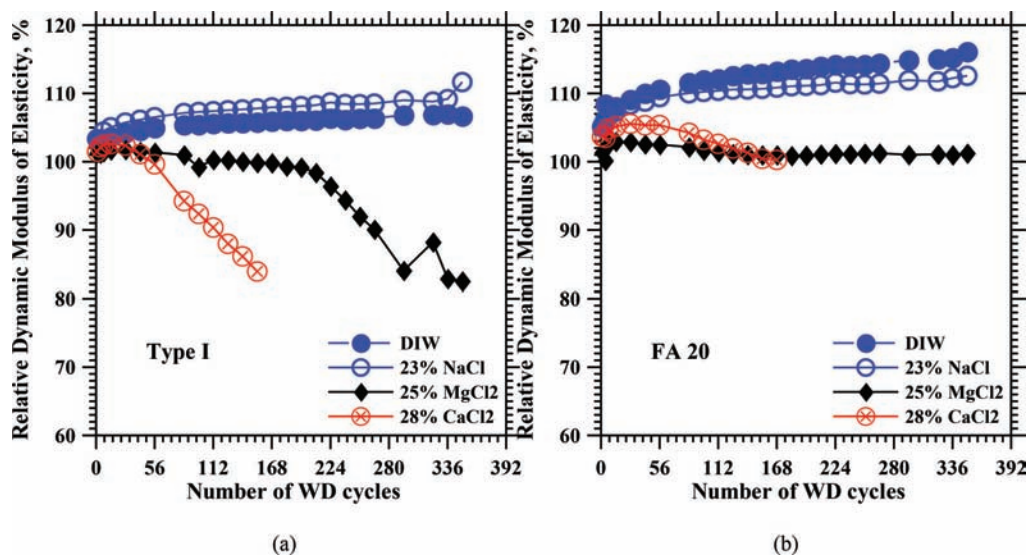


Figure 4.4 RDME values for (a) Type I, and (b) FA 20 specimens exposed to W/D regime.

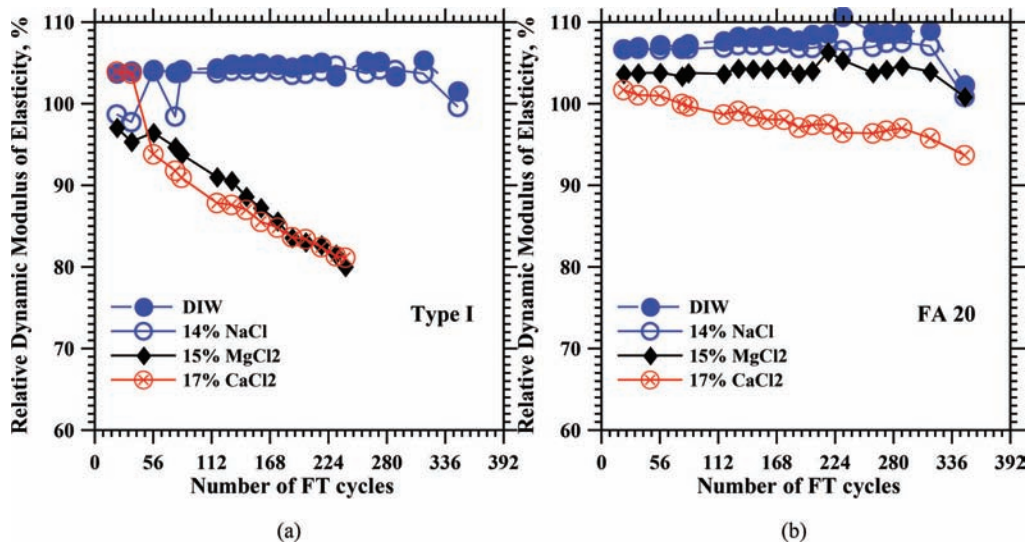


Figure 4.5 RDME Values for (a) Type I and (b) FA 20 specimens subjected to FT regime.

in these two exposure conditions. Type I specimens subjected to 23% NaCl solution exhibited 10% reduction in RDME values after 350 FT cycles and no reduction after 350 WD cycles. This indicates more susceptibility to deterioration under FT action as compared to WD action in case of NaCl solution. This difference is much more prominent for RDME values of Type I specimens exposed to CaCl₂ and MgCl₂ solutions.

For specimens exposed to 25% MgCl₂ solution, the RDME values reduces to 80% after 350 WD cycles while the same level of reduction was recorded after 240 FT cycles. Exceptionally, for Type I specimens exposed to 28% CaCl₂ solution, the WD exposure is found to be more damaging than the FT exposure, as RDME values dropped down to 80% level after only

168 WD cycles but it required 240 FT cycles to reach that level. So it is important to note that if concrete is expected to experience more WD conditions than FT conditions during its life, MgCl₂ solution would be beneficial as it can withstand more WD cycles as compared to CaCl₂ solution.

Figure 4.6 (b) shows the comparison for FA20 specimens exposed to different deicing solutions for the same number of FT and WD cycles. It can be seen that WD cycles improve RDME values to about 115% for exposure to DIW and NaCl solution while it reached to 100% during the same number of FT cycles. But exposure to MgCl₂ solution is not affecting RDME values for FA 20 specimens under both WD and FT regimes and thus fly ash improves the performance. In case of CaCl₂ solution, the reductions in RDME values

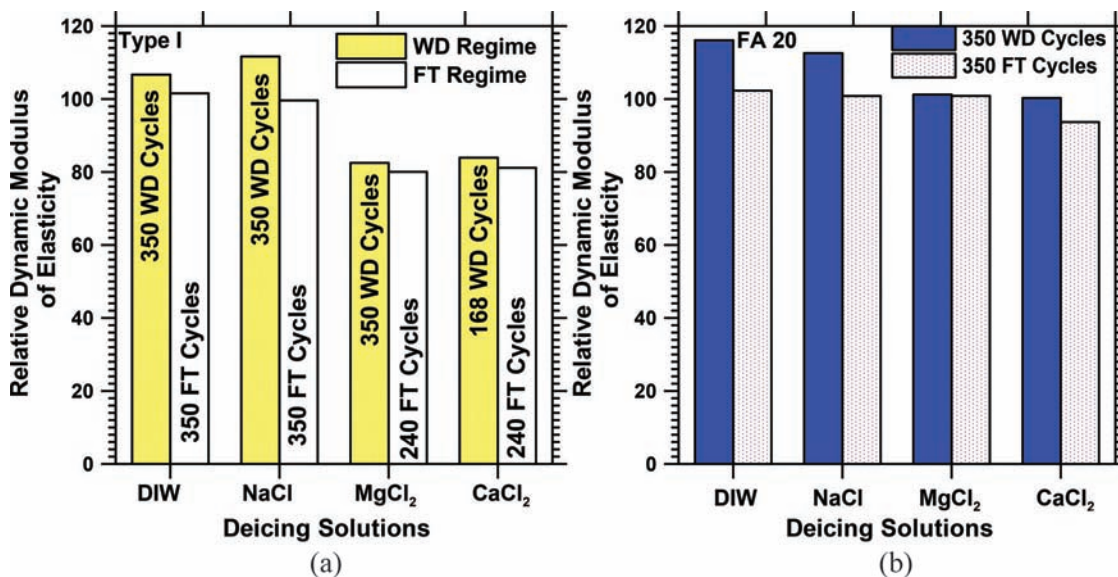


Figure 4.6 RDME values for (a) Type I and (b) FA 20 specimens subjected to WD and FT exposure.

are lower for FA 20 specimens than the Types I specimens for both WD and FT conditions.

4.3 Length Changes

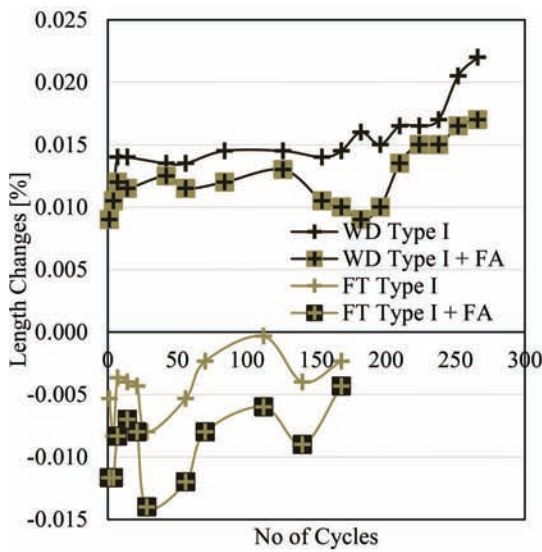
4.3.1 Deionized Water (DIW)

Figure 4.7 (a) illustrates the changes in length for concrete specimens exposed to 266 W/D and 168 F/T cycles, respectively in the presence of DIW. As seen from this figure; plain concrete expands slightly more than concrete with fly ash. Specimens with both types

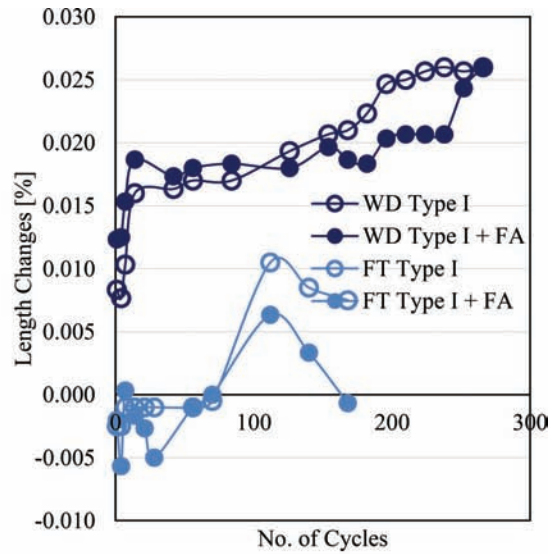
of binders experience shrinkage when subjected to F/T exposure condition throughout the test period. Specimens containing fly ash showed higher relative reduction in length than the Type – I concrete samples.

4.3.2 NaCl Solution

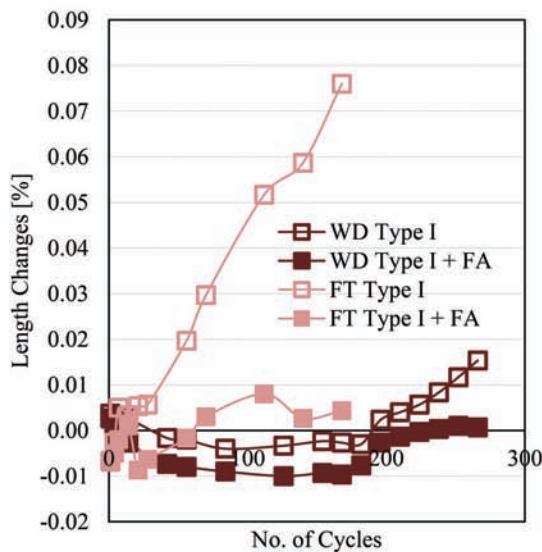
The summary of length changes for both (W/D & F/T) exposure regimes and both types of concrete (Type I and FA 20) subjected to sodium chloride solution is presented in Figure 4.7 (b). When we compare specimens subjected to W/D cycles with those exposed to



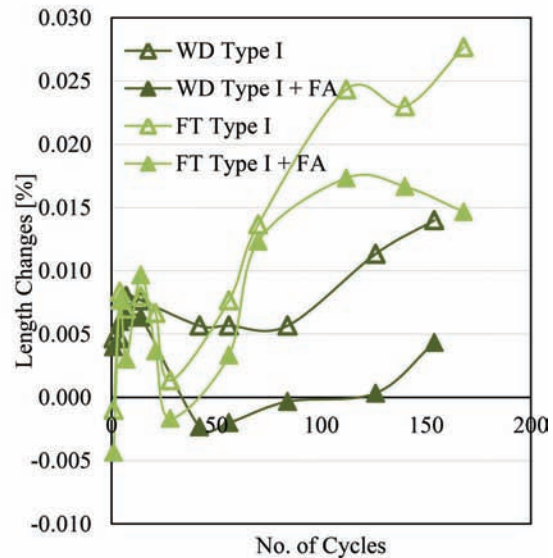
(a) Deionized water



(b) NaCl solution



(c) MgCl₂ solution



(d) CaCl₂ solution

Figure 4.7 Length changes (%) of test specimens subject to different exposure condition: (a) Deionized water, (b) NaCl solution, (c) MgCl₂ solution, and (d) CaCl₂ solution.

F/T cycles, it is evident that the first group (W/D cycles) of samples undergo a higher expansion during the same period of time.

4.3.3 $MgCl_2$ Solution

Figure 4.7 (c) shows changes in length for concrete specimens subjected to W/D and F/T cycles in the presence of 15% $MgCl_2$ solution. It is evident that plain concrete exposed to F/T cycles shows the highest expansion among all specimens exposed to other deicers. Unlike DIW and NaCl solutions, specimens subjected to $MgCl_2$ solution shows higher expansion for F/T exposure than the W/D exposure.

4.3.4 $CaCl_2$ Solution

The summary of length changes for all specimens exposed to the $CaCl_2$ solution is presented in graphical form in Figure 4.7 (d). The highest value of expansion (> 0.025) is noticed for plain concrete specimens subjected to F/T cycles. The same type of binder, however, subjected to W/D cycles shows smaller expansion after a comparable period of time. Again, the rate of expansion of specimens containing fly ash is lower than that of plain concrete specimens.

4.3.5 $NaCl + MgCl_2$ Solution

The summary of length changes for concrete specimens subjected to both types of exposure conditions in the presence of combined NaCl and $MgCl_2$ solution is presented in Figure 4.8 (a). The relative length changes for both Type - I and FA 20 concrete samples were higher in case of W/D exposure condition.

4.3.6 $NaCl + CaCl_2$ Solution

Figure 4.8 (b) presents length changes for concrete samples with and without fly ash that were subjected to W/D and F/T cycles in the presence of the combination of NaCl + $CaCl_2$ solution. From the graph it is easy to observe that specimens subjected to W/D cycles experience higher expansions at the beginning of the exposure but at the end of F/T cycles, there was not much difference in the expansions resulted from both W/D and F/T cycles.

4.3.7 $NaCl + Ice Ban^{\circledR}$ solutions

The summary of length changes for both types of exposure and both types of concrete subjected to NaCl + Ice Ban[®] is presented in Figure 4.8 (c). The highest expansion was observed for plain concrete samples exposed to F/T cycles for more than 56 cycles. The expansion of Type I specimens exposed to W/D cycles was proceeding at a more gradual rate which only increased after 250 cycles.

4.3.8 Comparison of Length Changes for Specimens Subjected to All Solutions

Figure 4.9 and Figure 4.10 show, respectively, length changes for plain concrete specimens and samples containing fly ash that were exposed to W/D conditions in the presence of various deicing/anti-icing chemicals. All plain concrete specimens, except for those exposed to 25% $MgCl_2$, show expansion during the W/D cycles. The highest increase in length (by about 0.03%) can be observed for concrete prisms that were exposed to a 23% NaCl and NaCl + Ice Ban[®]. The only solution that causes the relative reduction in length (up to 196 cycles) is a 25% solution of $MgCl_2$. After an initial (after 1 cycle) expansion of 0.004%, these specimens start to shrink. However, after 196 W/D cycles of exposure, specimens subjected to this deicer/anti-icer start expanding at a relatively steep rate. For FA 20 samples (Figure 4.10), the maximum expansion can be observed in the concrete prisms exposed to a 23% NaCl (0.03%) and then those subjected to NaCl + $MgCl_2$ (0.02%).

The length changes of the plain concrete specimens that were subjected to F/T cycles in various solutions are shown in Figure 4.11. All specimens except those subjected to deionized water have shown expansion. The highest length increase (0.08%) can be observed for specimens that were subjected to a 15% solution of $MgCl_2$. Another deicer/anti-icer that causes relatively high expansion of 0.04 after 168 cycles is NaCl + Ice Ban[®]. Similar increases in length (0.2%) can be observed for specimens that were subjected to F/T cycles and the combinations of: NaCl + $MgCl_2$ and NaCl + $CaCl_2$.

Figure 4.12 shows length changes for fly ash concrete specimens that were subjected to F/T cycles in various solutions. Overall, specimens with fly ash show low level of expansion. Almost no length changes have been observed for specimens subjected to NaCl and NaCl + Ice Ban[®]. The 17% solution of $CaCl_2$ causes the highest expansion (0.02%) among all specimens containing fly ash and exposed to F/T cycles.

4.4 Mass Changes

4.4.1 Deionized Water

The mass changes of concrete specimens subjected to W/D cycles while exposed to deionized water were higher than those experienced by concrete exposed to F/T cycles (Figure 4.13 (a)). After 168 of W/D the FA20 Concrete gained about 0.6% of mass whereas the plain concrete gained about 0.4% of mass.

4.4.2 NaCl Solution

The relative changes in mass of concrete prisms that were exposed to W/D and F/T cycles in the presence of NaCl solution are shown in Figure 4.13 (b). Concrete specimens with fly ash gained around 0.8% of their initial masses after 266 W/D cycles of exposure while

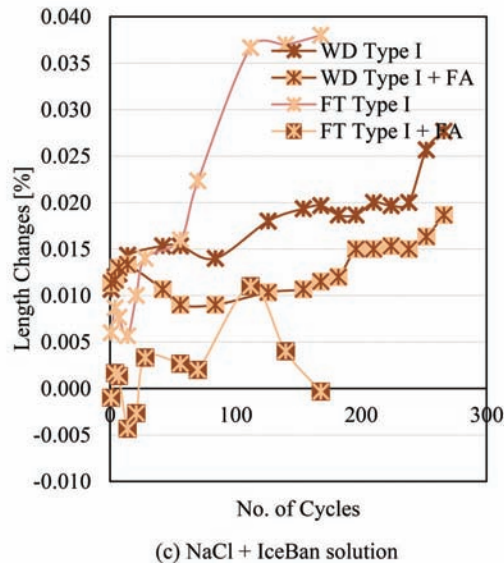
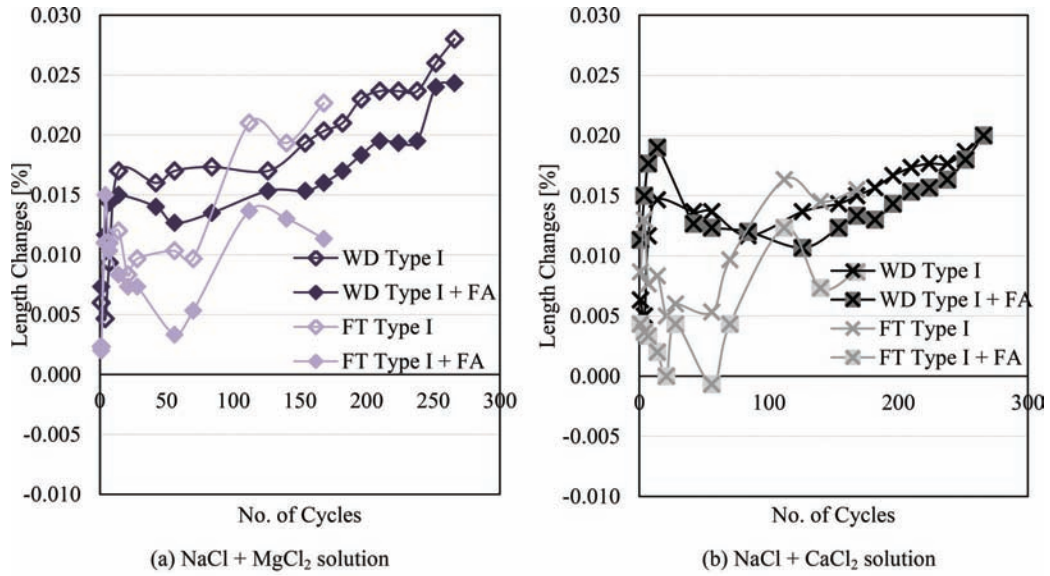


Figure 4.8 Length changes (%) of test specimens subject to different exposure condition: (a) NaCl + MgCl₂ solution (b) NaCl + CaCl₂ solution, and (c) NaCl + Ice Ban solution.

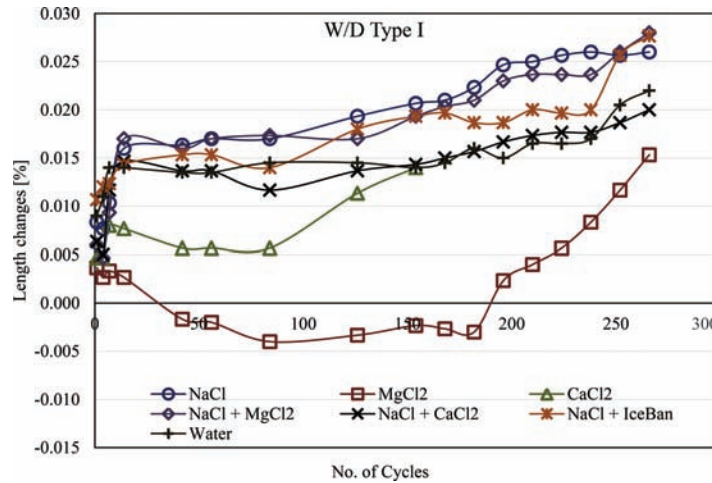


Figure 4.9 Length changes (%) of Type-I test samples subjected to W/D cycles.

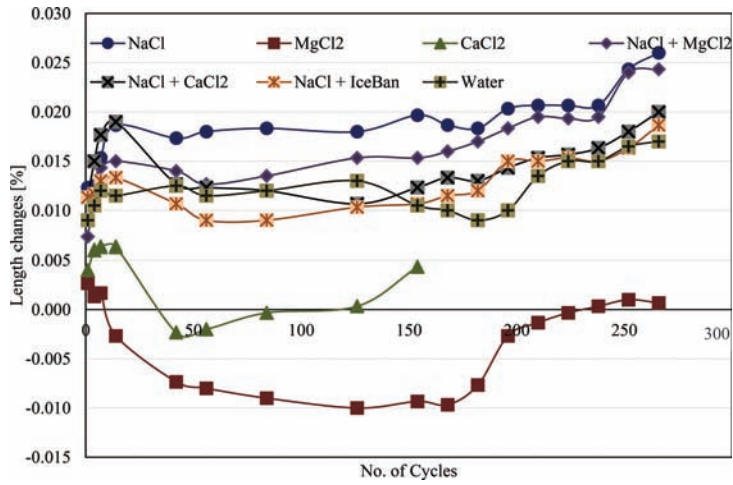


Figure 4.10 Length changes (%) of FA 20 test samples subjected to W/D cycles.

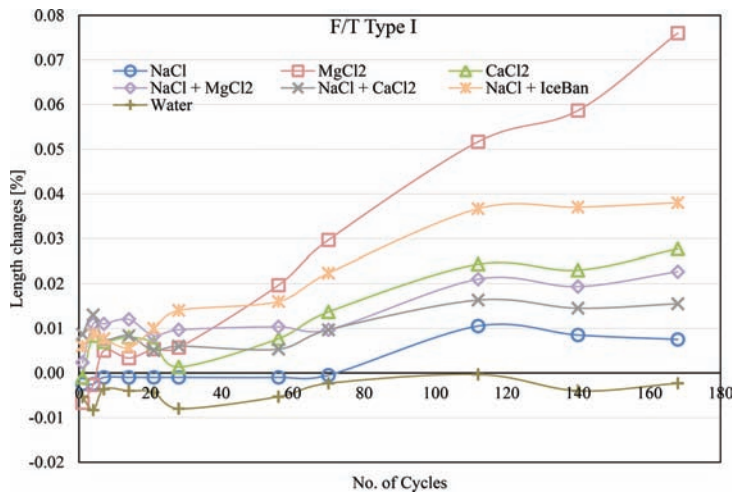


Figure 4.11 Length changes (%) of Type-I test samples subjected to F/T cycles.

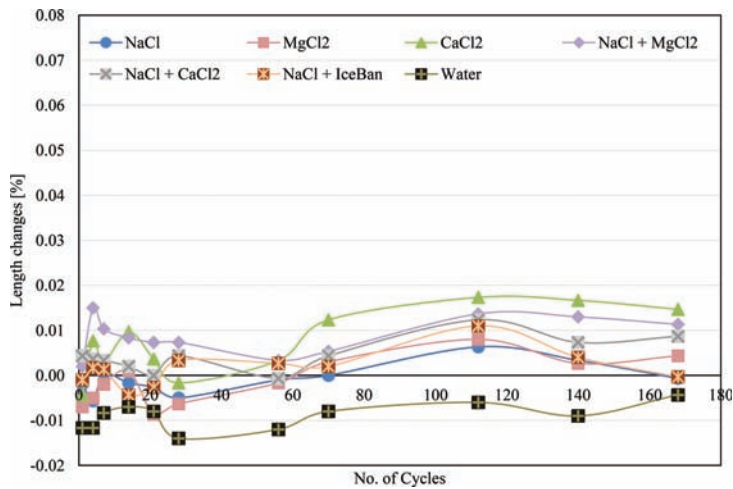


Figure 4.12 Length changes (%) of FA 20 test samples subjected to F/T cycles.

plain specimens gained around 0.7%. Concrete specimens that were exposed to W/D regime gained more mass than those subjected to F/T cycles. In contrast to what was observed during the W/D exposure, fly ash concrete exposed to F/T cycles gained less mass than plain concrete.

4.4.3 $MgCl_2$ Solution

The relative mass changes for concrete samples subjected to W/D and F/T cycles while exposed to

$MgCl_2$ solutions are shown in Figure 4.13 (c). The biggest relative mass change (about 1.7%) after 168 cycles of exposure can be observed for plain concrete subjected to F/T cycles. This is followed by relative mass changes of plain concrete exposed to W/D condition. It should be mentioned, however, that the increase in the relative mass gain of specimens exposed to W/D is much delayed with respect to that experienced by specimens in F/T exposure regime. For concrete containing fly ash the relative mass gains remain small (about 0.3%), irrespective of the exposure condition used.

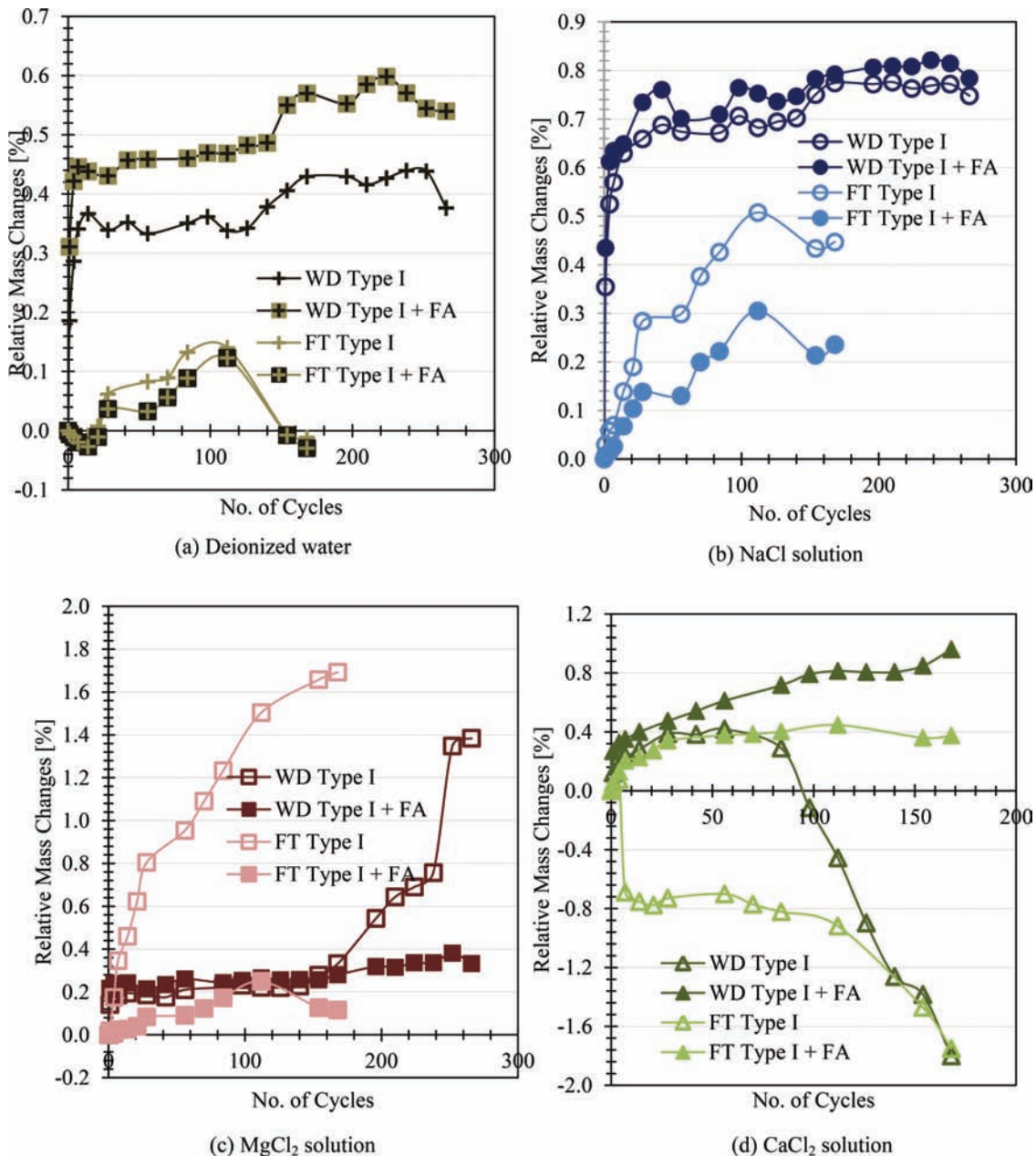


Figure 4.13 Mass changes (%) of samples subjected to different exposure condition (a) Deionized water, (b) NaCl solution, (c) $MgCl_2$ solution, and (d) $CaCl_2$ solution.

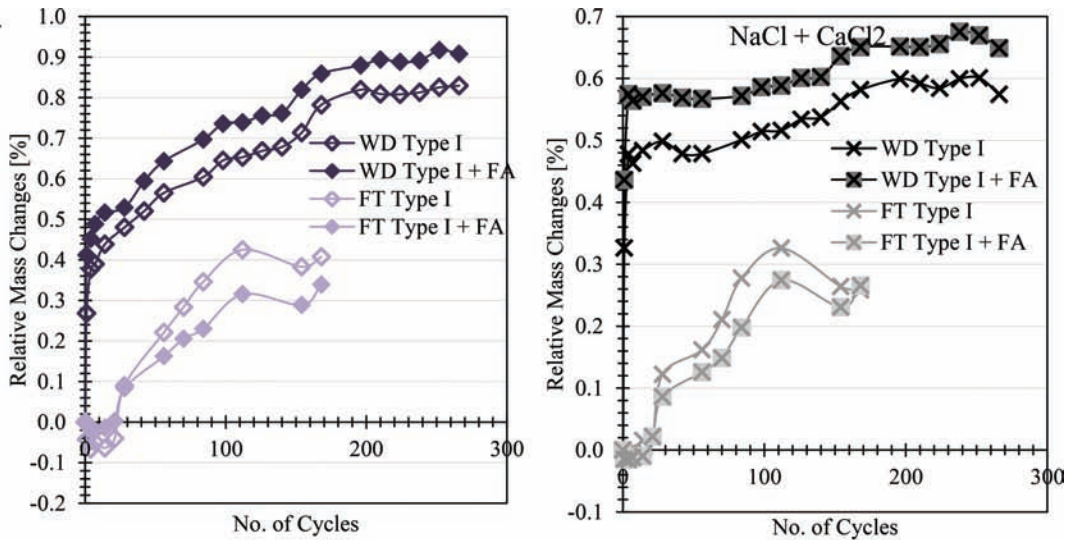
4.4.4 CaCl₂ Solution

The summary of mass changes for concrete prisms subjected to CaCl₂ deicing chemicals under both W/D and F/T exposure conditions is shown in Figure 4.13 (d). It can be seen that Type I concrete specimens start losing mass very early during the F/T cycles (initial drop about 0.8%). Subsequently, the mass of these specimens remains more or less constant for the next 160 cycles and then again starts decreasing with a drop in relatively value of almost 2% after ~166 cycles. Although the process of mass decrease for plain concrete exposed to W/D cycles started much later (after ~ 56 cycles) in comparison to the F/T exposure

(after ~ 4 cycles). The final value of mass reduction was also 2%.

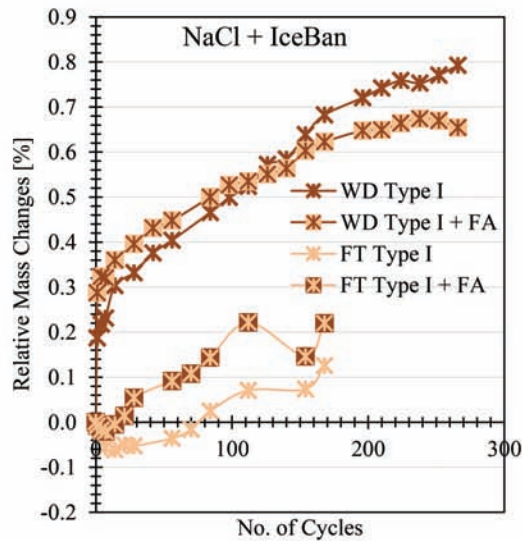
4.4.5 NaCl + MgCl₂ Solution

Figure 4.14 (a) shows the relative mass changes (%) of concrete samples exposed to NaCl + MgCl₂ solution. The specimens exposed to W/D cycles experience high (~0.5%) initial relative mass increase compared to specimens exposed to F/T cycles. Upon further exposure, that initial difference in mass gain is preserved, with curves for W/D exposure remaining more or less parallel and shifted by about 0.4% above the curves for F/T exposure.



(a) NaCl + MgCl₂ solution

(b) NaCl + CaCl₂ solution



(c) NaCl + IceBan solution

Figure 4.14 Mass changes (%) of samples subjected to different exposure condition (a) NaCl + MgCl₂ solution, (b) NaCl + CaCl₂ solution, and (c) NaCl + Ice Ban solution.

4.4.6 NaCl + CaCl₂ Solution

The effect of exposure to combined solutions of NaCl and CaCl₂ on the relative mass change of samples is shown in Figure 4.14 (b). It is noted that specimens exposed to W/D cycles experience around two-times higher mass gain than those subjected to F/T cycles. All concrete shows gains in mass, regardless of the type of concrete and regime. For concrete samples exposed to W/D cycles, the increase remains at about 0.5%, while that for concrete prisms subjected to F/T cycles remains at about 0.3% regardless of the type of binder that was used to prepare the specimens.

4.4.7 NaCl + Ice Ban Solution

The summary of mass changes for concrete with and without fly ash and exposed to sodium chloride with Ice Ban deicing chemicals is shown in Figure 4.14 (c). Concrete specimens that were subjected to W/D cycles show a much higher mass gain after 168 cycles (0.7% for Type-I and 0.6% for FA 20) then specimens subjected to F/T cycles (0.2% for Type-I and 0.1% for FA 20).

4.4.8 Comparison of Mass Changes for Specimens Subjected to All Solutions

Figure 4.15 and Figure 4.16 show, respectively, the relative changes in mass for Type I and FA 20 concrete prisms subjected to W/D cycles in the presence of various solutions. It can be observed that all specimens containing only Type I cement, except for those subjected to a 28% solution of calcium chloride gain, mass during the 266 W/D cycles of exposure. The behavior of the specimens subjected to CaCl₂ solutions

is drastically different from the rest. For this solution, after an initial gain in mass the concrete specimens start to lose mass and after 98 cycles show a mass lower than that observed at the beginning of exposure. Only after 168 W/D cycles, Type I concrete specimens subjected to CaCl₂ solutions lost around 1.8% of the initial mass. This finding is consistent with the visual inspections and RDME test outcomes as the samples exposed to CaCl₂ solutions showed extensive surface degradation during those tests.

The mass changes of the Type I and FA 20 concrete specimens that were subjected to F/T cycles and various solutions are shown in Figure 4.17 and Figure 4.18, respectively. Analyzing these graphs, it is easy to notice that the relative changes in mass for Type I concrete specimens that were exposed to F/T cycles in the presence of a 15% solution of MgCl₂ and a 17% solution of CaCl₂ are significantly different from the others. Specifically, the prisms exposed to 15% solution of MgCl₂ show continuous gain in mass whereas specimens exposed to calcium chloride solution show continuous decrease in mass. The lowest mass gain (close to 0) was observed for specimens that were immersed in sodium chloride + Ice Ban[®] and deionized water (Figure 4.17 and Figure 4.18).

To facilitate easier comparison between relative mass changes of Type I and FA 20 concrete specimens exposed to W/D and F/T cycles for about 266 days, all data collected after 266 cycles of exposure are presented respectively in Figure 4.19 (for W/D cycles) and Figure 4.20 (for F/T cycles).

4.5 Absorption Test

As already observed in section 3.4.4 of this report, the specimens used in this test were preconditioned by

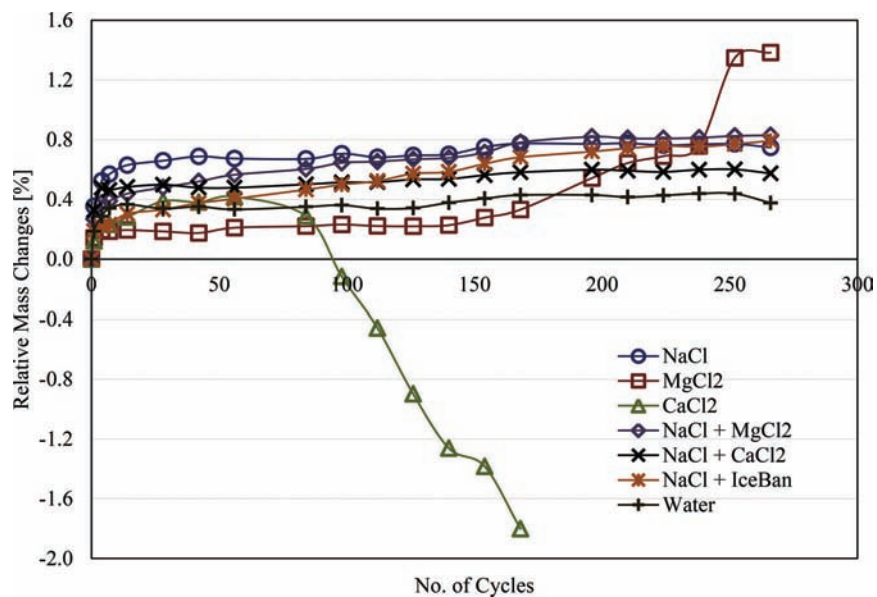


Figure 4.15 Relative mass changes (%) of Type I test samples subjected to W/D cycles.

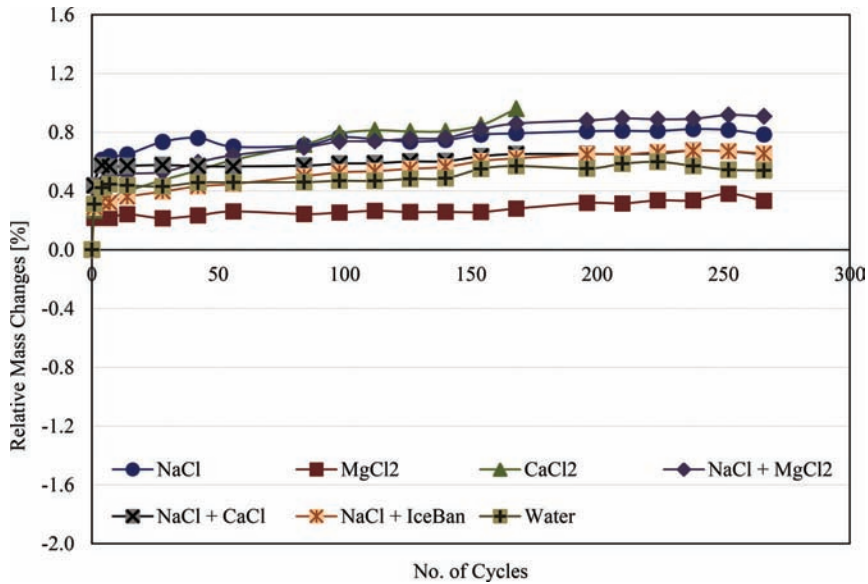


Figure 4.16 Relative mass changes (%) of FA 20 test samples subjected to W/D cycles.

two different methods. the first method involved placing one half of the specimens in the desiccator and exposing them for 3 days to temperature of $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $80\% \pm 3\%$ RH. This was followed by 15 days of air drying in the laboratory at 23°C and 50% RH. The second half of the specimens was preconditioned for 3 days in an environmental chamber set to maintain at 23°C and 50% relative humidity control.

The absorption values were calculated by the procedure described in section 3.4.4 using the measured mass changes for each of the specimens. These values were then plotted against square root of time and the slopes of the resulting plots yielded both, the initial and secondary rate of absorption. The individual plots of

absorption vs. the square root of time, along with the resulting slopes are given in Appendix B.

From Figure 4.21 it can be observed that specimens containing fly ash absorb less solution than those without it. Concrete with fly ash tends to have a more dense structure so ingress of the solution is more difficult. Also, specimens subjected to water and 23% sodium chloride have relatively high absorption. In fact, the absorption rate for sodium chloride specimen is slightly higher than that for water. Specimens in contact with 28% CaCl_2 and 25% MgCl_2 solutions experienced, respectively, medium and low absorptions. The lower absorption rate of specimens subjected to 25% MgCl_2 might be due to the formation of Brucite.

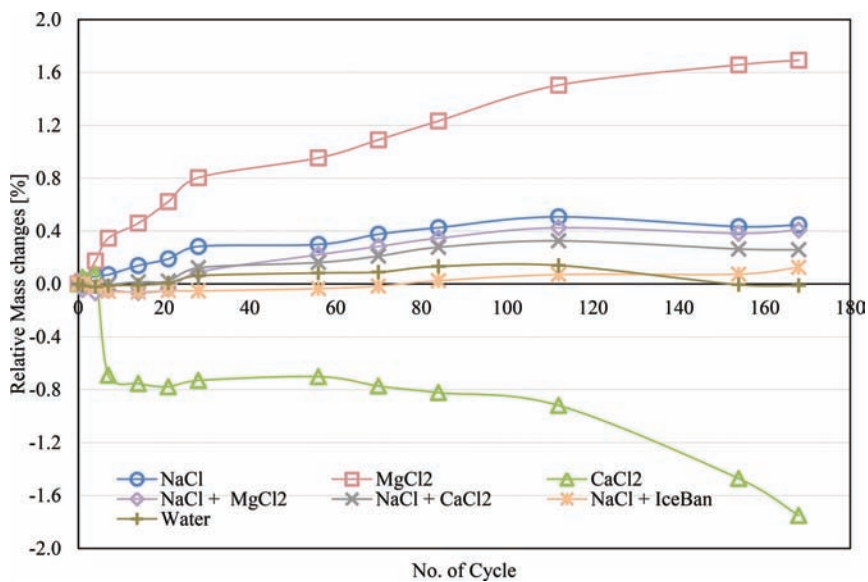


Figure 4.17 Relative mass changes (%) of Type I test samples subjected to F/T cycles.

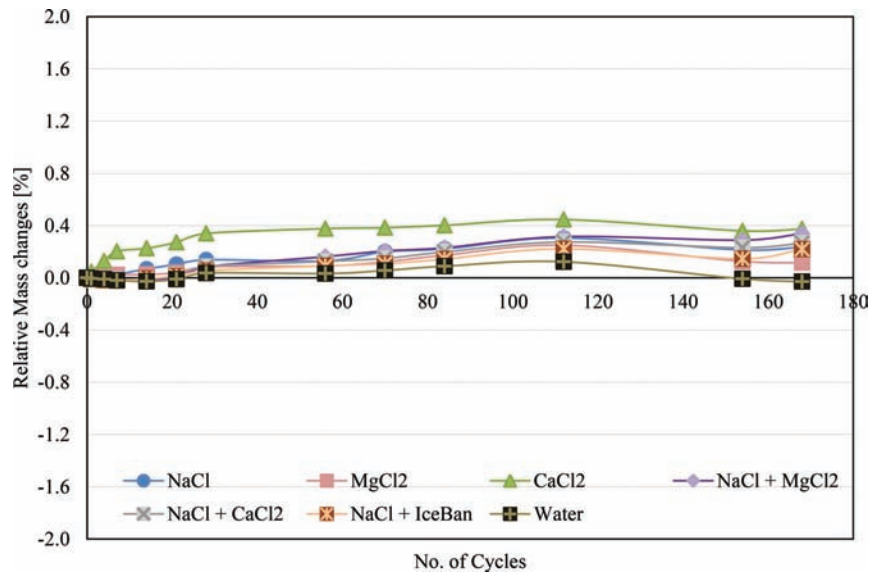


Figure 4.18 Relative mass changes (%) of FA 20 test samples subjected to F/T cycles.

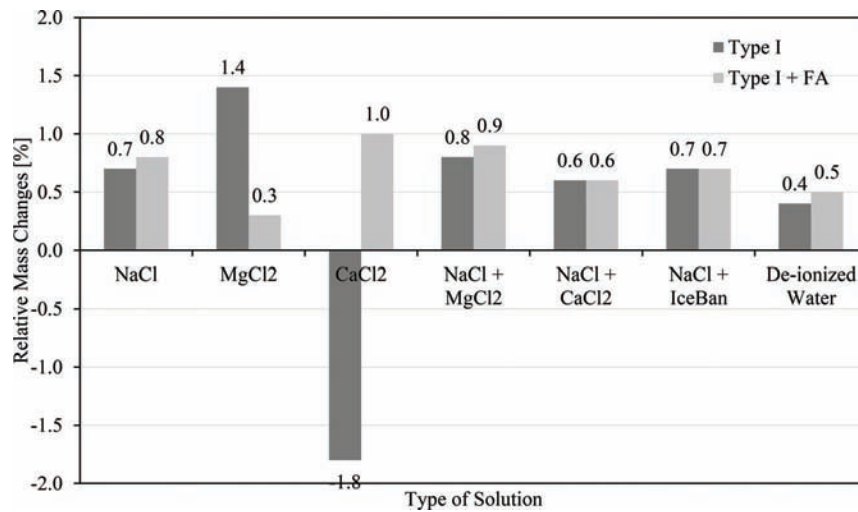


Figure 4.19 Relative mass changes (%) of concrete samples subjected to 266 W/D cycles.

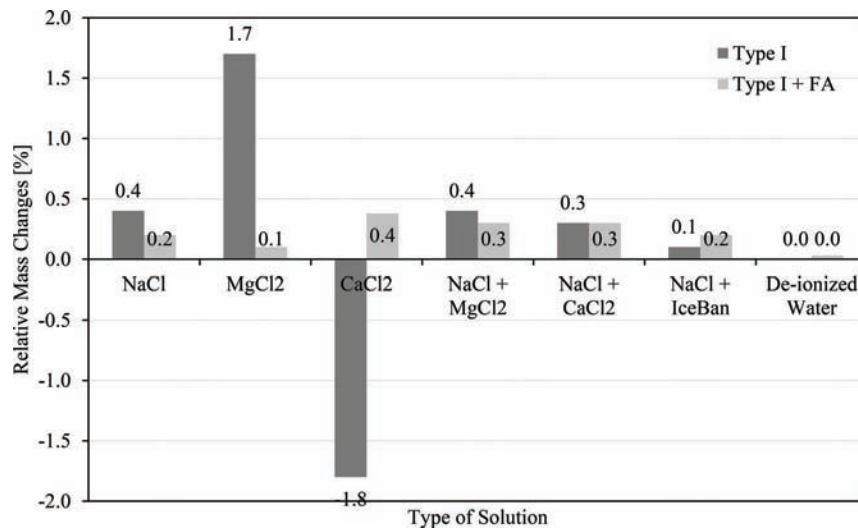


Figure 4.20 Relative mass changes (%) of concrete samples subjected to 266 F/T cycles.

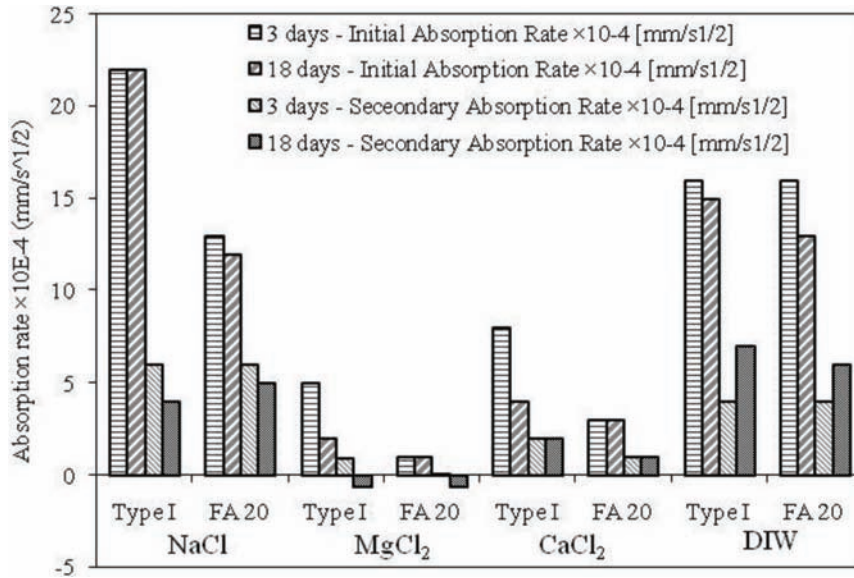


Figure 4.21 The Initial and the secondary rates of absorption for specimens exposed to different deicing solutions.

Microstructural investigation of the specimens subjected to MgCl₂ showed that Brucite was deposited in the air voids near the edges of the specimens which may slower the transportation of the liquids through the specimens (further discussed in 4.10). Also deposits of calcium oxychloride and portlandite have been found in specimens subjected to CaCl₂ solution which may also alter the absorption behavior of the samples.

4.6 Deicer Penetration

The purpose of this experiment was to determine what effect, if any, different preconditioning regimes will have on the depth of chloride ion penetration. The same preconditioning regimes as above used in the absorption test were also utilized in this experiment.

Those include; (a) 18 days of preconditioning (3 days at 50°C and 80% relative humidity + 15 days at 23°C and 50% relative humidity) and (b) 3 days of preconditioning at 23°C and 50% relative humidity. The chloride ion penetrations were measured for three different deicer/anti-icer solutions: 23% sodium chloride, 25% magnesium chloride and 28% calcium chloride.

Detailed results of the deicers penetration depths are given in Appendix C. Figure 4.22 and Figure 4.23 show the average penetration of chloride ions for respectively 3 days and 18 days preconditioning regime. It can be observed that the highest depth of penetration for both 3-days and 18 days preconditioned concrete specimens was associated with the 23% sodium chloride (NaCl) irrespective of the types of binder. At the same time, the lowest depth of penetration was caused by the 25%

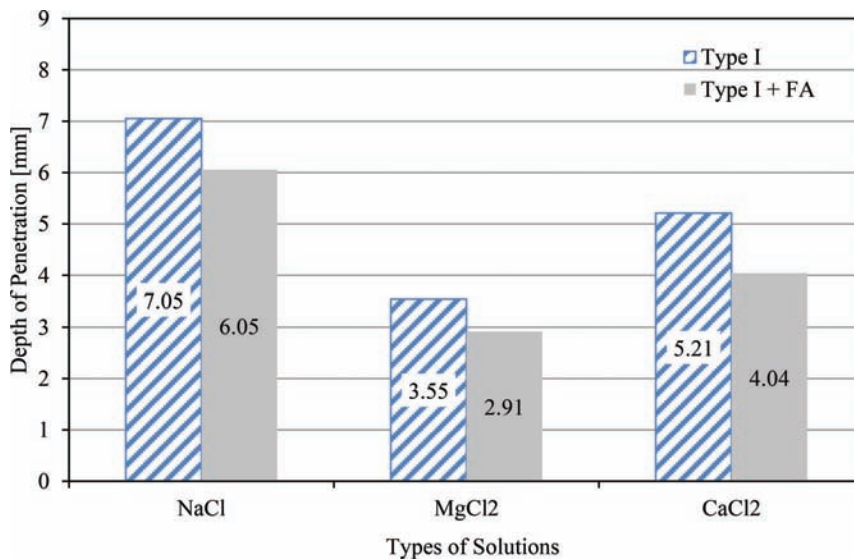


Figure 4.22 Average depth of chloride ion penetration for 3 days preconditioned specimens.

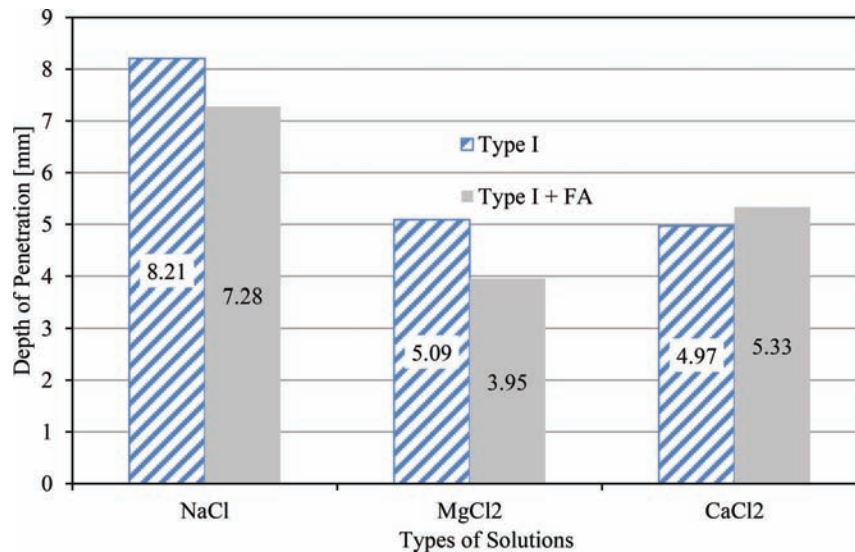


Figure 4.23 Average depth of chloride ion penetration for 18 days preconditioned specimens.

solution of $MgCl_2$. In most cases the depth of penetration was higher for Type I samples than in FA 20 samples. The differences in the total depth of chloride ion penetration between samples preconditioned for 3 days and 18 days were in range of 0.24 to 1.5 mm with samples preconditioned for 18 days typically experienced higher penetration. It should be noted that the measurement of the depth of penetration is very subjective, so the reported values should be treated only as an approximation. Overall, the differences in depth penetration are not significant and it can be interpreted as an error in subjective measurement. Based on these data it appears that conditioning of specimens for 3 days instead of 18 days will produce similar results.

4.7 Scaling Resistance

Four different types of deicing/anti-icing chemicals were used during this test. These include: 4% solution of sodium chloride (NaCl), 4% solution of sodium chloride (NaCl) + 0.1% solution of magnesium chloride ($MgCl_2$), 4% solution of sodium chloride (NaCl) + 0.1% solution of calcium chloride ($CaCl_2$) and 4% sodium chloride (NaCl) solution + 1.6% of agricultural deicer (Ice Ban®).

The mass losses of both types of concrete (Type I and FA 20) resulting from the scaling test are shown in Figure 4.24 and Figure 4.25. After 100 days of exposure, the maximum mass loss (4.6 g) was observed for FA 20 specimens subjected to the 4% NaCl solution. The lowest mass loss (0.28 g) was observed when Type I specimens were subjected to 4% of NaCl + Ice Ban®. For all types of systems the highest mass loss is observed at the beginning of the exposure. The slopes of the mass loss curves become more gradual after about 10 cycles. The initial rate of mass loss for specimens exposed to the sodium chloride plus calcium

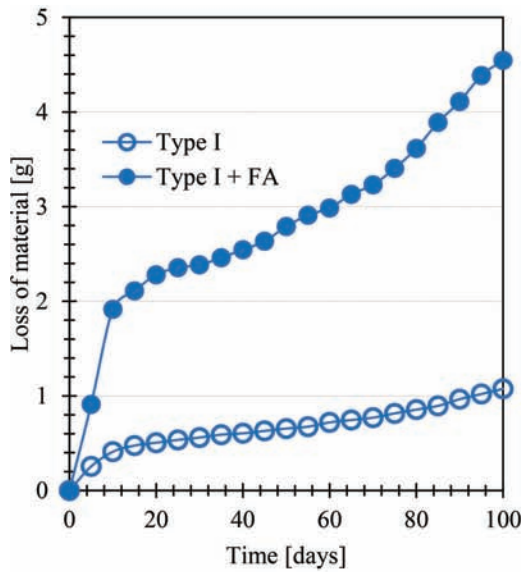
chloride solution is much lower than that observed for the solution of sodium chloride.

As can also be observed from these figures, in two cases (NaCl and NaCl + Ice Ban) mixtures containing fly ash are less resistant to scaling than plain mixtures. Lower resistance of concrete containing fly ash and exposed to NaCl could be the result of lower cement content (468 lbs/ yd^3) used in this specimens in comparison to 586 lbs/ yd^3 as was used for plain concrete and lower depth of penetration of NaCl compared to other deicers (see section 4.6). The addition of magnesium chloride based chemicals to sodium chloride didn't result in higher deterioration caused by scaling regardless the type of the binder. Appearances of the specimens subjected to scaling test is given in Appendix A.

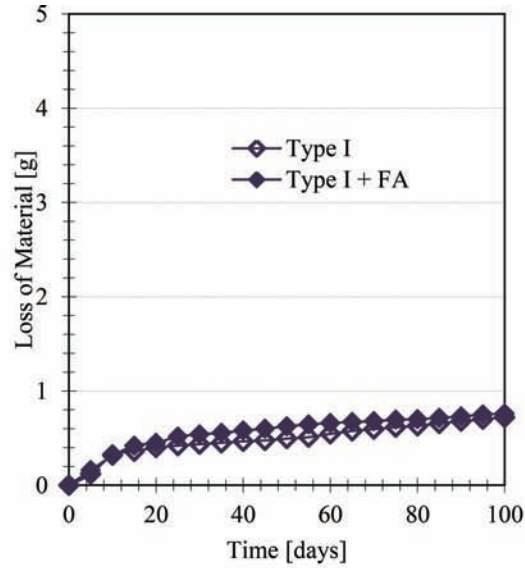
4.8 Compressive Strength

The results of the compressive test are reported for specimens exposed to two lengths of W/D cycles: (a) 168 cycles and (b) 350 cycles. Note: the specimens exposed to $CaCl_2$ solution were tested after 168 W/D cycles due to excessive surface scaling and generation of substantial amount of damaging as indicated by the ultrasonic pulse velocity (UPV) measurements described in section 4.9 of this report. Before starting the W/D exposure, all specimens were preconditioned for 3 days (after 28 days of lime water curing) in a control room with a temperature of 23°C and 50% relative humidity. Total of five solutions were incorporated in this experiment: deionized water (DIW), 23% NaCl, 28% $CaCl_2$, 25% $MgCl_2$ and lime water (SLW).

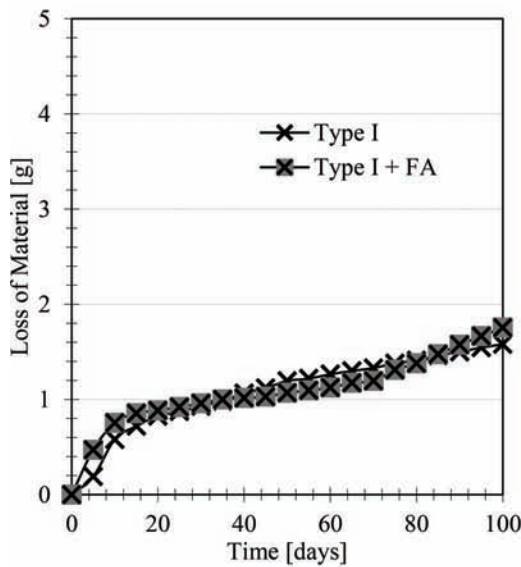
Figure 4.26 shows the compressive strengths for both Type I and FA20 specimens. There was no significant difference in compressive strength for Type I and FA20 specimens exposed to DIW, 23% NaCl solution and saturated lime water (SLW). However, some strength differences were observed for specimens exposed to



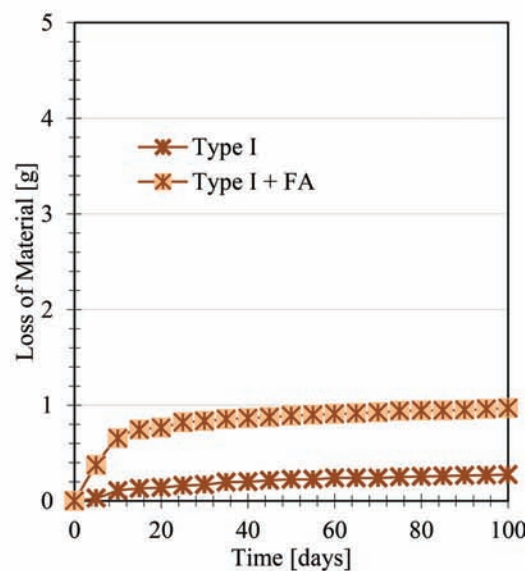
(a) 4% NaCl solution



(b) 4% NaCl + 0.1 % MgCl₂ solution



(c) 4% NaCl + 0.1 % CaCl₂ solution



(d) 4% NaCl + 1.6% IceBan solution

Figure 4.24 Mass losses of specimens subjected to scaling test in the presence of: (a) 4% NaCl solution, (b) 4% NaCl + 0.1% MgCl₂ solution, (c) 4% NaCl + 0.1% CaCl₂ solution and (d) 4% NaCl + 1.6% Ice Ban solution.

28% CaCl₂, and 25% MgCl₂ solutions. In case of 25% MgCl₂ solutions, FA 20 samples are found to provide more compressive strength than the Type I samples. Whereas, for 28% CaCl₂ solution, that compressive strength for Type I (8069 psi) samples are slightly higher than FA 20 (7678 psi) samples. In addition, although the strength loss for Type I specimens in 25% MgCl₂ solution was higher when compared to specimens in 28% CaCl₂ solution, it should be noted that the duration of exposure to MgCl₂ solution was more than 2 time longer (350 vs. 168 W/D cycles) than the duration of exposure in the CaCl₂ solution. It can be

therefore concluded that Type I specimens exposed to MgCl₂ under W/D conditions perform better than specimens exposed to CaCl₂ under identical exposure condition as reported by (18) this behavior can most likely be attributed to reduced penetration of MgCl₂ into the microstructure.

4.9 Ultrasonic Pulse Velocity (UPV) Measurements

The ultrasonic pulse velocity (UPV) method has been used to establish the residual strength of concrete and to quantitatively assess the damages sustained by

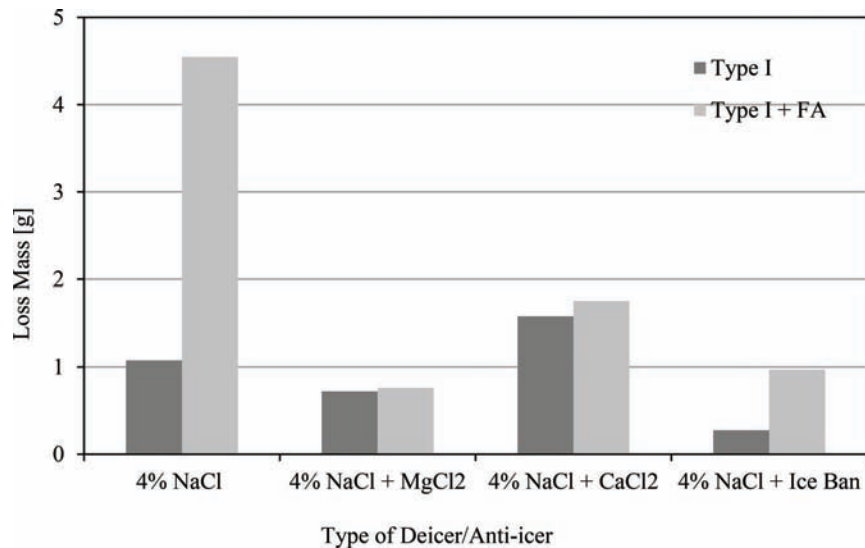


Figure 4.25 Mass losses of concrete specimens subjected to different deicing solutions.

concrete members. It is reported in (44) that UPV of concrete can indicate the extent of internal cracking of members damaged by freeze-thaw cycles. It was further stated that optical microscopy showed that freeze-thaw cycles result in uniformly distributed damages in concrete, whereas salt-scaling damages are more localized. Thus, the damage caused by freeze-thaw cycles reduce the UPV. Therefore, in this research changes in the UPV were monitored and compared to the degree of physical damage that was noted visually and quantified by measuring the relative dynamic modulus of elasticity (see section 4.2).

Figure 4.27 (a) shows average ultrasonic pulse velocity (UPV) values calculated from the results

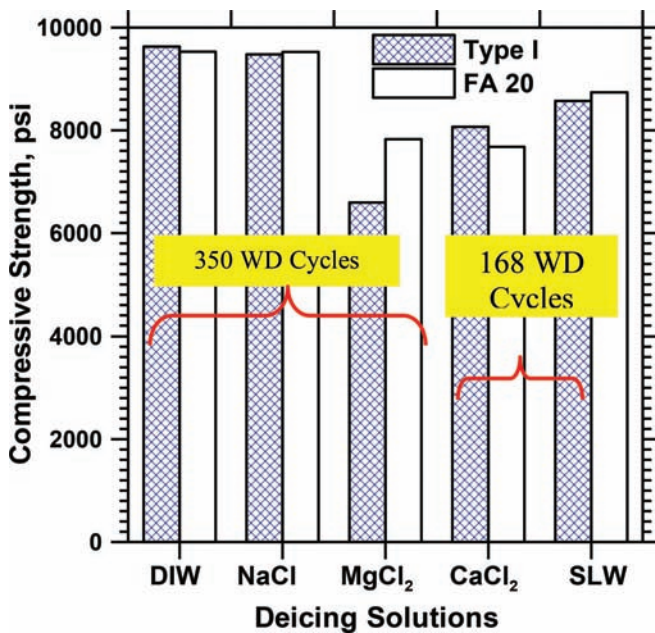


Figure 4.26 Compressive strengths for specimens exposed to different deicers under WD regime.

obtained for three Type I specimens exposed W/D cycles. It can be seen that for specimens exposed to DIW and 23% NaCl solution the values increased from 5.1 km/s at zero W/D cycle to about 5.3 km/s after about 336 W/D cycles, indicating no micro cracking took place in these specimens. However, not all specimens could be exposed to that many W/D cycles. As an example the W/D exposure of specimens stored in the CaCl₂ solution to be stopped after 168 cycles due to excessive surface scaling and sharp reduction in the value of relative dynamic modulus of elasticity (see section 4.2). With respect to UPV values, specimens exposed to 28% CaCl₂ solution started exhibiting downward trend after about 36 W/D cycles, and lost about 50% of the initial value (drop from 5.1 km/s to ~ 3.5 km/s) after 154 W/D cycles. This high (about 50%) drop of UPV is indicative of the internal degradation of the microstructure. For Type I specimens exposed to 25% MgCl₂ solution the reduction in UPV values began after 168 cycles and reached to about 4.4 km/s (about 12% reduction from the initial value of 5 km/s) after 294 W/D cycles. As mentioned earlier (section 4.8) the individual series of cylinders were tested for the compressive strength once the UPV measurements were no longer possible.

Figure 4.27 (b) shows average UPV values from two individual FA20 specimens exposed W/D cycles. It can be seen that, similar to Type I specimens, the UPV values of FA20 specimens exposed to DIW and 23% NaCl solution increased from the initial number of 5.0 km/s to about 5.2 km/s after about 336 WD cycles. The FA20 specimens exposed to CaCl₂ exhibited reduction of the UPV value from 5 km/s to about 4.6 km/s (about 8%) after 154 W/D cycles while those exposed to MgCl₂ decreased to about 4.6 km/s and 4.8 km/s (4%) after 336 W/D cycles.

In summary, the UPV measurements indicate that under the W/D exposure adopted in this research the

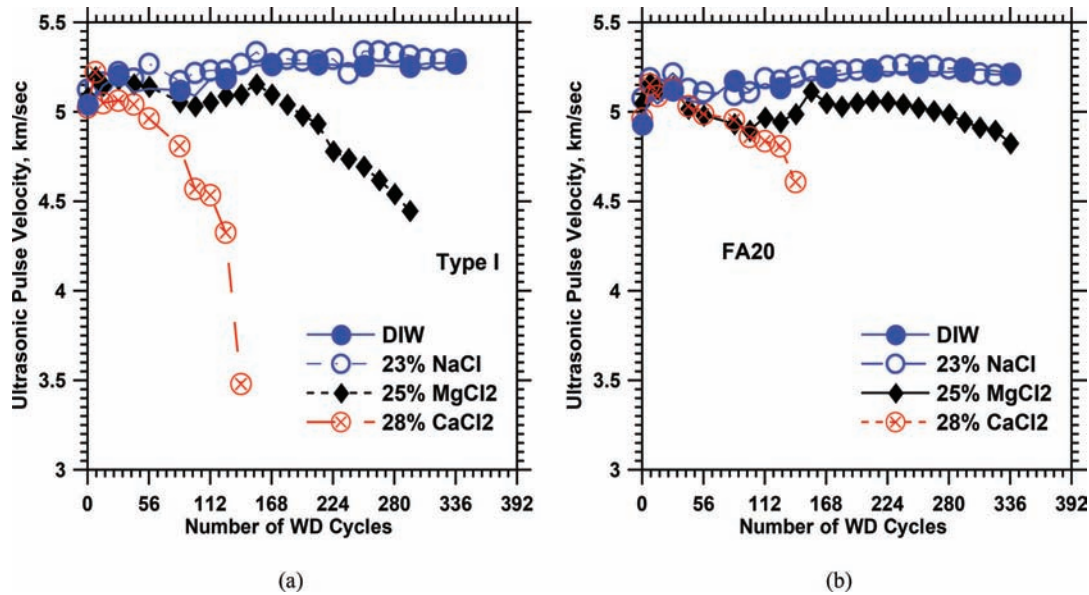


Figure 4.27 UPV for (a) Type I, and (b) FA 20 mixtures exposed to WD regime.

28% CaCl₂ solution is more harmful to Type I and also FA 20 concretes than 25% MgCl₂ solution.

4.10 Chloride Profile during Unidirectional Diffusion of Salt Solutions under W/D Regime

The chloride penetration profile for cylindrical specimens exposed to 28% CaCl₂ solutions was obtained after 168 W/D cycles. The corresponding profile for specimens exposed to 25% MgCl₂ solution was obtained after 350 W/D cycles. The results are shown in Figure 4.28. It can be seen that beyond the first 2 mm the concentrations are similar for all cases. Within the first 2 mm higher concentration was observed for Type I specimen exposed 25% MgCl₂ solution.

It is also important to note that in order to achieve similar level of chloride penetration, the specimens exposed to MgCl₂ required about twice as much time as specimens exposed to CaCl₂ solution. This can be explained by the slower absorption and penetration of 25% MgCl₂ solution as compared to CaCl₂.

4.11 Microstructural Changes in the Concrete Matrix

The microstructural changes due to the interactions of deicers with the hydrated cementitious matrix were evaluated by scanning electron microscopy (SEM) analysis. This section presents only the results of evaluation of changes in the microstructure results from exposure to CaCl₂ and MgCl₂ and Ice Ban+NaCl solutions since previous research indicated that these deicing solutions may have considerable detrimental effects on concrete microstructure compared to the other deicers. Previous study by Sutter and his co-workers (11) indicated that calcium chloride reacts with

calcium hydroxide to form hydrated calcium oxychloride (3CaO*CaCl₂*15H₂O). They also concluded that this type of reaction is occurring most efficiently in concrete exposed to freezing and thawing cycles, which is exactly the situation that requires the application of the deicers. These authors further reported that the formation of the calcium oxychloride is damaging to the concrete matrix as it generates disruptive hydraulic pressure. Figure 4.29 (a) shows such reaction product

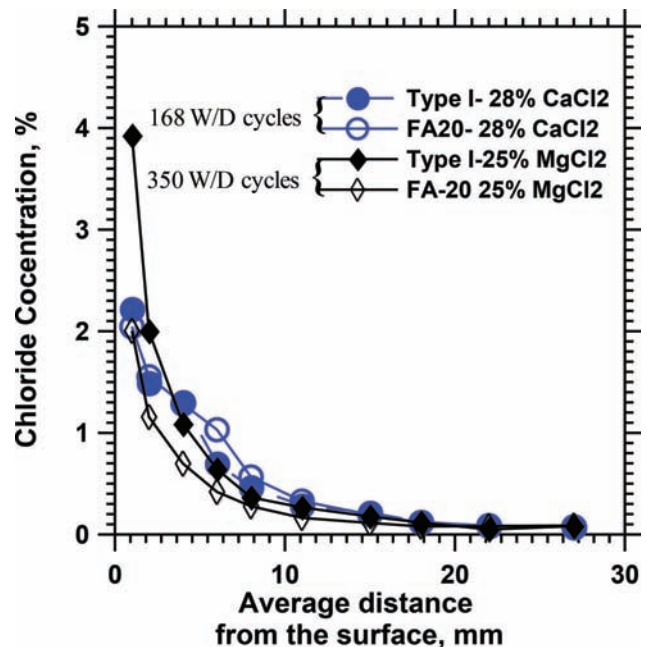
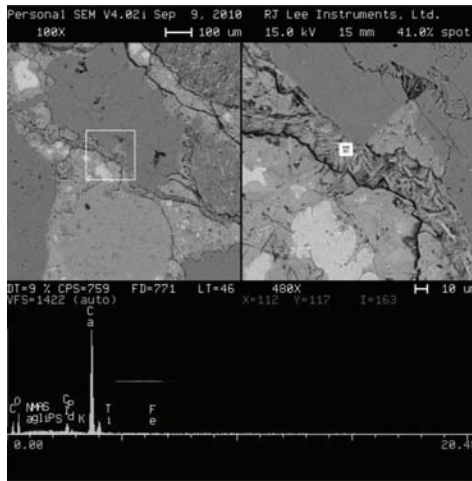
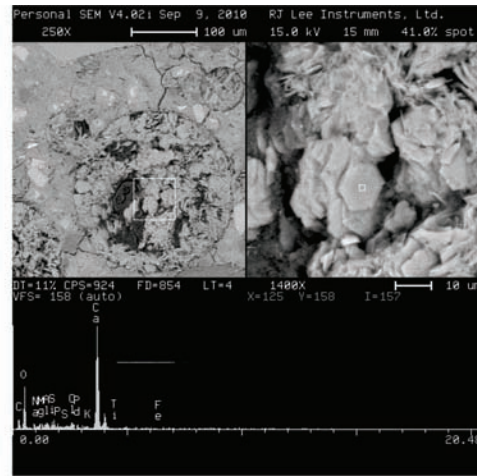


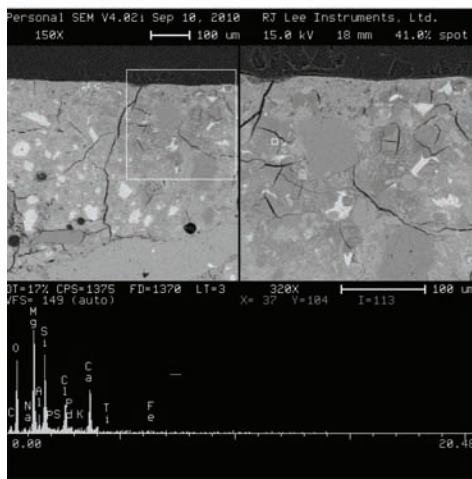
Figure 4.28 Penetration of acid soluble chlorides in specimens after 168 W/D cycles in CaCl₂ solution and 350 W/D cycles in MgCl₂ solution.



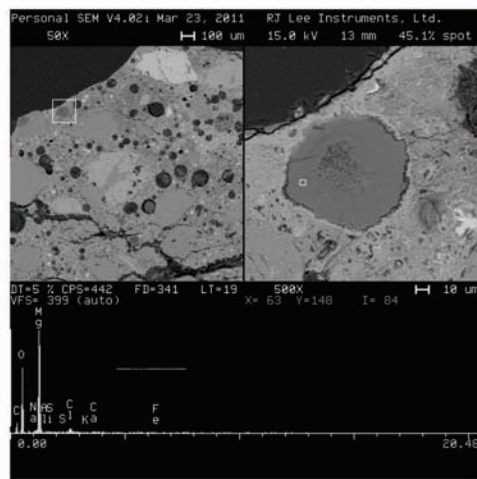
(a) EDX peaks shows the tracing of calcium oxychloride in Type I specimen subjected to 28 % CaCl₂ and W/D cycle



(b) Deposits of Ca(OH)₂ in Type I specimen subjected to CaCl₂ and W/D cycle



(c) MSH formation in type I specimen subjected to MgCl₂ and W/D cycles

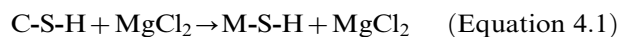


(d) Brucite formation in type I specimen subjected to MgCl₂ and FT cycles

Figure 4.29 Scanning Electron Micrograph of microstructure of specimens showing tracing of (a) Calcium oxychloride, (b) Calcium hydroxide, (c) MSH, and (d) Brucite formations.

in the microstructure of PC specimens exposed to 28% CaCl₂ solution under W/D regime. Also some deposits of Ca(OH)₂ was identified in the same specimen as shown in Figure 4.29 (b).

The MgCl₂ has been reported (11) to react with C-S-H gel and form non-cementitious M-S-H gel as illustrated by Equation 4.1. The formation of such product is shown in Figure 4.29 (c).



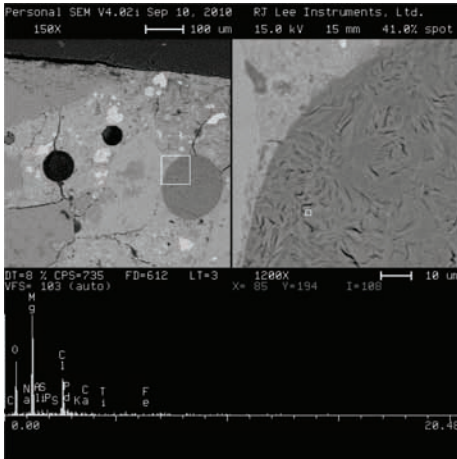
Another reaction identified as reportedly taking place in pastes exposed to MgCl₂ (11) is the depletion

of Ca(OH)₂ and formation of CaCl₂ and Mg(OH)₂ as illustrated by Equation 4.2.

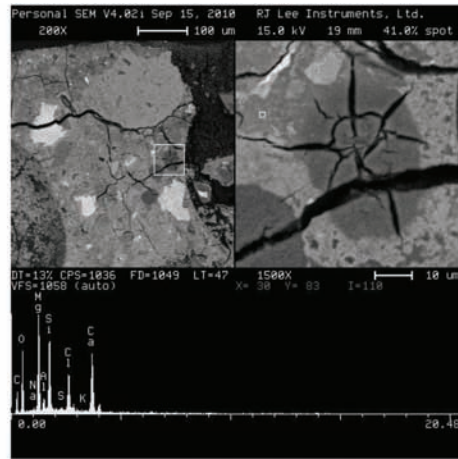


In this project, the formation of such Brucite (Mg(OH)₂) was identified in samples subjected to MgCl₂ deicer solution as shown in Figure 4.29 (d). Formation of magnesium oxychloride was also found in the sample subjected to MgCl₂ deicer solution (Figure 4.30 (a)).

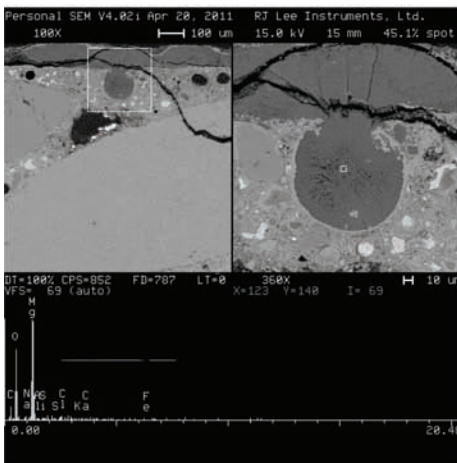
For the specimens subjected to Ice Ban+NaCl solution, deposits of Brucite were found in both FA



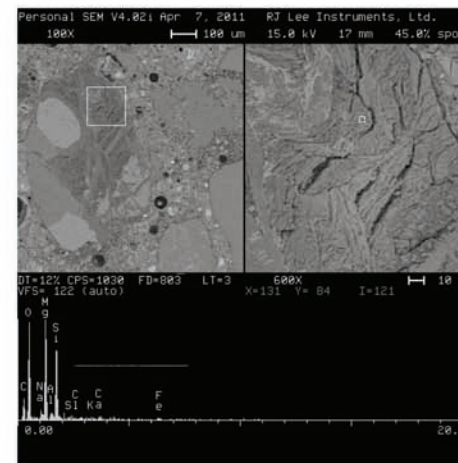
(a) Magnesium oxychloride formation in FA specimen subjected to $MgCl_2$ and W/D cycles



(b) Brucite formation in FA specimen subjected to IceBan and NaCl solution



(c) Brucite formation in Type I specimen subjected to IceBan and NaCl solution



(d) MSH formation in Type I specimen subjected to IceBan and NaCl solution

Figure 4.30 Scanning Electron Micrograph of microstructure of specimens showing tracing of (a) Magnesium oxychloride, (b) Brucite formation in FA specimen, (c) Brucite formation in Type-I specimen, and (d) MSH formation in the presence of Ice Ban solution.

and Type I specimens as shown in Figure 4.30 (b) and Figure 4.30 (c), respectively. Figure 4.30 (d) shows the formation of MSH in type I specimens subjected to Ice Ban + NaCl solution.

5. CONCLUSIONS

5.1 Effects of Different Deicers/Anti-icers on Concrete Properties

The summary of the effects of various deicers/anti-icers on concrete properties is presented in this section. Six different solutions were used in this study: sodium chloride, magnesium chloride, calcium chloride, sodium chloride + magnesium chloride, sodium chloride + calcium chloride, sodium chloride + Ice Ban®. All tests were performed on plain concrete specimens (containing Type I cement only) or fly ash concrete specimens (20% substitution by weight of cement with Class C fly ash).

5.1.1 Specimens Exposed to Deionized Water

Samples exposed to deionized water have found to provide consistent properties throughout the test without showing any severe sign of degradation. Both FA 20 and Type I specimens exhibited continuous increase in RDME values while subjected to W/D cycles in the presence of Deionized water. In case of F/T cycles, the RDME values increased initially but it showed sudden decrease at the end. Moreover, the specimens exposed to deionized water provided the maximum compressive strength (~9600 Psi) after 350 W/D cycles. Considering all the results of this study, it can be stated that deionized water did not exerted any detrimental effect on both Type I and FA 20 concrete specimens.

5.1.2 Specimens Exposed to Sodium Chloride (NaCl) Solution

Sodium chloride, NaCl immersed specimens show higher level of deterioration (as measured by the reduction in the RDME and mass changes) than the specimens immersed in deionized water. However, the observed level of deterioration was still much lower than that observed in cases when concrete samples were exposed to either calcium chloride or magnesium chloride solutions. No visible cracks can be observed in specimens exposed to sodium chloride solution after 275 W/D cycles and 168 F/T cycles.

The specimens exposed to NaCl experienced increase in mass mostly due to an increased rate of absorption of this solution and increase in the value of the RDME. In fact, the sodium chloride immersed specimens show the highest gain in this property among all deicers regardless of the type of concrete and exposure regime. The only test where specimens that were exposed to sodium chloride solution show worse results than the specimens exposed to other chemicals was the scaling test. However, even in this case the damage was rather superficial.

5.1.3 Specimens Exposed to Magnesium Chloride (MgCl₂) Solution

Concrete specimens that were subjected to MgCl₂ solution experienced relatively high (about 10% for W/D exposure and about 14% for F/T exposure) reduction in the RDME than the NaCl solution. The surface deterioration of magnesium chloride immersed specimens worsened with the increase in the exposure time and when examined after 275 cycles of W/D exposure the surface of the specimens showed multiple fine cracks. In addition, some loss of material was also evident, especially around the edge of plain concrete samples.

The only other deicer that resulted in larger relative modulus and mass losses than the MgCl₂ solution was calcium chloride (CaCl₂) solution. In addition, the onset of the reduction in RDME and in mass loss of specimens exposed to MgCl₂ solutions was much delayed when compared to the CaCl₂ solution.

5.1.4 Specimens Exposed to Calcium Chloride (CaCl₂) Solution

Samples exposed to calcium chloride (CaCl₂) solution resulted in the highest (15 to 17%) reduction in the RDME in comparison with other deicing solutions in this study. In case of plain concrete specimens, this reduction started very early (after about 28 cycles of W/D and about 7 cycles of F/T exposure). In addition, calcium chloride immersed specimens were the first ones to develop surface cracking and to experience loss of material along the edges.

It should be pointed out, however, that fly ash specimens exposed to CaCl₂ performed consistently better than the plain specimens. In absorption test, specimens that were subjected to the CaCl₂ solution resulted higher absorption values than the MgCl₂ solution, regardless of the type of binder.

5.1.5 Specimens Exposed to NaCl + MgCl₂ Solution

Performance of specimens subjected to combined solutions of NaCl and MgCl₂ was very comparable to the performance of specimens exposed to NaCl solution alone. The length and mass changes of the samples subjected to this combined solution are very similar to that of NaCl solution except these combined solution resulted in higher length changes at the end of F/T cycles.

5.1.6 Specimens Exposed to NaCl + CaCl₂ Solution

The results obtained for concrete specimens exposed to a combined solution of NaCl and CaCl₂ were very comparable to those obtained for NaCl alone. The only exception were the scaling test results where this exposure regime resulted in lower reduction in the mass of scaled material compared to NaCl alone.

5.1.7 Specimens Exposed to NaCl + Ice Ban® Solution

Concrete samples that were exposed to a combined solution of sodium chloride and Ice Ban® showed performance similar to that exhibited by specimens exposed to the two other combined solutions; especially during early stages of exposure cycles. However, in some cases (when evaluated near the end of the exposure period), the performance of the concrete subjected to this combined solution started to decline. For example, plain concrete samples that were exposed to F/T cycles in the presence of combined sodium chloride + Ice Ban® solution experienced higher rates of length changes (~0.038%) than those observed in specimens exposed to other combined deicers.

5.2 Effects of Fly Ash Addition to Concrete Specimens

Concrete specimens containing fly ash (as a partial replacement of cement) exhibited better performance when compared with the Type I specimens during most of the tests in this study. FA 20 specimens showed lower reduction in RDME values than the Type I specimens for both W/D and F/T exposure conditions. Moreover, all of the FA 20 specimens resulted in mass gain irrespective of the deicer type and exposure conditions. Whereas Type I specimens resulted in severe mass loss under both W/D and F/T regimes when soaked in CaCl₂ deicing solution. The only negative aspect of fly ash replacement was observed during the scaling test when FA 20 specimens resulted in higher mass loss than the Type I specimens.

5.3 Summary

The calcium chloride deicing solutions appear to be the most destructive with respect to concrete properties, regardless of the type of exposure regime and the type of binder used. The magnesium chloride deicing solution also showed higher level of damaging effects toward concrete compared with sodium chloride solution. With MgCl₂ the reduction in certain concrete properties starts manifesting itself much later than in the case of calcium chloride. Overall, the best performance (in terms of reducing the negative impact on concrete) was associated with the use of sodium chloride solutions, followed by the combined solution of sodium chloride with magnesium chloride and sodium chloride with calcium chloride. Specimens that were exposed to sodium chloride with Ice Ban® showed acceptable performance during the initial stages of the exposure cycles. However, long term exposure to this combined deicer resulted in an increased risk of deterioration, especially in plain concrete exposed to F/T conditions.

The addition of fly ash was found to have a positive influence on performance of the concrete, regardless of the type of deicer and exposure regime used. The only concrete property that was negatively impacted (although rather mildly) was scaling resistance. F/T

exposure conditions typically resulted in more severe distress than W/D regimes, even though the concentrations of deicers used for F/T tests were about 50% lower than those used during W/D tests. This confirms the finding from the literature that the combination of physical and chemical deterioration processes is often more severe than each of these processes alone.

6. RECOMMENDATIONS

Sodium chloride immersed specimens showed the best performance under exposure conditions used in the study; hence it is recommended that this deicer should be preferentially used for winter maintenance operation unless the expected temperatures are below 25°F. At the temperature below this limit the effectiveness of this solution will be reduced.

The use of combined solutions of either combinations of sodium chloride with magnesium chloride or sodium chloride with calcium chloride should be explored further. Based on preliminary results obtained during this research which only used relatively low concentration of MgCl₂ and CaCl₂, it seems that there may be a potential for improving the low temperature effectiveness of NaCl deicer without severely impacting the durability of concrete.

Finally it has been demonstrated that the use of fly ash can significantly improve the performance of concrete exposed to deicing chemicals though it showed minor negative impact on scaling resistance. However, based on the literature, slightly increased scaling tendency of concretes with supplementary cementitious materials can be successfully reduced by lowering the water cement ratio and by producing concrete with adequate air void system.

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APPENDIX A. TEST PARAMETERS AND RESULTS OF THE PREVIOUS STUDIES ON DEICER

TABLE A.1

Summary of Test Parameters and Results for Laboratory Concrete Mixes Exposed to Various Deicing Chemicals

Investigator	Mixture/Specimens	Solutions	Tests	Exposure Conditions	Observations	Findings
1	2	3	5	4	6	7
Khedr et al. (35)	PC concrete with air content: 0%, 3–4%, 4–5%, 5–7%, 7–9%; FA: siliceous river sand; CA: natural gravel	CaCl ₂ 5%	mass changes	F/T		calcium hydroxide dissolution; reduced pH; chloroaluminate formation
Collepari and Santagata (23)	10 × 10 × 10 cm; w/c=0.4/0.5/0.6; PC; PC+30%fly ash, PC+50% slag	CaCl ₂ 30%		5°C	concrete appeared to be severely damaged, even in the absence of F/T cycles, when non-air entrained concrete is produced with normal PC	calcium oxychloride formation
Marchand et al. (27)		NaCl				calcium hydroxide formation; chloroaluminate; CaCl ₂ formation
Wang et al. (18)	9 × 9 × 9 cm and 10 × 10 × 10 cm PC Type I/II, air cont. 6%, w/c=0.48, CA: limestone	NaCl 26.5%	XRD; SEM/EDX; mass changes; scaling; strength	W/D	some cracks observed; no precipitates; limited mass change; no scaling; less than 10% strength loss in comparison to water immersed specimens; small amount of mass gain, little scaling; little strength loss with increasing F/T cycles	calcium hydroxide formation; calcium hydroxide (CH) presence; leaching ettringite
		NaCl 13.3%		F/T		
		CaCl ₂ 37.9%		W/D	samples severely cracked; air voids filled by precipitates; high Cl ⁻ concentration in voids; gain a relatively large amount of mass; increasing scaling with W/D cycles; less than 10% strength loss in comparison to water immersed samples; 0–30 cycles mass gain (crystal precipitates); 30–40 significant mass loss (paste disintegration probably); increasing scaling with F/T cycles; dramatic strength loss compared to water samples	ettringite presence; Ca-Al-Cl-S hydrate; leaching of CH; leaching ettringite
		CaCl ₂ 9.5%		F/T		
Wang et al. (18)	10 × 10 × 10 cm PC Type I/II, air cont. 6%, w/c=0.48, CA: limestone	K Acetate 54.5% Agr.-deicing	mass changes; strength	W/D	limited mass changes; lower strength loss than paste significantly mass loss; existing of micropores; lower strength loss than paste	
Darwin et al. (40)	3 × 3 × 12 in. prisms; Type I/II PC w/c = 0.45; air content 6%	NaCl 3%, 15% MgCl ₂ 3.3%, 16% CaCl ₂ 3.8%, 18% CMA 4.9%, 23%	modulus of elasticity and physical appearance	W/D	at lower concentration a relatively small negative impact on properties of concrete, at 15% greater, but still small at 3.3% measurable damage; at 16% a significant changes at 3.8% a relatively small negative impact on properties of concrete; at higher concentration significant changes at lower concentration measurable damage to concrete; at higher concentration a significant changes	

TABLE A.1
(Continued)

Investigator	Mixture/Specimens	Solutions	Tests	Exposure Conditions	Observations	Findings
1	2	3	5	4	6	7
Kozikowski et al. (37)	Type I/II cement 5.5% or 3% air content; w/c = 0.42 or 0.44, respectively; 12 × 12 × 3 in. slabs - scaling; cores from the scaling slabs - wicking	NaCl 4%; 30% MgCl ₂ 30% NaCl 4%; 30% MgCl ₂ 30%	scaling	F/T	after 50 cycles damage observed only for concrete with 3% air content and exposed to 4% NaCl; 30% NaCl didn't freeze at -18C no damage observed due to lack of ability to freeze at -18C significant crystal formation; mass increase due to salt deposit; no significant damage (microscopical examination) little to no crystallization; mass decrease (at 23C) due to mild chemical attack; mass increase at 4C; no significant damage (microscopical examination)	
Sutter et al. (11)	cylinders 2-in × 4-in with FA and GBFS; w/c=0.4, 0.5, 0.6; OTTAWA SAND Type I cement	NaCl 17.8% CaCl ₂ 17% MgCl ₂ 15%	petrographic analysis; EDX	constant temp of 40°F	no deterioration after 84 days after 56 days of exposure expansion and cracking; after 84 days severely deteriorated after 56 days of exposure expansion and cracking; after 84 days severely deteriorated	calcium oxychloride formation; calcium hydroxide dissolution brucite formation; calcium oxychloride formation; calcium hydroxide dissolution
Sutter et al. (42)	cylinders w/c = 0.4, 0.5, 0.6;	NaCl 17.8% MgCl ₂ 15%	petrographic analysis	cyclic temp. -15 to 135°F	no visible cracking after 7 and 14 days no visible cracking after 7 and 14 days	salt crystallization; calcium hydroxide dissolution; alteration of C-S-H; osmotic pressure salt crystallization; calcium hydroxide dissolution; alteration of C-S-H;

Note: W/D = wetting & drying; F/T = freezing & thawing.

TABLE A.2
Tests on Mortar Specimens Subjected to Various Deicing/Anti-icing Chemicals

Investigator	Mixture/Specimens	Solutions	Tests	Exposure Conditions	Results	Observation
1	2	3	4	5	6	7
Hoffman et al. (32)	Discs 65 mm in diameter and 5 mm high; PC w/c 0.5	NaCl 20%	thermogravimetric analysis	F/T		calcium hydroxide dissolution; monosulphate; Friedel's Salt
Kozikowski et al. (37)	Type I/II cement; w/c = 0.48	MgCl ₂ 30%	petrographic analysis; SEM	immersion in solution	bar that was immersed for 2.5 years didn't have significant distress	brucite formation; alteration of C-S-H

Note: F/T = freezing & thawing.

TABLE A.3
Summary of Test Parameters and Results for Laboratory Pastes Exposed to Various Deicers

Investigator	Mixture/Specimens	Solutions	Methods	Exposure Conditions	Results	Observation
1	2	3	5	4	6	7
Chatterji (34)	4 × 4 × 16 cm, PC, w/c = 0.5	CaCl ₂ 30%	X-ray examination	constant 40° C, 5° C, 20° C	severity of CaCl ₂ attack decreases with increasing temperature and above 40° C concrete is not affected	monochlorohydrate formation; calcium hydroxide dissolution; crystallization
Wang et al. (18)	5 × 5 × 5 cm PC Type I/II, w/c = 0.4	NaCl 13.3% CaCl ₂ 9.5%	mass changes; scaling; strength	F/T	minimal mass gain; little scaling; little strength loss with increasing F/T cycles 0-30 cycles mass gain (crystal precipitates and fluid adsorption in the cracks); 30-40 drastic mass loss; increasing scaling with F/T cycles; comparable scaling with concrete samples; considerable strength loss	

TABLE A.5
Summary of Test Parameters and Results for Field Concrete Exposed to Various Deicers

Investigator	Mixture/Specimens	Solutions	Methods	Exposure Conditions	Results	Observation
1	2	3	4	5	6	7
Cody et al. (38)	12 × 12 × 25 mm blocks with dolomite coarse aggregates	NaCl 3 M or 0.75 M CaCl ₂ 3 M or 0.75 M MgCl ₂ 3 M or 0.75 M	visual using binocular microscope	F/T	Benign severely damaged	calcium hydroxide dissolution; chloroaluminate formation brucite formation; M-S-H formation
Cody et al. (38)	12 × 12 × 25 mm blocks with dolomite coarse aggregates	NaCl 3 M or 0.75 M CaCl ₂ 3 M or 0.75 M MgCl ₂ 3 M or 0.75 M	visual using binocular microscope	W/D	Benign severely damaged	calcium hydroxide dissolution; chloroaluminate formation brucite formation; M-S-H formation
Lee et al. (36)	12 × 12 × 25 mm blocks with dolomite coarse aggregates	NaCl 3 M or 0.75 M CaCl ₂ 3 M or 0.75 M	visual using binocular microscope	continuous soak	Benign	calcium hydroxide dissolution; chloroaluminate formation
Lee et al. (36)	3 × 1.5 × 1.5 cm blocks with dolomite coarse aggregates	MgCl ₂ 3 M or 0.75 M NaCl 0.75 M CaCl ₂ * 2H ₂ O	petrographic analysis; SEM; EDAX	W/D	the most destructive least deleterious	brucite formation; M-S-H formation calcium hydroxide dissolution; chloroaluminate formation; trichloroaluminate formation brucite and M-S-H formation; calcium hydroxide dissolution; calcium chloride hydrate
	3 × 1.5 × 1.5 cm blocks with dolomite coarse aggregates	MgCl ₂ * 6H ₂ O			after 23 cycles rapid deterioration	brucite and M-S-H formation; calcium hydroxide dissolution; formation of portlandite; chloroaluminate formation
		NaCl	petrographic analysis; SEM; EDAX	F/T	more deleterious than DW	calcium hydroxide dissolution; chloroaluminate formation; trichloroaluminate formation brucite and; M-S-H formation; calcium hydroxide dissolution; chloroaluminate formation; calcium chloride hydrate
		0.75 M CaCl ₂ * 2H ₂ O			less deleterious than in W/D	brucite and M-S-H formation; calcium hydroxide dissolution; formation of portlandite; chloroaluminate formation

Note: W/D = wetting and drying; F/T = freezing and thawing.

APPENDIX B. SCALING TEST SPECIMENS



Figure B.1 Appearance of specimens that were subjected to scaling test in the presence of 4% solution of sodium chloride (NaCl) after 100 cycles of exposure (left – Type I; right – FA) sodium chloride with magnesium chloride.

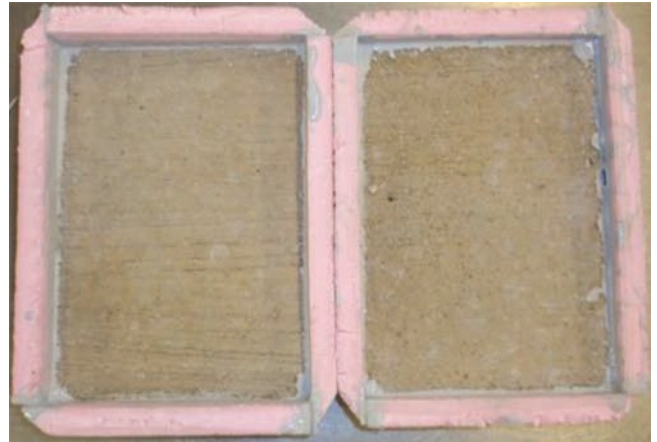


Figure B.3 Appearance of the specimens that were subjected to scaling test in the presence of the combination of sodium chloride and calcium chloride (NaCl + CaCl₂) after 100 cycles of exposure (left – Type I; right – FA).



Figure B.2 Appearance of the specimens that were subjected to scaling test in the presence of the combination of sodium chloride with magnesium chloride (NaCl + MgCl₂) after 100 cycles of exposure (left – Type I; right – FA).

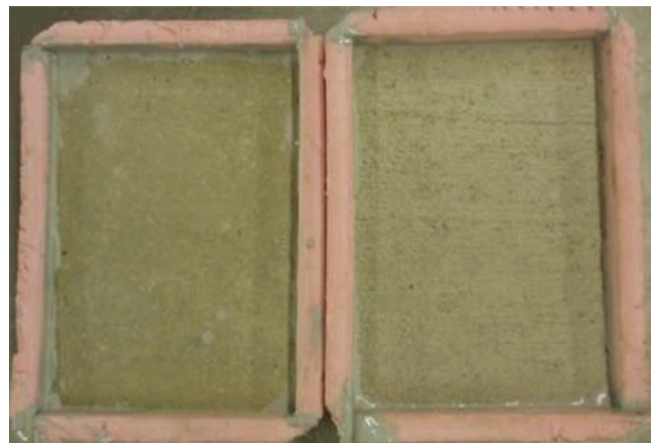


Figure B.4 Appearance of the specimens that were subjected to scaling test in the presence of the combination of sodium chloride and Ice Ban[®] after 100 cycles of exposure (left – Type I; right – FA).

APPENDIX C. ABSORPTION OF CONCRETE SPECIMENS

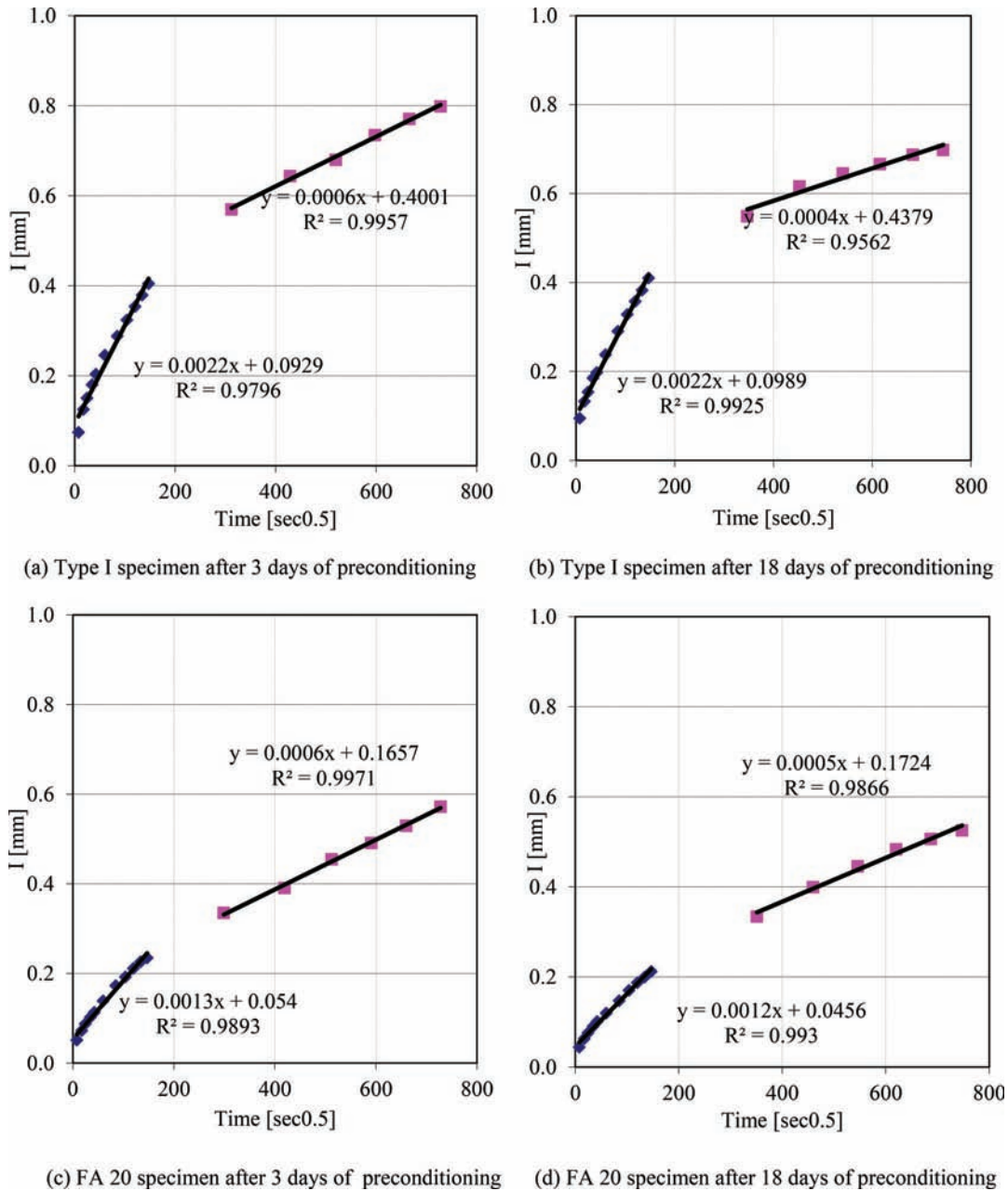


Figure C.1 Absorptions of concrete specimens when subjected to 23% NaCl: (a) Type I specimen in 3 days preconditioning, (b) Type I specimen in 18 days preconditioning, (c) FA 20 specimen in 3 days preconditioning, (d) FA 20 specimen in 18 days preconditioning.

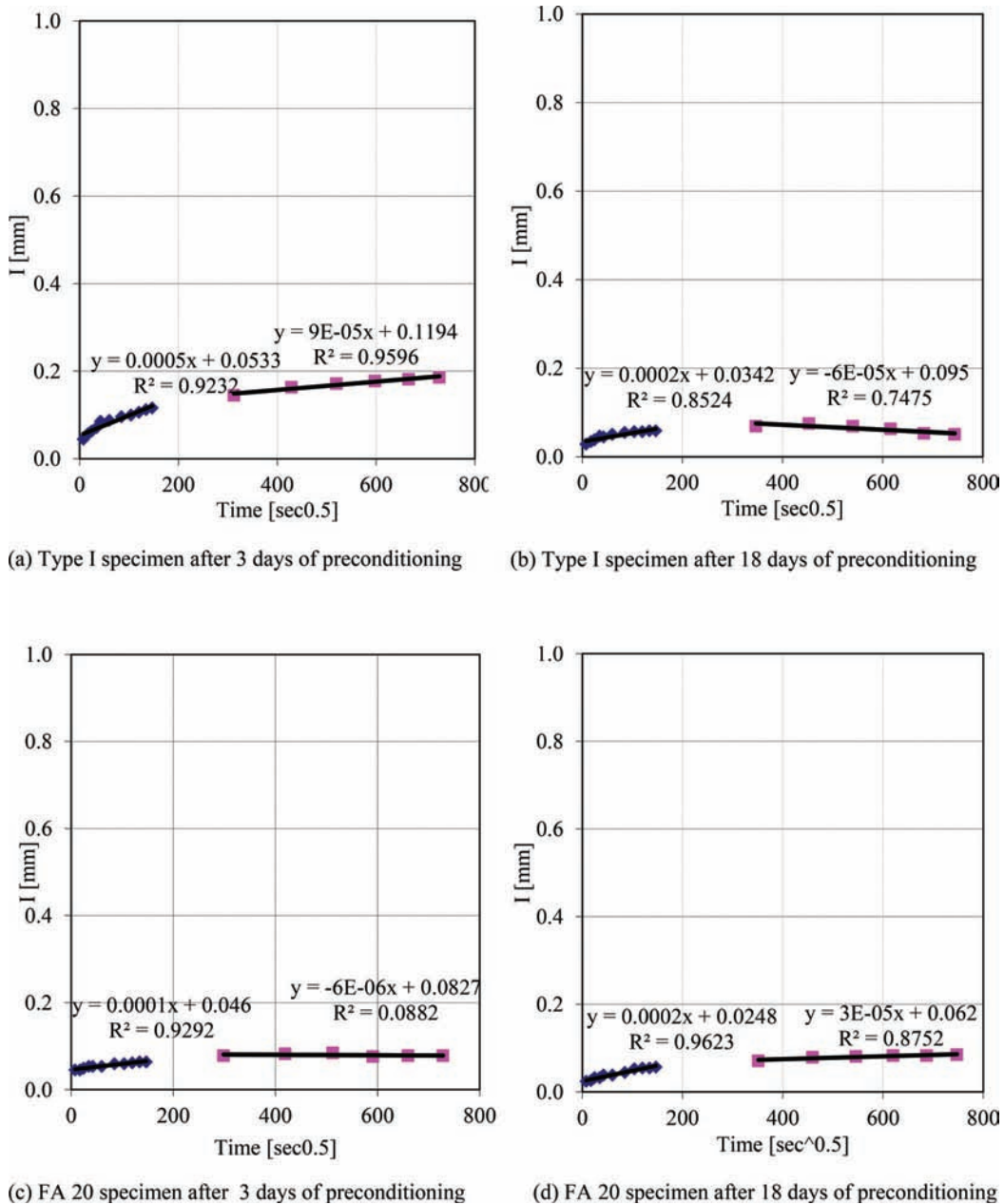


Figure C.2 Absorption of concrete specimens when subjected to the solution of 25% $MgCl_2$: (a) Type I specimen after 3 days of preconditioning, (b) Type I specimen after 18 days of preconditioning, (c) FA 20 specimen after 3 days of preconditioning, (d) FA 20 specimen after 18 days of preconditioning.

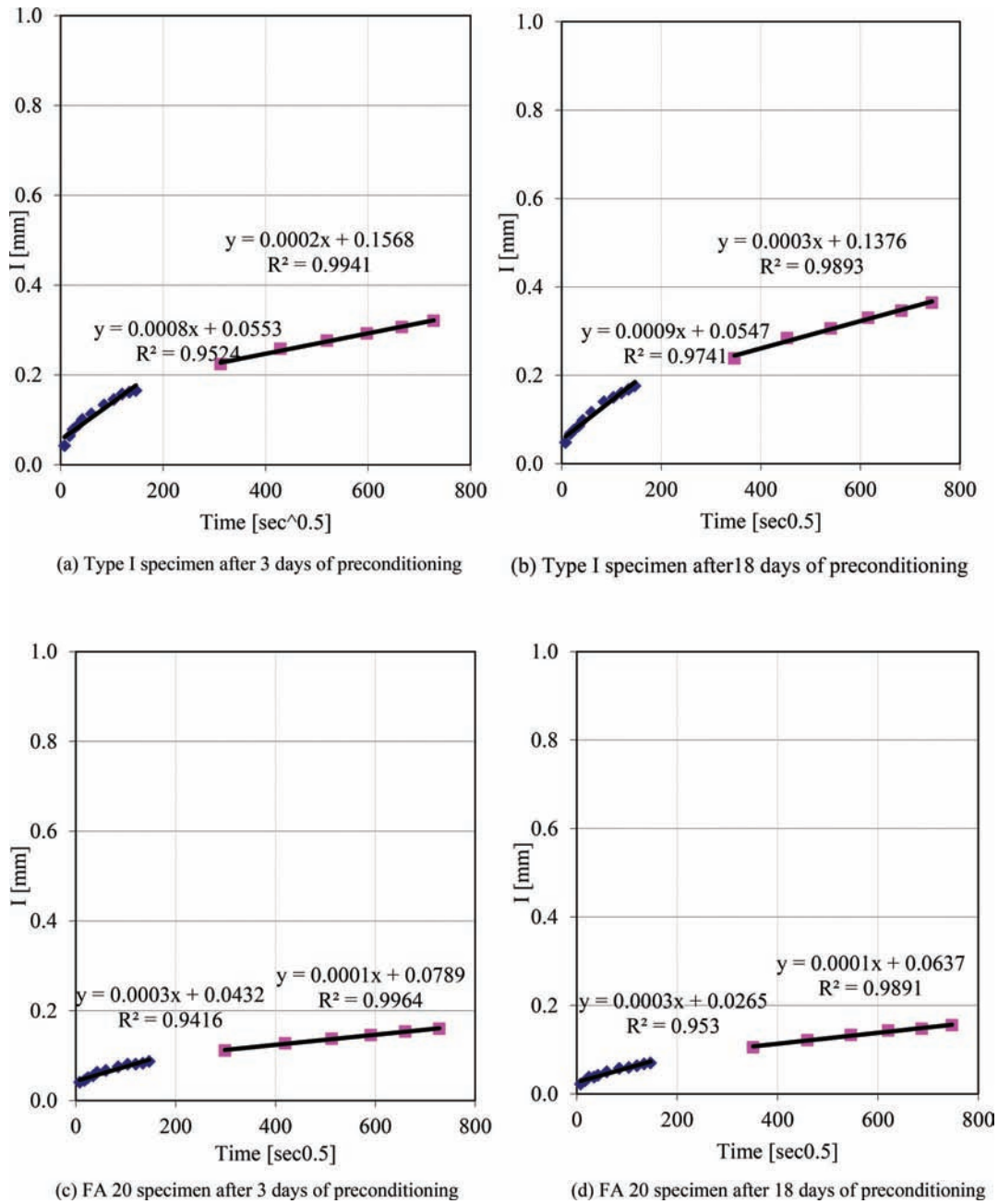


Figure C.3 Absorption of concrete specimens when subjected to 28% CaCl₂: (a) Type I specimen after 3 days of preconditioning, (b) Type I specimen after 18 days of preconditioning, (c) FA 20 specimen after 3 days of preconditioning, (d) FA 20 specimen after 18 days of preconditioning.

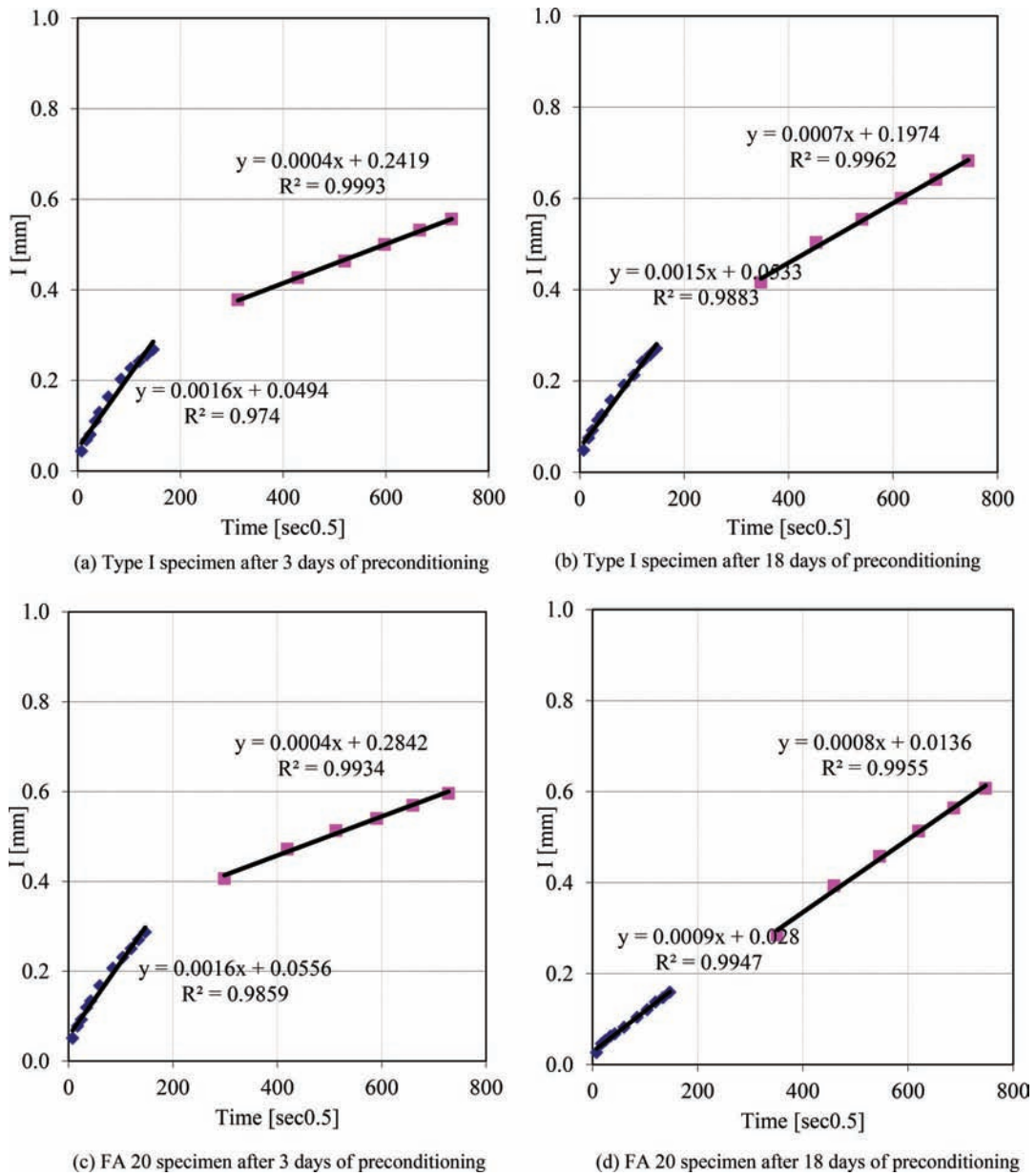


Figure C.4 Absorption of concrete specimens when subjected to Deionized Water: (a) Type I specimen after 3 days of preconditioning, (b) Type I specimen after 18 days of preconditioning, (c) FA 20 specimen after 3 days of preconditioning, (d) FA 20 specimen after 18 days of preconditioning.

APPENDIX D. DEPTH OF CHLORIDE IONS PENETRATION

TABLE D.1
Depth of Penetration for Concrete Specimens Subjected to 23% Solution of Sodium Chloride (NaCl)

	3 Days Preconditioning				18 Days Preconditioning			
	Type I		Type I + FA		Type I		Type I + FA	
	6.64	6.08	6.17	15.17	7.55	6.54	4.84	4.17
	6.75	5.42	5.76	5.21	8.35	6.72	5.99	6.64
	7.15	7.34	5.89	6.58	8.65	7.73	6.71	7.85
	7.28	8.38	6.16	6.73	8.91	8.90	8.19	8.29
	7.56	9.99	11.84	7.69	9.69	9.74	9.60	8.72
Average	7.06	7.05	5.94	6.17	8.64	7.78	6.96	7.59
Average	7.05		6.06		8.21		7.28	

TABLE D.2
Depth of Penetration of 3 Days Preconditioned Plain and Fly Ash Concrete Specimens Subjected to 25% Solution of Magnesium Chloride (MgCl₂)

	3 Days Preconditioning				18 Days Preconditioning			
	Type I		Type I + FA		Type I		Type I + FA	
	2.88	6.16	2.38	3.18	3.30	5.10	3.35	3.31
	3.17	3.38	0.00	3.33	3.56	5.39	3.45	3.75
	3.40	3.38	3.01	3.65	5.13	5.56	3.97	3.76
	4.43	3.51	3.50	3.99	5.29	5.62	4.63	4.16
	4.70	4.65	4.02	4.54	6.85	5.83	4.75	4.53
Average	3.67	3.42	2.17	3.66	4.66	5.52	4.02	3.89
Average	3.55		2.91		5.09		3.95	

TABLE D.3
Depth of Penetration of 3 Days Preconditioned Plain and Fly Ash Concrete Specimens Subjected to 28% Solution of Calcium Chloride (CaCl₂)

	3 Days Preconditioning				18 Days Preconditioning			
	Type I		Type I + FA		Type I		Type I + FA	
	6.30	6.28	4.86	5.43	4.00	3.88	4.17	3.46
	3.92	5.09	2.68	3.38	4.48	5.13	4.63	3.84
	5.01	5.58	4.35	4.31	4.67	5.33	5.39	5.71
	5.84	5.82	4.80	4.72	4.74	5.45	6.30	6.12
	7.29	6.90	5.01	5.74	5.95	5.69	9.98	7.05
Average	4.92	5.50	3.94	4.14	4.63	5.30	5.44	5.22
Average	5.21		4.04		4.97		5.33	

About the Joint Transportation Research Program (JTRP)

On March 11, 1937, the Indiana Legislature passed an act which authorized the Indiana State Highway Commission to cooperate with and assist Purdue University in developing the best methods of improving and maintaining the highways of the state and the respective counties thereof. That collaborative effort was called the Joint Highway Research Project (JHRP). In 1997 the collaborative venture was renamed as the Joint Transportation Research Program (JTRP) to reflect the state and national efforts to integrate the management and operation of various transportation modes.

The first studies of JHRP were concerned with Test Road No. 1—evaluation of the weathering characteristics of stabilized materials. After World War II, the JHRP program grew substantially and was regularly producing technical reports. Over 1,500 technical reports are now available, published as part of the JHRP and subsequently JTRP collaborative venture between Purdue University and what is now the Indiana Department of Transportation.

Free online access to all reports is provided through a unique collaboration between JTRP and Purdue Libraries. These are available at: <http://docs.lib.purdue.edu/jtrp>

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