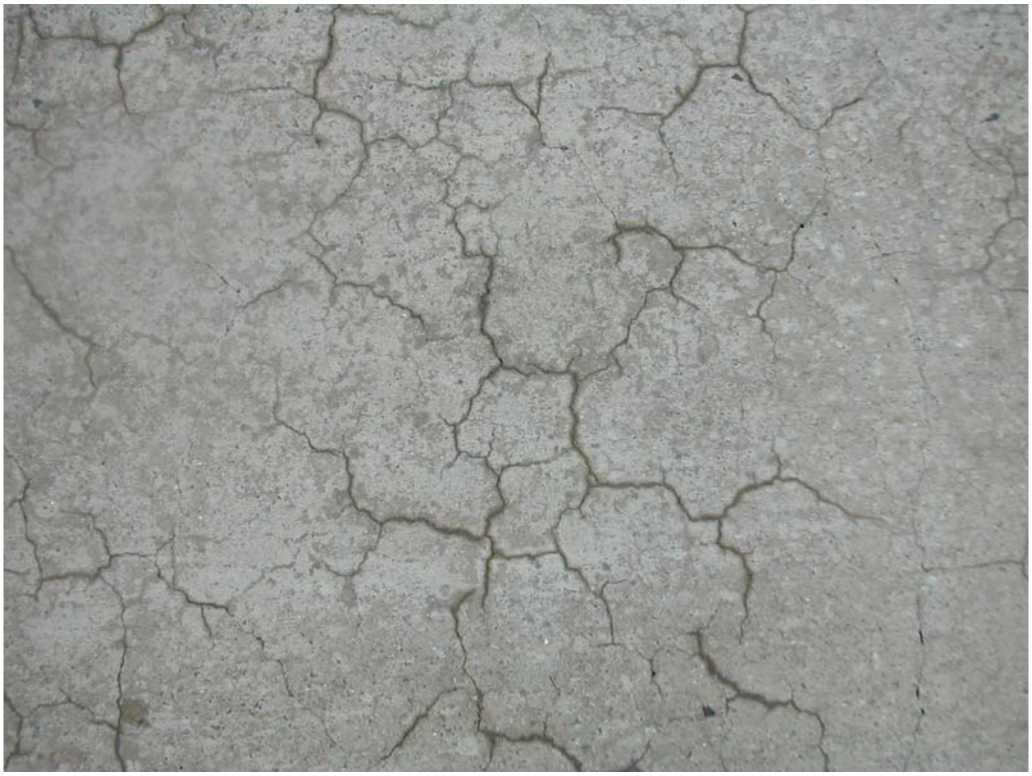
An *IPRF* Research Report
Innovative Pavement Research Foundation
Airport Concrete Pavement Technology Program

Report IPRF-01-G-002-03-9

Potential for Acceleration of ASR in the Presence of Pavement Deicing Chemicals



Programs Management Office
5420 Old Orchard Road
Skokie, IL 60077

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Principal Investigators

Prasada Rao Rangaraju, Ph.D., P.E.
Department of Civil Engineering
Clemson University
Clemson, SC 29634

Jan Olek, Ph.D., P.E.
School of Civil Engineering
Purdue University
West Lafayette, IN 47907

Programs Management Office
5420 Old Orchard Road
Skokie, IL 60077

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EXECUTIVE SUMMARY

Recent observations of premature deterioration of runways, taxiways and other airfield concrete pavements at certain airports in the United States have suggested the possible role of airfield deicing and anti-icing chemicals in causing or accelerating the distress. Based on limited investigation conducted on these affected pavements, alkali-silica reaction (ASR) was suspected to be the principal reason for the observed deterioration. In order to understand the potential influence of these anti-icing and deicing chemicals on triggering ASR in concrete, the IPRF 03-9 research study sponsored by Innovative Pavements Research Foundation (IPRF) was initiated. The principal objective of this study was to determine if selected airfield pavement deicing chemicals such as potassium acetate, sodium acetate, sodium formate and potassium formate have a potential to cause and/or accelerate ASR in concretes containing reactive aggregates.

This research study was comprised of a *preliminary investigation* followed by a *comprehensive testing program*. In the preliminary investigation, a modified ASTM C 1260 test method was developed and evaluated to assess interactions between deicing chemicals and mortar bar test specimens containing reactive and non-reactive aggregates. After establishing the viability of the proposed test method to identify deleterious interactions between deicer solutions and reactive aggregates, a comprehensive, in-depth testing program was conducted. The main part of this testing program involved performing a series of standard and modified ASTM C 1260 (mortar bar) tests and ASTM C 1293 (concrete prism) tests. The test specimens were prepared using different aggregates (both reactive and non-reactive) in combination with low-alkali and high-alkali cements. Once cured, the specimens were exposed to various commercial-grade airfields deicer solutions and to 1N sodium hydroxide solution which was used as a reference solution. Changes in length and dynamic elastic modulus of test specimens were monitored over periods of time and the influence of the exposure condition (type of solution, temperature and length of exposure) on the microstructure and composition of reaction products were also evaluated. In addition, analyses of pore solution were conducted to determine the causes behind the observed deterioration of test specimens. Finally, changes in the pH values of the deicer solutions were also monitored to study their interactions with test specimens.

The results of this study provide strong evidence that both mortar and concrete test specimens with reactive aggregates were attacked by all the deicer solutions studied. However, the magnitudes and rates of expansion depended on specific combination of aggregate mineralogy, cement alkali content and deicer solution type. Mortar bar and concrete prisms with non-reactive aggregates did not exhibit any significant signs of alkali-silica reactivity when exposed to either deicer solutions or to 1N sodium hydroxide solution.

Among the different deicers evaluated, potassium acetate caused the most severe attack in test specimens with reactive aggregates. While other deicers were aggressive, the degree of attack was dependant more on the aggregate mineralogy. With respect to cement alkalinity, when exposed to deicer solutions the test specimens with high-alkali cement showed more rapid rate of deterioration than those with low-alkali cement. However, test specimens with low-alkali cement showed comparable levels of expansion and deterioration at later ages in the tests. The microstructure of test specimens exposed to deicer solution was characterized by extensive cracking in the paste, at paste-aggregate interface and in the aggregate grains. The nature of cracking in test specimens, and the frequency with which reaction products were observed, depended on the specific combination of aggregate and deicer solution. The ASR gel was observed to be present within air-voids in paste and cracks in paste and aggregate. Frequently, ASR gel was found to completely infuse the paste adjacent to a reacted aggregate grain and/or cracks in paste. Also, in test specimens containing highly reactive aggregate (NM rhyolite) and exposed to potassium acetate deicer solution, the paste microstructure was found to be significantly altered in the vicinity of the aggregate grains.

One of the significant findings of this study was the observation of rapid and dramatic increase in the pH values of deicer solutions upon interacting with mortar and concrete test specimens. It was determined (through separate investigation) that these pH changes were affected by the interaction of calcium hydroxide (one of the primary hydration products of portland cement) with the deicer solution. In particular, very high pH levels (~14.00 or higher) were observed in potassium acetate and potassium formate deicer solutions. While, in theory, these high pH levels in deicer solutions can be viewed as perhaps triggering ASR in test specimens containing reactive aggregates, results from analysis of pore solution expressed from concrete exposed to deicer solutions do not support this hypothesis.

The analysis of pore solutions expressed from concretes exposed to deicers for occurrence of various ions (Ca^{+2}, Na^+, K^+, SO_4^{-2}, CH_3COO^-, $HCOO^-$ and OH^-) indicated that the principal cations and anions present were alkali (Na^+, K^+) and acetate (CH_3COO^-) or formate ($HCOO^-$) ions, respectively. Surprisingly, the OH^- ion concentrations in expressed pore solutions of all specimens exposed to deicer solutions were found to be well below what is typically expected to trigger ASR reactions in concrete. In light of these contradicting observations, the authors believe that the ASR reaction mechanisms associated with deicer solutions may be distinctly different from the traditional ASR caused by alkali hydroxides.

While additional investigation is necessary to unravel the underlying mechanisms of the observed distress, some preliminary recommendations based on the modified ASTM C 1260 test method are made to identify aggregates that may potentially react in the presence of the airfields deicer solutions. Findings from this research study suggest that aggregates that exhibit mortar bar expansions over 0.1% at 16 days in the modified ASTM C 1260 test method (i.e. soaked in the deicer solution) should be considered as potentially reactive in the presence of the deicers investigated. It should be noted that the recommendations from this study are based on a few tests with a limited number moderate to highly reactive aggregates, two cements and one representative deicer from each of the main formulations used on airfields. The suggested expansion limits should be reevaluated when results from tests on larger data sets of aggregates and cements become available. Findings from this study also suggest that modified ASTM C 1293 test would be able to identify aggregates that may potentially be reactive in presence of deicer solutions. However, additional research is needed to validate the expansion limits as well as to decipher some secondary interactions between the hydrated compounds and deicer solutions that may be contributing to the observed expansion. In addition, a separate study should be conducted to evaluate if the nature of the hydration products as well as the type and location of distress in the field concrete correlates with the findings obtained form laboratory tests.

1. INTRODUCTION

1.1. PURPOSE

Recent observations of some prematurely distressed airfield concrete pavements by Federal Aviation Administration (FAA) have suggested that the deicing and anti-icing chemicals used for winter time maintenance may have caused the observed distress. Based on the limited visual evidence of the distress and the nature of the materials involved, it was suspected that the distress was related to alkali-silica reaction (ASR) in concrete. In addition, the increased intensity of the distress at locations that received the most frequent applications of the deicing and anti-icing chemicals further reinforced the likelihood of interactions between these chemicals and the concrete. This research study was initiated to investigate the potential of selected airfield pavement deicing and anti-icing chemicals to induce ASR in concrete and to develop an interim test protocol to screen materials that are susceptible to these chemicals.

1.2. BACKGROUND

Chemical deicing and anti-icing agents are routinely used for ice and snow removal operations in many airports across the world. In the past, chemicals such as urea, ethylene glycol (EG), propylene glycol (PG), and blends of PG and urea have been successfully used on airfield pavements as deicing and anti-icing agents. However, environmental concerns arising from high biological oxygen demands of glycols and urea in runoff streams, and concerns with the toxicity of these chemicals to aquatic life have lead to regulations on such uses of glycols and urea [1, 2]. In response to these limitations, a new generation of deicers was developed in the early 1990s, which were based on alkali-acetate and alkali-formate formulations. Since that time deicers and anti-icers such as potassium acetate, sodium acetate, potassium formate and sodium formate have seen enormous growth in their uses as anti-icing and deicing agents on airfield pavements.

Coincidentally, in last 15 years an increasing number of airfield pavements have reported premature deterioration in airfield concrete pavements. Investigations into the deterioration of several commercial concrete airfield pavements indicated Alkali-Silica Reaction (ASR) to be one of the principal reasons for deterioration. The airfields investigated included: Colorado Springs Airport (COS), Denver International Airport (DEN), Salt Lake City International Airport (SLC), Detroit Metropolitan International Airport (DTW), Hartsfield-Jackson Atlanta International Airport (ATL), Greenville-Spartanburg International Airport (GSP), Memphis International Airport (MEM) and others.

In some of these airports, including COS, DEN, SLC and DTW it has been suspected that the exposure of the concrete pavement to the alkali-acetate and alkali-formate deicers may have played a role in either triggering or accelerating ASR distress. Figures 1 and 2 show the typical ASR distress observed in airfield concrete pavements exposed to deicing chemicals.

FIGURE 1. ASR DISTRESS IN CONCRETE PAVEMENT AT DENVER INTERNATIONAL AIRPORT

FIGURE 2. ASR DISTRESS IN CONCRETE PAVEMENT AT COLORADO SPRINGS AIRPORT

ASR is a chemical reaction that occurs when alkali hydroxides present in pore solution of concrete react with certain forms of amorphous or poorly crystalline silica present in aggregates to form an ASR gel. The ASR gel being hygroscopic tends to absorb moisture and expand. When the tensile stresses generated by the expansion of ASR gel exceed tensile strength of concrete, cracking and subsequent deterioration occur in concrete pavements.

The main source of alkalis in concrete is portland cement. However, other sources of alkalis such as mix water, supplementary cementitious materials and deicing salts have known to contribute to the occurrence of ASR in concrete. Although considerable research has been conducted in past on studying the influence of various factors that affect ASR, including some deicing chemicals such as sodium chloride and calcium chloride, no published literature is available on the effects of alkali-acetate and alkali-formate deicers on causing ASR.

Considering that the use of acetate and formate based deicing formulations on airfield pavements is expected to continue, because of their effectiveness and environmentally friendly nature, it is imperative that the effect of these deicers on durability of concrete pavements be established. In particular, the potential of these chemical agents to trigger or accelerate ASR in concrete pavements needs to be ascertained and appropriate ASR mitigation measures be identified to minimize premature deterioration due to deicer-induced distress.

1.3. OBJECTIVES

The principal objectives of this research study are:

1. To determine the potential of alkali-acetate and alkali-formate based deicing and anti-icing agents to cause ASR in airfield pavement concrete containing susceptible aggregate.

2. To develop a test protocol to screen aggregate materials susceptible to deicer-induced ASR, if the deicing/anti-icing chemicals are found to cause ASR distress.

3. To develop recommendations for potential changes to existing specifications for evaluating aggregate materials for use in construction of rigid airfield pavements.

1.4. SCOPE OF THE RESEARCH

The scope of this study was limited to evaluating four common airfield pavement anti-icers and deicers that are formulated with the following active ingredients:

1. Potassium Acetate
2. Sodium Acetate
3. Sodium Formate
4. Potassium Formate

In this study, mortar and concrete test specimens were prepared with aggregates that had an established history of alkali-silica reactivity. For this purpose, four sources of reactive aggregates and two sources of non-reactive aggregates were selected. The aggregates included the following:

Reactive Aggregates:

1. Rhyolite from New Mexico (Las Placitas Gravel Pit, NM; Lafarge Aggregates)
2. Siliceous Limestone from Ontario, Canada (Spratt Quarry, Ontario, Canada)
3. Argillite from North Carolina (Gold Hill Quarry, NC; Vulcan Materials)
4. Quartzite from South Dakota (Sioux Falls Quarry, SD; L.G. Everist, Inc.)

Non-Reactive Aggregates:

1. Ottawa Sand from Illinois (ASTM C 778 Standard Sand; U.S. Silica Company)
2. Dolomite from Illinois (Thornton Quarry, IL; Material Service Corporation, Inc.)

In order to assess the influence of cement alkali content on any observed distress in these studies, a high-alkali cement (0.82% Na2Oeq.) and a low-alkali cement (0.31% Na2Oeq.) were used with each combination of aggregate and deicer.

In the absence of any established test methods to assess the influence of deicing chemicals on the ASR potential of aggregates, modified versions of standard ASTM test procedures (ASTM C 1260 and ASTM C 1293) were developed and adopted in this study. The details of these modified test methods are described in the Experimental Test Methods section (Section 3.2). Based on the findings from this research study, recommendations on potential changes to specifications and guidelines for evaluation of deicing chemicals for their potential to cause ASR in concrete have been developed.

2. LITERATURE REVIEW

2.1. DEICING AND ANTI-ICING CHEMICALS

Deicing chemicals were first used in the 1930s for snow and ice removal, but it was not until the 1960s that their use became widespread after winter maintenance personnel learned about its effectiveness [3]. Today, deicers are a necessary and accepted part of winter maintenance programs on both highways and airfield pavements to facilitate safe movement of traffic. Deicing chemicals are also widely used on aircraft to prevent snow and ice from adhering to the aircraft body so as to ensure safe operational control of the aircrafts.

Pavement deicing chemicals or “deicers” are chemicals that are sprayed or applied on pavements to melt ice or snow accumulated on the pavement surface. Anti-icing chemicals or “anti-icers” are chemicals that are applied on pavement surfaces or on aircraft bodies before a precipitation event to prevent ice or snow from adhering to their surfaces.

When chemicals are used as anti-icers, they are sprayed on bare pavement surface before a precipitation event, such that these chemicals melt snow and ice immediately upon precipitation to form brine. The resulting brine has a lower freezing temperature than pure water; this prevents ice or snow from adhering to the pavement surface. Similarly, when chemicals are used as deicers they are sprayed on the accumulated ice or snow on the pavement. The deicers melt the ice to form brine. The resulting brine penetrates through the remaining ice to reach the pavement surface, where it works to undercut and debond the ice from the pavement surface. This process aids in easy removal of the accumulated ice and snow by subsequent mechanical brushes.

Typically, the deicers used on highway pavements and bridges have included chemicals such as sodium chloride, calcium chloride, magnesium chloride, calcium magnesium acetate, and others. In airfield applications the use of chloride based deicers is discouraged, due to the corrosive effects of these chemicals on the metal components of the aircraft.

In the past, typical deicing and anti-icing chemicals used on airfield pavements included non-chloride based chemicals such as urea, ethylene glycol (EG), propylene glycol (PG), and blends of PG and urea. However, due to environmental concerns associated with increased biochemical oxygen demand on the receiving waters and the toxicity effects of these deicing chemicals on aquatic fauna and flora, their use as pavement deicers in airfields has been strongly discouraged [4]. In response to the increasing need for environmentally benign deicers a new generation of deicers emerged in the early 1990s, which were based on alkali-acetate and alkali-formate formulations. Since that time deicers and anti-icers such as potassium acetate, sodium acetate, potassium formate and sodium formate have seen an enormous growth in their use on airfield pavements.

Depending on the specific function for which a given chemical formulation is used, certain chemicals such as potassium acetate are used both as deicing as well as anti-icing agents. In this report both deicing and anti-icing chemicals will be referred to as “deicing chemicals” or simply as “deicers”, as their effects on durability of concrete are considered to be similar regardless of the specific mode of application in field conditions.

2.2. CHEMICAL ATTACK OF DEICERS ON CONCRETE

Chloride-based deicers such as sodium chloride and calcium chloride are widely known to cause and accelerate corrosion of reinforcement in concrete. In addition, these deicers have also been found to exacerbate other distress mechanisms in concrete such as conventional ASR, chemical attack, and scaling. In particular, concrete containing supplementary cementing materials such as fly ash and slag are found to be vulnerable to excessive scaling in presence of deicing chemicals such as sodium chloride and calcium chloride, under certain conditions [5]. Research has also shown that deicing chemicals such as calcium chloride can result in formation of complex calcium-oxychloride phases [6]. The formation of similar disruptive oxychloride phases has been observed in mortars exposed to magnesium chloride deicer solutions [7]. Studies have shown that chloride based deicing chemicals were found to promote decalcification of cement paste and alteration of other hydration products such as ettringite into chloroaluminates [8, 9].

Calcium magnesium acetate (CMA), has recently gained attention as a non-chloride based deicer for use on bridge decks and other reinforced structures to alleviate problems associated with corrosion of reinforcement. Studies on the effects of CMA on durability of concrete have shown that CMA deicer solutions result in significant degradation of the cement paste matrix, resulting in loss in mass and strength of the concrete [10, 11]. In their studies, Lee et al. and Wang et al. found magnesium-bearing deicers such as CMA and magnesium chloride to cause severe deterioration in cement paste specimens through formation of brucite (magnesium hydroxide) and non-cementitious magnesium silicate hydrate [8, 9].

Published literature on the effects of alkali-acetate and alkali-formate deicers on durability of concrete is limited. In their studies on effects of deicers on concrete, Wang et al. found that potassium acetate deicer did not cause any scaling of concrete, and was benign compared to other chloride-based deicers evaluated [9].

2.3. INFLUENCE OF CHLORIDE-BEARING DEICERS ON ASR IN CONCRETE

ASR is one of the common durability problems in concrete. ASR is a chemical reaction in concrete that occurs between certain reactive siliceous components in aggregates and the highly alkaline concrete pore solution. This reaction produces a hygroscopic reaction product, often referred to as ASR gel. The mechanism that leads to cracking and deterioration of concrete is typically not the production of the ASR gel itself, but its expansion in the presence of moisture, particularly in restricted spaces such as cracks in aggregates. The high pH environment required for the siliceous aggregates to react is typically generated from the dissolution of alkali sulfates and other alkali-bearing phases in cement. In some cases the alkalis may be supplied from other components of concrete such as supplementary cementing materials (SCMs) [12], admixtures, or in some instances from within the aggregate itself [13-16]. External sources of alkalis such as from marine exposure and from application of deicing salts such as sodium chloride have also been found to trigger ASR [17-23].

Extensive research has been carried out by Chatterji et al. and others concerning the influence of the most common deicer – sodium chloride (NaCl) – in initiating or aggravating ASR in concrete [17]. In these studies, it has been shown that the degree of deterioration depends on such factors as the alkali and C_3A contents of the cement, the concentration of the NaCl solution, and the temperature at which testing is conducted. Interestingly, Chatterji et al. have noticed in their studies that solutions of alkali-salts produced greater expansions due to ASR in test specimens than solutions of alkali-hydroxides of the same concentrations [17]. The findings from Chatterji et al. were confirmed in work conducted by Kawamura and Ichise [20]. It is believed that the excessive expansions generated in mortars containing reactive aggregate and exposed to chloride-bearing solutions were due to combination of chloroaluminate formation along with acceleration of ASR. In contrast, Berube et al. concluded that the occurrence of chloroaluminates is primarily responsible for increased expansions observed in presence of sodium chloride solutions [23].

2.4. INFLUENCE OF ALKALI-ACETATE AND ALKALI-FORMATE DEICERS ON ASR IN CONCRETE

After nearly 65 years of research on ASR since its discovery in 1940 by Stanton [24], and after 12 International Conferences on the subject, and despite several thousand published papers and reports, concern with the possible influence of other kinds of deicers, such as alkali-acetate and alkali-formate deicers, on ASR is virtually non-existent in published literature.

It is estimated that more than 10 million gallons of the potassium acetate liquid deicer and over 14,000 metric tons of solid deicers (sodium acetate and sodium formate) are applied annually on airfield pavements and non-commercial applications in the United States alone [Susan Royer Baum, Personal Communication, July 8, 2005]. The influence of these chemicals on concrete pavements, in particular their effect on inducing ASR in those pavements has not been previously established. This lack of information is partly due to the relatively short history of the use of these deicers. Potassium acetate, the most widely used deicing chemical on airfield pavements across the world, was introduced into the European market only in 1988 and into the United States only in the early 1990s [25]. Of additional concern is that the use of potassium acetate is rapidly spreading to structures other than airfield pavements, including bridge decks and parking garages. Several state agencies and some owners of parking garages across the country are embracing automated deicing systems, in which sensors embedded in pavements monitor the pavement surface conditions, and automatically trigger the dispensing of the liquid deicers [26-30]. The possible influence of these automated deicing systems and of the deicers used in these systems on the durability of the concrete structures remains to be seen.

It is well known that typical ASR distress takes a number of years to manifest in field conditions, depending on the reactivity of the aggregate and on exposure conditions. Concrete airfield pavements being the first concrete structures exposed to the new-generation deicers are beginning to show the distress after prolonged exposure.

In light of the growing concerns associated with deteriorating concrete pavements in airfields, in May 2004 FAA through Innovative Pavement Research Foundation (IPRF) initiated a research study to investigate the problem. The intent of this investigation was to determine if alkali-acetate and alkali-formate deicers have a potential to initiate and/or accelerate ASR in concrete, and determine the effectiveness of typical ASR mitigation measures against the effect of these deicers.

3. EXPERIMENTAL PROGRAM

3.1. RESEARCH APPROACH

The research approach adopted in this study can be summarized in the following steps:

1. Select representative deicers which are widely used by airports across the United States.

2. Select representative aggregates that have an established history of being either reactive or non-reactive in nature.

3. Develop preliminary proposed test methods and conduct investigations to validate these proposed test methods of evaluating the ASR potential of the aggregates in presence of deicing chemicals.

4. Evaluate the reactivity of aggregates in presence of deicing chemicals using the proposed test methods.

5. Determine the extent of physical deterioration in the mortar and concrete test specimens exposed to deicing solutions by measuring the loss in dynamic elastic modulus of the specimens during the course of testing.

6. Study the microstructure and composition of the reaction products in mortar and concrete test specimens using scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX), and analyze the composition of the pore solution expressed from test specimens.

7. Study the changes in the composition of the soak solution employed in the test methods by monitoring its pH before and after storing the test specimens in the solution.

8. Develop an understanding of the mechanism of distress.

9. Develop recommendations on evaluating aggregates in presence of deicers, based on the findings from the research study.

Traditionally, standard test methods such as those described in ASTM C 1260 and ASTM C 1293 are used to assess the potential reactivity of an aggregate source. However, in this research study the factor being investigated was potential of an external environment (i.e. the presence of deicing chemical solutions) to trigger deleterious ASR in concrete. In order to accomplish this objective, the standard test procedures were modified.

The principal modification to the test methods involved soaking the test specimens in a deicer solution of a defined concentration, instead of the storage conditions described in the standard test procedures. The experimental approach involved subjecting the test specimens to deicer solutions, and monitoring the length-change behavior of the test specimens. The results from the modified test methods would then be compared to the results from the standard test methods to evaluate the influence of the deicer solutions in triggering ASR. At the end of the test the microstructure and composition of the reaction products would be studied using SEM and EDX.

3.2. TEST METHODS

3.2.1. Standard ASTM C 1260 Test

In this test method, mortar bars (25 mm x 25 mm x 285 mm) with embedded gage studs are cast, and cured for 24 hours in a moist curing room. After demolding, the bars are cured for an additional 24 hours in an 80ºC water-bath. At the end of water-bath curing, the bars are transferred to an 80ºC bath of 1N sodium hydroxide solution. Periodic length-change measurements are taken over the course of subsequent 14 days and percent expansions are calculated.

Based on the guidance provided in ASTM C 33, mortar bar expansions less than 0.1% at 16 days after casting are typically considered to represent results with non-reactive aggregates in the standard ASTM C 1260 test. Expansions greater than 0.2% at 16 days are considered to represent results with potentially reactive aggregates. Expansions between 0.1% and 0.2% require additional confirmation by concrete prism test (ASTM C 1293 test) or from past field performance. In the present study, the length-change measurements were taken beyond the standard 16 days, to 30 days so as to verify the performance of different aggregates at later ages.

FAA Advisory Circular 150/5370-10B – Standard for Specifying Construction of Airports – considers aggregate to be reactive if expansions in mortar bars subjected to standard ASTM C 1260 test exceeds 0.1% at 16 days [31]. This limit is modified on a regional basis.

For instance, the revised AC 150/5370-10B specification employed by the Northwest Mountain Region Airports Division considers aggregate to be reactive if the expansion of mortar bars in the standard ASTM C 1260 test exceeds 0.1% at 30 days after casting. When the use of pavement deicing chemicals such as potassium acetate solutions is anticipated, a modified ASTM C 1260 test is employed to assess the reactivity of the aggregate [32]. In the modified ASTM C 1260 test, the mortar bars are soaked in a deicer solution after the initial curing regimen, instead of 1N sodium hydroxide solution. When deicer usage is anticipated, the aggregate is considered reactive if expansion of mortar bars in the modified ASTM C 1260 test exceeds 0.08% at 30 days after casting. The tighter specifications may be justified on airfield pavements, where concerns and consequences arising from Foreign Object Debris (FOD) are serious.

In the present investigation, an aggregate is considered reactive if the expansions of mortar bars exceed 0.1% at 16 days after casting, in the standard or modified ASTM C 1260 test methods. However, the expansion results will also be evaluated against the more stringent expansion limits imposed by the revised AC 150/5370-10B standards specified by the Northwest Mountain Regions Airport Division, where applicable.

3.2.2. Modified ASTM C 1260 Test

In the modified ASTM C 1260 test proposed for this research, the mortar bars are soaked in a deicer solution of a defined concentration, instead of the standard 1N sodium hydroxide solution. The intent of this test as applied in this study is to evaluate the potential of the deicer soak solutions to cause ASR in mortar bar test specimens containing reactive aggregates. The specific concentrations of the deicer soak solutions employed in this test were:

- 50% wt. solution of potassium acetate (6.4 molar concentration)
- 50% wt. solution of potassium formate (7.84 molar concentration)
- Saturated solution of sodium acetate at room temperature (4.66 molar concentration)
- Saturated solution of sodium formate at room temperature (5.92 molar concentration)

The choice of using 50% wt. solutions of anti-icers and saturated solutions of deicers as soak solutions in the modified ASTM C 1260 and ASTM C 1293 tests was based on practical and realistic considerations. In routine anti-icing operations, 50% wt. solutions of potassium acetate and potassium formate are used over the concrete pavement surface; whereas in deicing operations solid deicers such as sodium acetate are applied on snow or ice to melt it. Though the melting action of snow and ice will dilute the concentration of the deicers, it is very likely that with repeated applications of the deicers and through repeated cycles of freezing and thawing and wetting and drying, the pore solution of concrete in the near-surface zone would go through periodic cycles of dilution and concentration. Similarly, with deicers such as sodium acetate and sodium formate, the worst possible exposure condition to which a concrete pavement would be exposed is a saturated solution of the deicer. Therefore, the use of 50% wt. solution of anti-icers and room-temperature saturated solutions of the deicers was considered to represent realistic, yet severe exposure conditions for investigating the influence of deicers.

Other than modifications to the soak solution composition, the casting and the subsequent storage regime applied to the test specimens is identical to the procedure described in the standard ASTM C 1260 test method. Expansion of mortar bars exceeding 0.1% at 16 days after casting was considered to represent aggregates of unacceptable reactivity.

3.2.3. Standard ASTM C 1293 Test

The standard ASTM C 1293 test procedure calls for preparation of concrete prisms with the aggregate in question (either coarse or fine aggregate) along with a non-reactive supplementary aggregate (fine or coarse aggregate). The cement to be used in this test is required to have a minimum alkali content of 0.9% ± 0.1% $Na_2O_{eq.}$ Sodium hydroxide is added to the mix water, if needed so as to raise the alkali content of the concrete mix to 1.25% $Na_2O_{eq.}$ by mass of cement. After initial curing, the concrete prisms are stored in sealed containers that maintain a high degree of relative humidity. The sealed containers are then placed in a 38°C environment. Periodic length-change measurements are taken up to one year. A level of expansion greater than 0.04% at one year is indicative of the reactive nature of the aggregate.

The ASTM C 1293 recommends storing the concrete prisms in 5-gallon pail buckets in a vertical orientation during the course of the test. This methodology typically allows for storage of 3 concrete prisms in each bucket. However, in the present study four concrete prisms were to be tested for each standard (and modified) ASTM C 1293 test. One of the four prisms was to be used as a sacrificial prism to assess changes in the microstructure of concrete and for expression of pore solution at periodic intervals. In this regard, the traditional 5-gallon pail was considered to be not suitable for the modified ASTM C 1293 test due to excessive weight of bucket resulting four prisms and soak solution. Therefore, to circumvent this issue a shoe-box type container of the type that is typically used in ASTM C 1260 tests was selected. In order to determine if the sample orientation would cause any significant impact on the observed expansions in the concrete prisms, a parallel set of standard ASTM C 1293 tests were conducted on each aggregate in both types of storage containers. The tests conducted in 5-gallon pails are referred to as "control-vertical" and the tests conducted in the shoe-box type container are referred to as "control-horizontal" in the graphs shown in the Results section of this report (Section 6.1).

3.2.4. Modified ASTM C 1293 Test

In this modified test method, the standard ASTM C 1293 test procedure was modified by soaking the concrete prisms in deicer solutions, instead of exposing them to a 100% relative humidity environment. For liquid runway deicers, the soak-solution used was representative of the concentration actually used in field applications. For instance, in case of potassium acetate based deicer a 50% wt. solution (6.4 M) was used as a soak solution. For solid runway deicers, saturated solutions of solid chemicals, i.e. 4.66 molar solution for sodium acetate and 5.92 molar solution for sodium formate, both representing saturation at room temperature, were employed as the soaking medium. For the reference test specimens in the modified ASTM C 1293 procedure, 1N sodium hydroxide solution was used as the soak-solution.

In this study, two series of samples were prepared that are referred to as the high-alkali (HA) series and the low-alkali (LA) series. In the HA series, the concrete prisms were prepared as per the standard procedure by boosting the alkali-content of the mix in the concrete up to 1.25% Na_2O. In the LA series, a parallel set of samples were prepared without addition of any external alkali to the mix; the cement used in this series being a low-alkali cement. In this test method, it was assumed that expansions in deicer exposed-concrete prisms exceeding 0.04% strongly suggested significant negative interactions between concrete and deicer solution.

3.2.5. Dynamic Modulus of Elasticity

The physical distress in mortar bars and concrete prisms was quantified by measuring the dynamic modulus of elasticity (DME). The DME values were determined using the resonant frequency method based on impulse excitation technique as per ASTM E 1876-01. A GrindoSonic™ instrument was used in determining the resonant frequencies of mortar bars and concrete prisms.

3.2.6. pH of Soak Solution

It is recognized that for ASR to occur in concrete a high pH environment (high concentration of hydroxyl ions) is essential. In standard ASTM C 1260 tests, the presence of a 1N sodium hydroxide soak solution provides a high pH environment. However, in case of the modified

ASTM C tests (with deicer soak solutions), the pH of typical deicer solutions by themselves are well below that of 1N sodium hydroxide solution.

In order to determine if any changes in pH occur due to potential interaction between deicer soak solutions and hydration products of cement, the pH of soak solution exposed to specimens in modified ASTM C 1260 and ASTM C 1293 tests was periodically monitored. The pH of the soak solution was determined using an Oakton pH 110 meter with a low-sodium error and a high salt electrode, calibrated to buffer solutions with pH 4, 7, 10, and 12.45.

3.2.7. SEM and EDX Investigation

Scanning Electron Microscopy (SEM) in back-scattered mode and Energy Dispersive X-ray analysis (EDX) were conducted on polished sections of mortar bars and concrete prisms recovered from the standard and modified ASTM C 1260 and ASTM C 1293 tests. The SEM-EDX investigation as part of this research study was conducted at Purdue University using an ASPEX SEM Instrument.

The samples for the SEM-EDX at Purdue were retrieved from the mortar bars or concrete prisms by slicing the test specimens using a slow-speed diamond saw (or by taking chunks of very weak specimens). These samples were dried at 50° C and then embedded using Spurr ultra low-viscosity resin. The impregnated small samples were then lapped on a series of diamond embedded discs of progressively decreasing diamond sizes to 1200 grit (mean particle size of 5 microns). The specimens were then polished using diamond paste spread on polishing cloths. The diamond sizes in the pastes used were progressively finer, with the final polish being accomplished using 0.25 micron diamond paste. The polished samples were then coated with a layer of palladium to avoid charging effects.

3.2.8. Pore Solution Expression and Analysis

3.2.8.1. Pore Solution Expression

3-month and 6-months old concrete specimens previously tested for expansion using the modified ASTM C 1293 method were used for expression of pore solution. After slicing sections of concrete prisms from standard and modified ASTM C 1293 tests, the specimens for pore solution expression were tightly sealed with plastic foil after wrapping with wet towels (soaked in deicer solution and then wrung out) to prevent pore solution loss during shipment. Just before the start of the squeezing process the samples were crushed in laboratory crusher. After crushing, some of the loose coarse aggregate grains were removed from the specimens to increase the paste content in the sample. The pore fluid expression device designed by Barneyback and Diamond was used for pore solution expression [33]. The apparatus (shown in Figure 3) has an inner specimen chamber with a diameter of 2 inches.

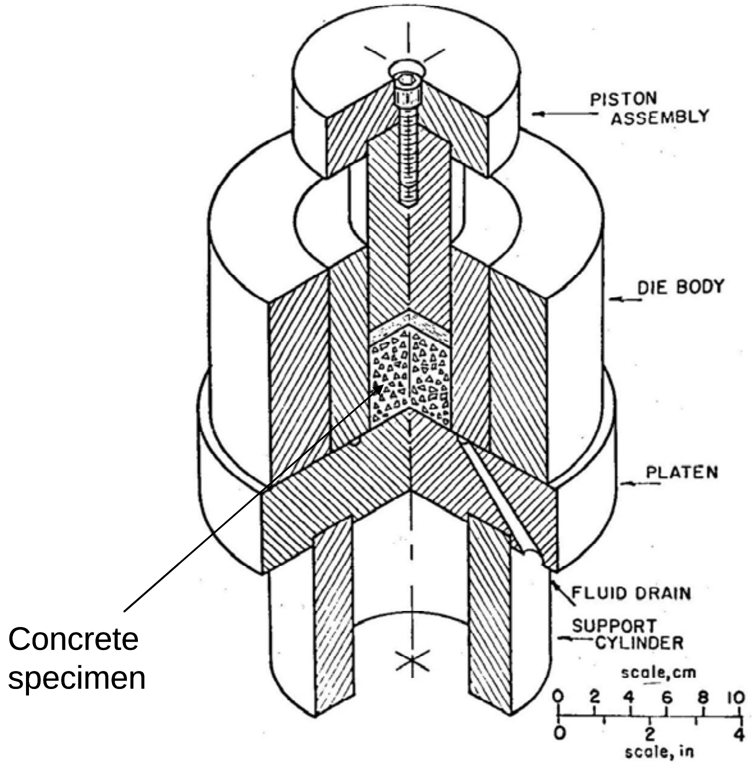


FIGURE 3. ISOMETRIC HALF-SECTION OF PORE FLUID EXPRESSION DEVICE [33]

The crushed sample was placed in the die chamber and the Teflon sealing pad was placed between the top of the sample and the piston to provide an even loading surface and to prevent small particles form getting between the wall of the die and the piston. Such particles, if present, will result in damage to both the piston and the wall of the die. The entire assembly (die with the specimen, piston, and a spacer) was then placed in the compression testing machine. A compressive load of 250,000 lbs (resulting in a stress of 80,000 psi) was applied to the piston at the rate of about 20,000 lbs per minute. Immediately before the start of the pore solution expression the surfaces of the die, the piston and the platen were sprayed with film of fluorocarbon lubricant to decrease the frictional effects. After the initial load application, several additional cycles of load were applied; these involved decreasing the load to 175,000 - 220,000 lbs and then increasing it back to 250,000 lbs to increase the yield of the pore fluid. The pore fluid expressed from the concrete was collected using two plastic syringes attached to a drain at the bottom of the die (see Figure 4).

After completion of the pore solution expression, the syringes were removed form the die and the fluid was immediately transferred to polyethylene bottles which were then tightly sealed. Before, after, and between each squeezing the equipment was cleaned with de-ionized water and paper towels, then dried with acetone to remove any water present within the die.

FIGURE 4. DIE ASSEMBLY WITH ATTACHED POLE FLUID COLLECTION SYRINGES.

3.2.8.2. Pore Solution Analysis

Expressed pore solutions were analyzed for their Na^+, K^+, Ca^{2+}, OH^-, SO_4^{-2}, CH_3COO^- contents. Na^+, K^+ and Ca^{2+} ion concentrations were determined using the Atomic Absorption/Emission Spectrophotometer (Varian® SpectrAA – 20) operated in the emission mode using an air–acetylene flame. The wavelengths used were: 422.7 nm for Ca^{2+}; 766.5 nm for K^+; and 589.0 nm for Na^+. The collected pore solutions were diluted with de-ionized water to obtain concentrations in the proper operating range for each of the analyses. For determination of Ca^{2+} concentration, a 10,000 ppm solution containing La^{3+} ions was introduced to both the standard and the pore solution samples so as to eliminate the influence of acetylene – air flame on calcium absorbance depletion.

The OH^- ions concentration was determined by titrating the solution with a 0.0954N HCl using phenolphthalein as an indicator. The reason for using phenolphthalein indicator was that upon addition of H^+ ions the acetates form acetic acid – acetate salt buffer; accordingly, an indicator that changes color above the pH of the buffer is needed. The phenolphthalein indicator changes color in the pH range of 10.0 – 8.2. Methyl red, commonly used for OH^- ions titrations, undergoes a color change in the pH range of 6.2 – 4.4, below the pH level at which acetate buffer is established. Accordingly, an accurate end point is not possible with the Methyl red indicator.

To perform the titration, a small amount (between 0.1 to 1.0 ml) of the pore solutions was removed from the storage bottle using a high-accuracy 100 micro-liter syringe and was diluted to about 50 cc. Three drops of phenolphthalein indicator solution were then added. The titration process, involving stepwise addition of standardized acid solution, was continued until the solution became colorless.

The SO_4^{2-} and CH_3COO^- ion concentrations of the expressed solution were determined with ion chromatography.

3.3. TEST MATERIALS

3.3.1. Anti-icers, Deicers and Reagents

The specific anti-icers investigated in this study were solutions of either potassium acetate or potassium formate. The deicers investigated were solid pellets composed of sodium acetate or sodium formate. Commercial anti-icing and deicing chemicals were used in the modified ASTM C 1260 and ASTM C 1293 tests. However, in some of the tests in the preliminary investigations, reagent grade potassium acetate, sodium acetate and sodium formate were used in preparing the soak solutions for mortar bars. Results from the modified ASTM C 1260 tests using reagent grade chemicals were compared to the results from the tests with commercial grade deicing chemicals to assess any effects of other additives such as corrosion-inhibiting agents, dyeing agents, etc. that are typically added to commercial deicing and anti-icing agents.

The soak solutions employed in the modified ASTM C 1260 and ASTM C 1293 tests were either the liquid anti-icers solutions as employed in field conditions, or for the solid deicers, saturated solutions of solid deicers prepared at room temperature. The concentrations of these soak solutions used in this study were as follows:

- 50% wt. solution of potassium acetate (6.4 molar concentration)
- 50% wt. solution of potassium formate (7.84 molar concentration)
- Saturated solution of sodium acetate at room temperature (4.66 molar concentration)
- Saturated solution of sodium formate at room temperature (5.92 molar concentration)

The reasoning behind the use of these anti-icers and deicers at the selected concentrations was previously discussed in the Section 3.2.2.

Reagent grade sodium hydroxide (NaOH) pellets were used in this study to prepare the 1N sodium hydroxide soak solution used for conducting the standard ASTM C 1260 tests.

3.3.2. Cement

In this study a high-alkali Type 1 cement (Na_2O_{eq} = 0.82%.) and a low-alkali Type 1 cement (Na_2O_{eq} = 0.31%.) were used. The chemical composition of the cements and their autoclave expansions are provided in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF CEMENTS USED IN THE STANDARD AND MODIFIED ASTM C 1260 AND ASTM C 1293 TESTS

Oxide	**High-Alkali Cement (%) (HA)**	**Low-Alkali Cement (%) (LA)**
SiO_2	19.74	20.3
Al_2O_3	4.98	5.0
Fe_2O_3	3.13	3.4
CaO	61.84	64.45
MgO	2.54	1.2
SO_3	4.15	2.8
LOI	1.90	1.85
$Na_2O_{equivalent}$	0.82	0.31
K_2O	0.84	0.36
Na_2O	0.27	.07
Insoluble Residue	0.25	0.17
C_3A	8.97	7.20
C_3S	46.6	63.76
Autoclave Expansion (%)	0.12	0.08

3.3.3. Aggregates

In this study, reactive coarse aggregates from four sources representing various mineralogies and levels of reactivity were selected. In addition, one non-reactive coarse aggregate was used for reference. The four reactive aggregates used were:

- **Spratt Limestone –** This aggregate was obtained from Spratt quarry in Ontario Province of Canada. It consists primarily of calcite with minor amounts of dolomite, which are not alkali-reactive, plus about 10% acid- insoluble residue. The latter contains reactive component, which is reported to consist of 3% to 4% of microscopic chalcedony and black chert, which is finely dispersed in the matrix [34]. This aggregate has an established history of being alkali-silica reactive in field structures and has been used as a reference aggregate in many ASR studies.
- **NM Rhyolite –** This reactive gravel was obtained from the Las Placitas Gravel Pit from the Bernalillo County in New Mexico. This aggregate primarily consists of rhyolite and has shown very high levels of reactivity [35].
- **NC Argillite –** This aggregate is a quarried material from the slate belt of North Carolina from the Gold Hill Quarry in North Carolina. This aggregate primarily consists of reactive metatuff/argillite. This aggregate has an established history of poor field performance in several bridge structures in North Carolina [36].
- **SD Quartzite –** This aggregate is obtained from crushing quarried rock from Sioux Falls quarry, located in the southeastern South Dakota. This aggregate consists of strained

quartz grains that are cemented with interstitial secondary quartz cement. The interstitial matrix also contains microcrystalline quartz, hematite and kaolinite. This aggregate has an established history of being reactive in concrete pavements in Minnesota and South Dakota [37].

The non-reactive coarse aggregate is a quarried dolomite from Thornton, Illinois, that has an established history of good field performance and has been used a reference non-reactive aggregate in laboratory studies [38]. The non-reactive fine aggregate used in this study was the standard Ottawa sand from Illinois, U.S.A. Table 2 shows the basic physical properties of all the aggregates used in this study.

TABLE 2. PROPERTIES OF AGGREGATES

Aggregate Property	**Spratt, Limestone**	**SD, Quartzite**	**NC, Argillite**	**NM, Rhyolite**	**IL, Dolomite**	**IL, Ottawa Sand**
Water absorption,%	0.456	0.42	0.344	1.087	2.12	0.0
Bulk specific gravity (OD)	2.69	2.51	2.75	2.60	2.66	2.65
Bulk specific gravity (SSD)	2.706	2.52	2.76	2.63	2.71	2.65
Dry Rodded Unit weight, kg/m^3	1568.3	1557.62	1566	1585.25	1563.7	---

3.4. SAMPLE NOTATION

In this study, the low-alkali and high-alkali cements are identified as LA and HA, respectively. Potassium acetate, sodium acetate, sodium formate, and potassium formate deicer solutions are identified as KAc, NaAc, NaFr and KFr respectively. 1N sodium hydroxide solution is identified as 1N NaOH. The aggregate sources are identified as NM - Rhyolite from New Mexico; Spratt - Spratt Limestone; NC – North Carolina argillite; SD - Quartzite from South Dakota.

3.5. TEST MATRIX

Tables 3 and 4 show the test matrix for standard and modified ASTM C 1260 and ASTM C 1293 tests. In this study a total of 74 mortar bars (standard and modified ASTM C 1260) tests and 50 concrete prism (standard and modified ASTM C 1293) tests were conducted.

TABLE 3. EXPERIMENTAL PROGRAM TO EVALUATE DEICING CHEMICALS USING MODIFIED AND STANDARD ASTM C 1260 TEST PROCEDURE WITH HIGH-ALKALI AND LOW-ALKALI CEMENTS

Test	**Soak Solution**	**Non-Reactive Aggregate**	**Reactive Aggregate**			
		Standard Ottawa Sand	Spratt Lime-stone	NC Argillite	NM Rhyolite/ Andesite	SD Sioux Quartzite
Standard ASTM C 1260 Test	Sodium Hydroxide	X	X	X	X	X
Modified ASTM C 1260 Test (using HA Cement)	Potassium Acetate	X	X	X	X	X
	Sodium Acetate	X	X	X	X	X
	Sodium Formate	X	X	X	X	X
	Potassium Formate	X	X	X	X	X
Modified ASTM C 1260 Test (using LA Cement)	Potassium Acetate	X	X	X	X	X
	Sodium Acetate	X	X	X	X	X
	Sodium Formate	X	X	X	X	X
	Potassium Formate	X	X	X	X	X

Of the 74 mortar bar tests, 24 tests were conducted as part of a preliminary investigation to study the potential of alkali-hydroxide leaching from mortar bars into soak solution, and to establish the validity of the proposed modified ASTM C 1260 test method. In addition, the influences of temperature of testing and concentration of soak solutions on the expansion of mortar bars were investigated. The results from the preliminary testing are presented in Section 4. The remainder of the standard and modified ASTM C 1260 tests, i.e. 50 tests, were conducted to investigate the potential of the four deicing chemicals and 1N NaOH solution to cause ASR in mortar bar test specimens prepared with each of the five aggregates. In these tests, the influence of alkali content of the cement was investigated by testing mortar bars prepared with both high-alkali cement and low-alkali cement.

A total of 50 concrete prism tests (standard and modified ASTM C 1293 tests) were conducted. Of these tests, 5 concrete prism tests were conducted as per the standard ASTM C 1293 procedure to establish the aggregate reactivity. The remainder of the 45 concrete prism tests was based on modified ASTM C 1293 procedure, described previously.

All of the modified ASTM C 1293 tests were conducted with concrete prisms stored in horizontal orientation in shoe-box type containers that were tightly sealed. In these tests the effects of 1N NaOH solution and three deicer soak solutions (potassium acetate, sodium acetate, and sodium formate) on expansion of concrete prisms were investigated. Potassium formate was not considered in this study due to the relative unavailability of this anti-icer in the United States. In these tests, the influence of both high-alkali and low-alkali cements on the expansions of concrete prisms were studied. It should be noted that the standard ASTM C 1293 tests were conducted only on concrete prisms prepared with high-alkali cement as required by the standard test procedure.

TABLE 4. EXPERIMENTAL PROGRAM TO EVALUATE DEICING CHEMICALS USING STANDARD AND MODIFIED ASTM C 1293 TEST PROCEDURE WITH HIGH-ALKALI AND LOW-ALKALI CEMENTS

Specimen Type	**Soak Solution**	**Non-Reactive Aggregate**	**Reactive Aggregate**			
		IL Dolomite	Spratt Lime-stone	NC Argillite	NM Rhyolite/ Andesite	SD Sioux Quartzite
Standard ASTM C 1293 Test Program						
Reference	None(Horizontal*)	X	X	X	X	X
	None (Vertical*)	X	X	X	X	X
Modified ASTM C 1293 Test Program on Concrete Prisms Using High-Alkali Cement (with alkali content of mix boosted to 1.25% Na_2O)						
Reference	Sodium Hydroxide	X	X	X	X	X
Test	Potassium Acetate	X	X	X	X	X
	Sodium Acetate	X	X	X	X	X
	Sodium Formate	X	X	X	X	X
Modified ASTM C 1293 Test Program on Concrete Prisms Using Low-Alkali Cement (without any boost to alkali content of the mix)						
Reference	Sodium Hydroxide	X	X	X	X	X
Test	Potassium Acetate	X	X	X	X	X
	Sodium Acetate	X	X	X	X	X
	Sodium Formate	X	X	X	X	X

* "Horizontal" and "Vertical" refer to orientation of concrete prism in the storage container

3.6. MORTAR AND CONCRETE PROPORTIONS

Mortars for the test specimens in the standard and modified ASTM C 1260 tests were prepared using 2.25 parts of fine aggregate with 1 part of cement by weight at a water-to-cement ratio of 0.47. The fine aggregate used in the mortars was prepared from crushing the coarse aggregates and sieving and washing to meet the gradation requirements specified in the standard ASTM C 1260 test method. The proportions of materials used in preparing the concrete prisms and the properties of fresh concrete are given in Table 5. The coarse aggregate was graded to meet the requirements as specified in the standard ASTM C 1293 test method.

TABLE 5. CONCRETE MIXTURE PROPORTIONS USED IN PREPARATION OF CONCRETE PRISMS FOR THE STANDARD AND MODIFIED ASTM C 1293 TESTS (PER CUBIC METER).

Materials	**Coarse Aggregate Type**				
	Spratt (Reactive)	**NM (Reactive)**	**SD (Reactive)**	**NC (Reactive)**	**IL Dolomite (Non-reactive)**
Cement, kg/m^3	420	420	420	420	420
Fine agg, kg /m^3	678	630	608	703	669
Coarse agg, kg/ m^3	1102	1121	1094	1099	1117
Water, kg/ m^3	182.7	182.7	182.7	182.7	182.7
W/C	0.435	0.435	0.435	0.435	0.435
Agg/Cem	4.24	4.17	4.06	4.29	4.25
Density, kg/m^3	2383	2355	2305	2405	2389
Actual density, kg/m^3	2401	2399	2350	2442	2410
Actual cement, kg/m^3	423	427	427	426	423
Slump, mm	65	115	50	50	50

Note: 2.33 kg/m^3 of reagent grade sodium hydroxide was added to the mix water in concrete prepared with high-alkali cement as per the standard ASTM C 1293 requirement. This resulted in a total alkali content of 1.25% Na_2O by mass of cement in the concrete mixture.

4. PRELIMINARY INVESTIGATION

4.1. PURPOSE OF PRELIMINARY INVESTIGATION

The intent of the preliminary investigation was to determine if the proposed modified ASTM C 1260 test procedure (mortar bar test method) would clearly identify any deleterious expansions in mortar bars containing reactive aggregates in presence of deicer salt soak solutions. To this end, four parallel sets of experiments were conducted to address specific issues raised by the IPRF technical panel. These issues included:

1. Impact of leaching of alkali hydroxides from mortar bars into deicer soak solution on the observed expansions in the mortar bar tests.

2. Influence of temperature of test (80º C vs. 38º C storage temperature) on the expansion behavior of mortar bars.

3. Influence of concentration of deicer soak solution on expansion behavior of mortar bars.

4. Compare effects of commercial deicing chemicals and equivalent reagent grade chemicals on the expansion behavior of mortar bars.

The primary purpose of the leaching study was to determine if any leaching of alkali ions (Na^+, K^+), hydroxyl ions (OH^-), or calcium ions (Ca^{++}) would occur from the mortar bars into soak solutions. Subsequently, the impact of any such leaching on the observed expansions was to be assessed. Although similar concerns exist with the proposed modified concrete prism test, due to time restraints it was decided to restrict the scope of the preliminary study to the accelerated mortar bar study.

In addition to these issues, it was observed early on in the investigation that a rapid jump in the pH of the deicer soak solutions was observed after the introduction of the mortar bars into them. Characterizing the pH jump in the deicer solution was considered important to properly address any deleterious effects of these solutions on mortar bars. Also, the interaction of the deicer solutions with reagent grade calcium hydroxide was investigated as part of the effort to explain the pH increase phenomenon.

A summary of principal findings from the preliminary study are presented below.

4.2. SUMMARY OF FINDINGS

4.2.1. Leaching Study

This study was conducted to determine if any leaching of alkali hydroxides or calcium from the mortar bars into the soak solutions occurred, during the course of testing in the modified ASTM C 1260 test, and if so what influence such leaching may have had on the expansion of mortar bars. For this purpose, mortar bars using Spratt limestone were prepared with both high-alkali and low-alkali cements and soaked in deicer solutions, 1N sodium hydroxide solution and plain deionized water for a period of 14 days. The concentrations of OH^-, Na^+, K^+, and Ca^{++} ions developed in the soak solutions were determined after 14 days of mortar-bar immersion, and the results were compared to concentration of these ions in solutions in which no mortar bars were immersed. The findings from this study indicated:

1. Based on comparison of OH^- concentration measurements in plain solution (before contact with mortar bars) and soak solutions (i.e. after contact with mortar bars for 14 days) using traditional titration techniques (with methyl red indicator for detecting the end point), it was observed that:

    - For mortar bars exposed to 1N NaOH solution (i.e. in the standard ASTM C 1260 test) a net diffusion of OH^- ions from the soak solution into the mortar bars was observed.

    - For mortar bars exposed to deionized water, a net leaching of OH^- ions was observed to occur from the opposite direction, i.e. from the mortar bars into the deionized water.

    - For mortar bars exposed to deicer solutions (KAc, NaAc, NaFr and KFr), all of which are highly concentrated solutions, the measurement of OH^- ion concentration using traditional titration techniques with the methyl red dye to detect the end point proved to be challenging. Additional testing using phenolphthalein indicator dye in the titration gave a very different end point. Based on the measurements with phenolphthalein indicator as end point, it appeared that the OH^- concentration in all deicer soak solutions increased when mortar bars were immersed in it, i.e. that there is a net leaching of OH^- ions from mortar bars into deicer soak solutions. However, independent investigations to study the interaction of calcium hydroxide, a common hydration product of portland cement, with each of the four deicer solutions indicated that a significant and rapid jump in pH of the deicer solutions occurred, suggesting an increase in the OH^- concentration of the deicer solution. Further investigation of these interactions was beyond the scope of the research study. In light of these complex interactions, the authors believe that it would be premature to conclude that the observed increase in the OH^- concentration of deicer solution was attributable to leaching of OH^{--} ions from the pore solutions of the mortar bars and additional investigation is needed.

2. Based on comparison of Na^+ and K^+ ion concentrations in plain solution (before contact with mortar bars) and in soak solutions (i.e. after contact with mortar bars for 14 days), it was observed that:

    - For mortar bars exposed to 1N NaOH solution, there is a net influx of Na^+ ions into the mortar bars.

    - For mortar bars exposed to deionized water, there is a net leaching of Na^+ and K^+ ions from the mortar bars into the deionized water, as anticipated.

- For mortar bars exposed to deicer solutions, there was a net influx of the primary cation (either Na^+ or K^+ depending on the specific deicer used) from the soak solution into the mortar bar.

3. Based on comparison of Ca^{++} concentrations in plain solution (before contact with mortar bars) and soak solutions (i.e. after contact with mortar bars for 14 days), it was observed that virtually no calcium leached out of mortar bars into soak solution in case of 1N NaOH and all the deicer soak solutions (< 5 ppm). However, in case of mortar bars exposed to de-ionized water, at 14 days of immersion over 350 ppm of Ca^{++} was observed in the soak solution.

In this investigation changes in concentrations of acetate and formate ions in the soak solutions were not measured.

Figures 5A and 5B shows the influence of different anti-icer and deicer solutions, 1N NaOH solution and deionized water on the expansion of Spratt limestone mortar bars prepared with high-alkali and low-alkali cements, respectively. It is observed from these results that significant expansions occurred in mortar bars containing reactive aggregate, when exposed to all of the deicer solutions and 1N NaOH, and no expansion was observed when exposed to deionized water. It should be noted that in these tests certain intermediate length-change measurements were avoided to not interfere with the leaching study. It was concluded from these results that leaching of OH^- and other ions was not a concern in this test method. **From these findings it was concluded that the modified ASTM C 1260 test method as proposed in this study was a viable test procedure in identifying the deleterious effects of deicer solutions on mortar bars containing reactive aggregates.**

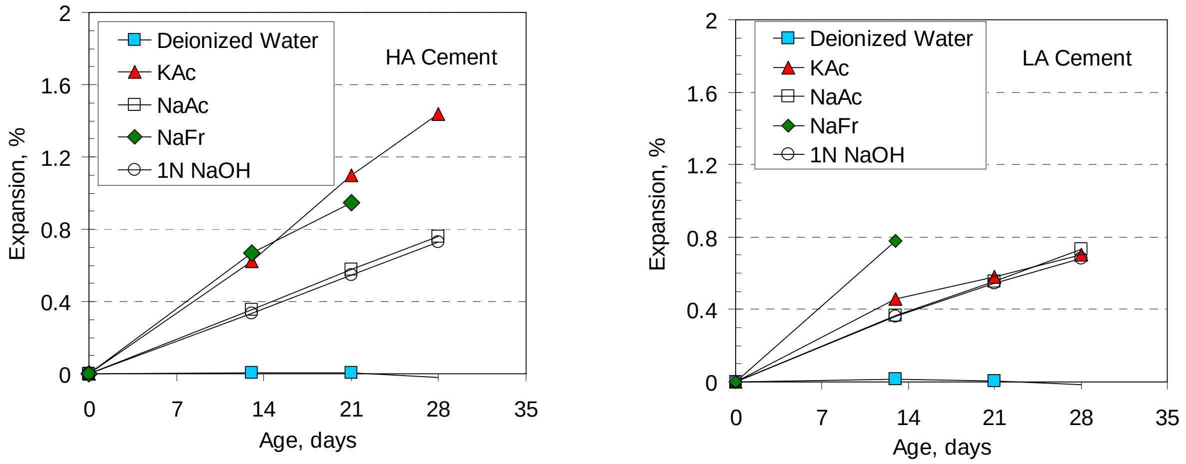


Fig. 5A. Fig. 5B.

FIGURE 5. INFLUENCE OF DIFFERENT DEICER SOAK SOLUTIONS, 1N NaOH AND DEIONIZED WATER ON EXPANSION OF MORTAR BARS CONTAINING REACTIVE SPRATT LIMESTONE AGGREGATE WITH HIGH-ALKALI AND LOW-ALKALI CEMENTS.

4.2.2. Effect of Concentration of Deicer Soak Solution on Expansion of Mortar Bars in the Modified ASTM C 1260 Tests

In this investigation, the effect of varying the concentration of potassium acetate deicer solution on expansion of mortar bars in the modified ASTM C 1260 test was investigated using Spratt limestone as the reactive aggregate. These tests were conducted on mortar bars prepared with both high-alkali and low-alkali cements.

Figures 6A and 6B shows the influence of concentration of KAc deicer solution on the expansion of Spratt limestone mortar bars prepared with high-alkali and low-alkali cements, respectively.

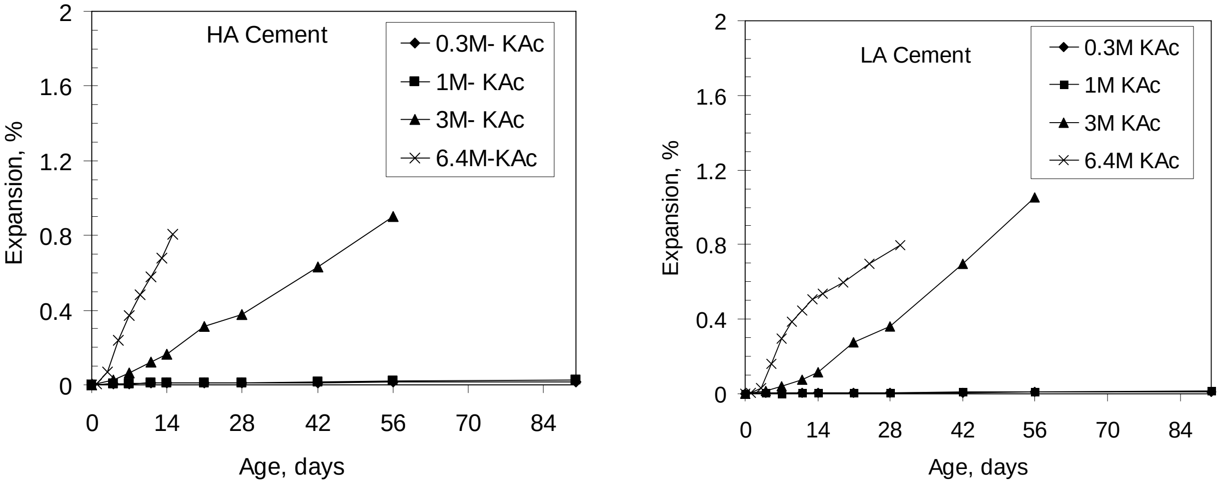


Fig. 6A. Fig. 6B.

FIGURE 6. FIGURE EXPANSIONS OF MORTAR BARS PREPARED WITH SPRATT AGGREGATE AND HA CEMENT AND SOAKED IN 0.3M, 1M, 3M AND 6.4M SOLUTIONS OF KAc

It was observed from these results that the expansion decreased with decrease in concentration of the potassium acetate deicer solution. The commercially available potassium acetate deicer – a 50% wt. solution at 6.4 molar concentration, resulted in the highest expansion in mortar bars with both low-alkali and high-alkali cements.

While the 3 molar potassium acetate deicer solution caused expansion in mortar bars of only slightly over 0.1% at 14 days, substantial expansion in mortar bars was observed at later ages (i.e. beyond 14 days), regardless of the alkali content of the cement used. Mortar bars soaked in 1 molar and 0.3 molar concentration potassium acetate deicer solutions did not exhibit any expansion with either of the two cements investigated in this study.

4.2.3. Effect of Temperature of Test on Expansion of Mortar Bars in the Standard and Modified ASTM C 1260 Tests

In this study, the effect of temperature of testing (80° C vs. 38° C) on the expansion observed in mortar bars exposed to 1N sodium hydroxide or to deicer solutions in the standard and modified

ASTM C 1260 tests was investigated. In addition, the influence of alkali content of the cement on mortar bar expansion was also observed in this investigation. Figure 7 show the results from this investigation.

It is observed from these results that in tests conducted with a storage temperature of 80º C, rapid expansion in mortar bars (< 7 days) was observed in the presence of all of the deicer solutions and of 1N NaOH solution, regardless of the alkali content of the cement. However, in tests conducted with a storage temperature of 38ºC, very little expansion took place in mortar bars exposed to either deicer solutions or 1N NaOH solution at ages up to 28 days, regardless of the alkali content of the cement used. However, at later ages (> 6 months) significant expansion occurred in mortar bars exposed to all of the deicer solutions and 1N NaOH solution. Depending on the specific soak solution used in the test, the expansions observed between six months to one year in mortar bars stored at 38º C were comparable to those in mortar bars at 14 days stored at 80º C. Based on these observations, it was concluded that the effect of the increased temperature in the modified ASTM C 1260 test was to primarily accelerate the rate of reactions involved.

4.2.4. Comparison of Effects of Commercial Grade and Reagent Grade Deicing Chemicals on Expansion of Mortar Bars in the Modified ASTM C 1260 Tests

In this investigation, the effects of potassium acetate and sodium acetate solutions prepared from commercial grade and reagent grade chemicals on expansion of Spratt limestone mortar bars were studied, using the modified ASTM C 1260 tests. In these tests, the concentration of both commercial grade and reagent grade chemical solutions were maintained identical. This study was undertaken to assess any effects of other additives in commercial grade deicing chemicals on the expansions observed.

Figures 8 and 9 show the results from tests with potassium acetate and sodium acetate solutions, respectively. It was observed from these results that both commercial grade and reagent grade potassium acetate caused significant distress in mortar bars containing reactive aggregates and were comparable to each other. However, the precise levels of expansions observed in mortar bars exposed to commercial and reagent grade chemicals differed slightly, depending on the specific deicer chemical considered.

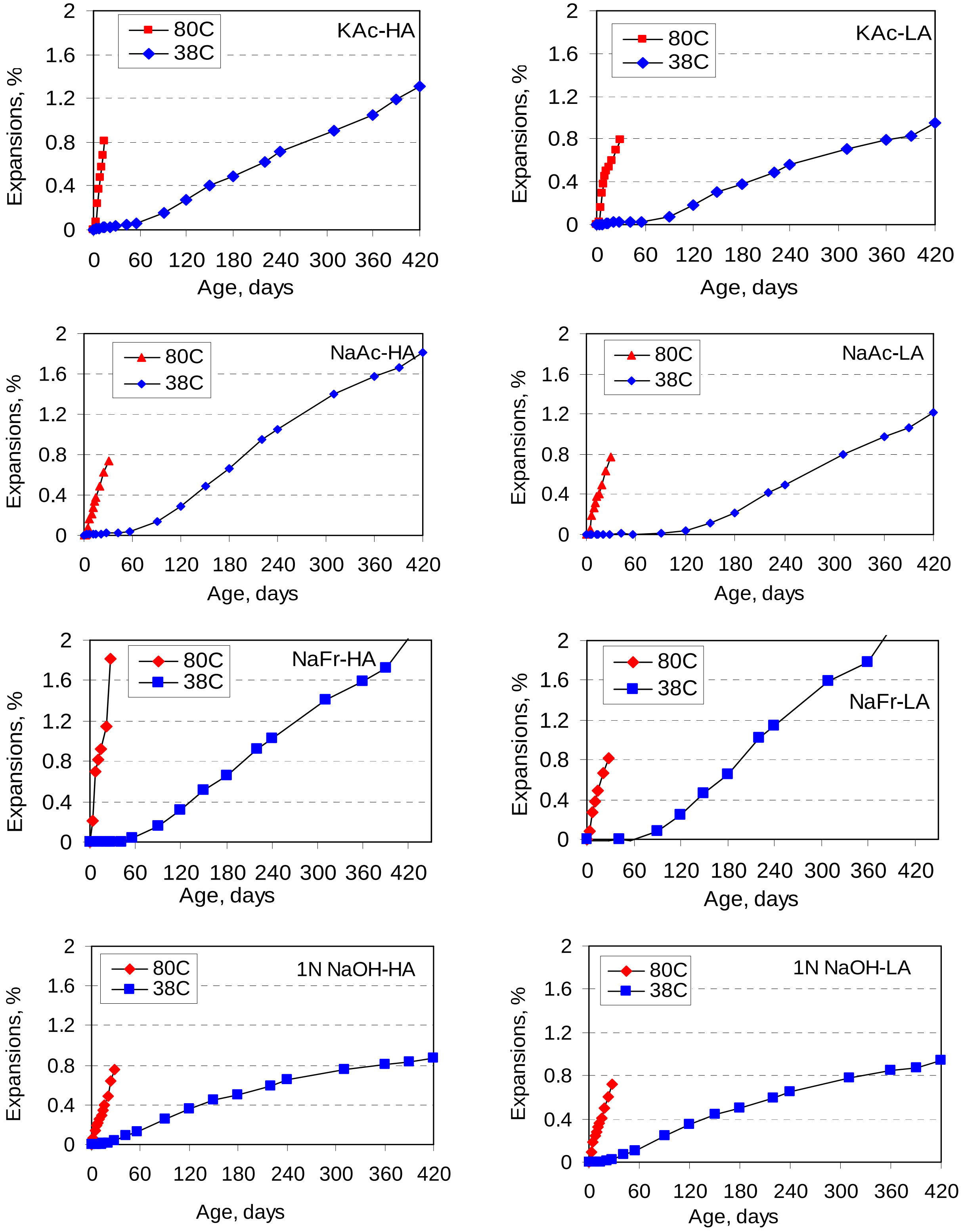


Fig. 7A (High-Alkali)

Fig. 7B (Low-Alkali)

FIGURE 7. INFLUENCE OF STORAGE TEMPERATURE, TYPE OF SOAK SOLUTION AND ALKALI CONTENT OF CEMENT ON EXPANSION OF SPRATT MORTAR BARS

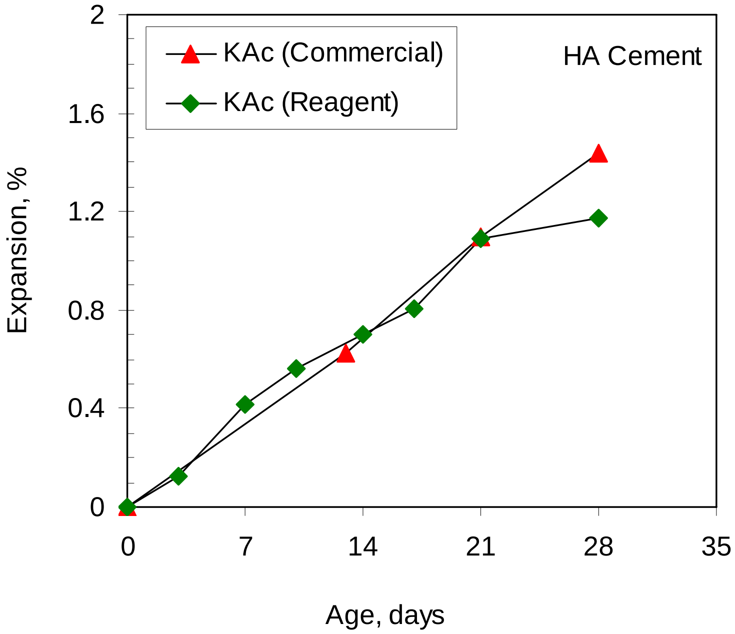


FIGURE 8. COMPARISON OF EXPANSIONS OF SPRATT LIMESTONE MORTAR BARS WITH HIGH-ALKALI CEMENT AND SOAKED IN 6.4 MOLAR SOLUTIONS OF REAGENT AND COMMERCIAL DEICER GRADE POTASSIUM ACETATE.

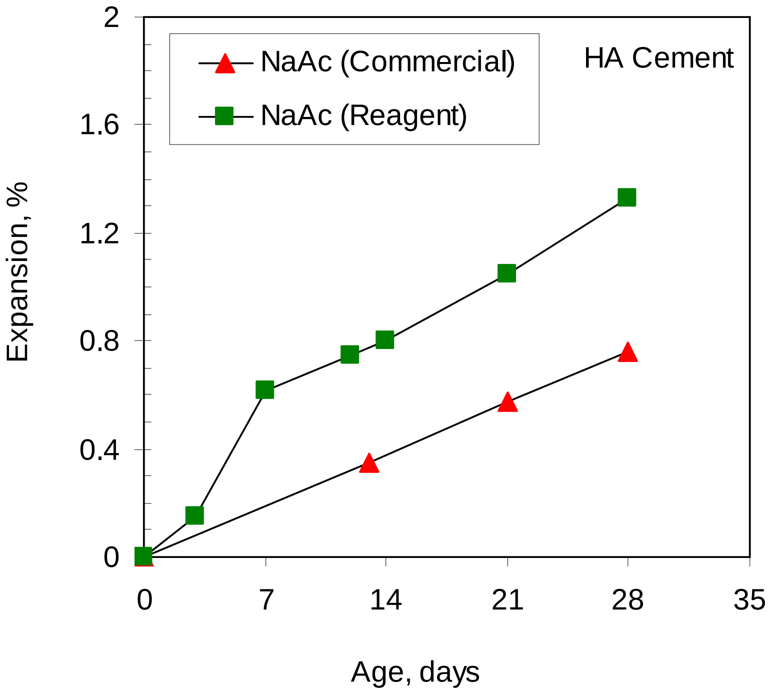


FIGURE 9. COMPARISON OF EXPANSIONS OF SPRATT LIMESTONE MORTAR BARS WITH HIGH-ALKALI CEMENT AND SOAKED IN ROOM TEMPERATURE SATURATED SOLUTIONS OF REAGENT AND COMMERCIAL DEICER GRADE SODIUM ACETATE.

5. RESULTS AND ANALYSIS OF DATA FROM MORTAR BARS TESTS

This section presents details of the results obtained from the standard and modified ASTM C 1260 tests conducted on both reactive and non-reactive aggregates (see Table 3 for test matrix). The specific results presented in this section include:

1. Length-change measurements of mortar bars
2. Dynamic modulus of elasticity of mortar bars
3. pH changes observed in soak solutions of standard and modified ASTM C 1260 tests
4. Microstructure of mortar bars

5.1. LENGTH-CHANGE MEASUREMENTS OF MORTAR BARS

5.1.1. Standard ASTM C 1260 Test

Figures 10 and 11 show expansions of mortar bars containing Spratt limestone, NC argillite, SD quartzite and NM rhyolite aggregates in the standard ASTM C 1260 test, using low and high alkali cements, respectively. Also, expansion of mortar bars with non-reactive Ottawa sand is included in the Figures for comparative purposes.

It is apparent from figures 10 and 11 that mortar bars with each of the four reactive aggregates show expansion well over 0.1% at 14 days of soaking, which indicates highly reactive nature, regardless of the alkali level of the cement. In contrast, mortar bars with Ottawa sand showed virtually no expansion with either high or low alkali cements in the standard ASTM C 1260 tests.

5.1.2. Modified ASTM C 1260 Test

5.1.2.1. Influence of Potassium Acetate-Based Deicer Soak Solution on Mortar Bar Expansion

Figures 12 and 13 show the expansion behavior of Spratt limestone, NC argillite, SD quartzite and NM rhyolite aggregates and Ottawa sand in the modified ASTM C 1260 tests, with low-alkali and high-alkali cements, respectively. In these tests potassium acetate deicer soak solution was employed.

It is observed from these figures that all the reactive aggregates mortar bars soaked in potassium acetate deicer showed deleterious levels of expansion (>> 0.1% at 14 days), regardless of the alkali content of the cement used. On comparing the expansions of mortar bars soaked in potassium acetate solution with those soaked in 1N sodium hydroxide solution, it is evident that Spratt limestone, NM rhyolite and SD quartzite aggregates showed considerably greater expansion in potassium acetate solution at any age, regardless of the alkali content of the cement used. However, for NC aggregate, mortar bars with low-alkali cement showed somewhat less expansion in potassium acetate solution compared to 1N sodium hydroxide solution, while bars containing with high-alkali cement followed the same trend as the other reactive aggregates.

For the reference Ottawa sand, mortar bars soaked in potassium acetate solution showed expansions of only 0.05% and 0.06% with low and high-alkali cements, respectively. These expansions are slightly higher than observed with 1N sodium hydroxide soak solution for the non-reactive Ottawa sand (0.014% - low-alkali cement and 0.015% - high alkali cement) but, they are still low enough for this aggregate to still be considered non-reactive.

5.1.2.2. Influence of Sodium Acetate-Based Deicer Soak Solution on Expansions of Mortar Bars

Figures 14 and 15 show the expansions of all the four reactive aggregates and the reference non-reactive aggregate in the modified ASTM C 1260 tests with low-alkali and high-alkali cements, respectively, where sodium acetate deicer soak solution was used.

It is observed from these figures that all four reactive aggregates showed very high levels of expansion in the sodium acetate deicer solution, regardless of the alkali content of the cement. Indeed, mortar bars containing NM rhyolite aggregate expanded more than 1% within 3 days of exposure to the sodium acetate soak solution. However, mortar bars prepared with the non-reactive Ottawa sand showed very minimal expansions (0.034% for low-alkali cement, 0.023% of high-alkali cement), even when the mortar bars are soaked up to 28 days.

Comparing the expansions of mortar bars soaked in 1N sodium hydroxide solution (see Figures 10 and 11) with those soaked in sodium acetate solutions (see Figures 14 and 15), it is evident that sodium acetate solution has considerably more aggravating influence than 1N NaOH solution.

5.1.2.3. Influence of Sodium Formate Deicer Soak Solution on Mortar Bar Expansion

Figures 16 and 17 show the length-change observed for mortar bars soaked in the sodium formate deicer solution in the modified ASTM C 1260 test, with high and low alkali cements, respectively. It is seen from these figures that, regardless of the alkali content of the cement used, the mortar bars exhibited significant expansions in presence of sodium formate deicer solution, i.e. expansions greater than 0.7% at 14 days, with additional expansions occurring subsequently. Again, the mortar bars prepared with the Ottawa sand did not show any significant expansion (0.006% at 14 days), regardless of the alkali content of the cement used.

Comparing the results from Figures 16 and 17 with those of Figures 10 and 11, it is evident that mortar bars containing reactive aggregates showed significantly higher level of expansion in presence of sodium formate deicer solution than 1N sodium hydroxide solution. However, the degree of increase in expansion in sodium formate deicer solution varied with the specific aggregate in question. The mortar bars containing non-reactive Ottawa sand did not exhibit significant expansion in either the 1N sodium hydroxide solution or the sodium formate deicer solution. Similar behavior was observed in presence of the low-alkali cement.

5.1.2.4. Influence of Potassium Formate Deicer Soak Solution on Mortar Bar Expansion

Figures 18 and 19 show the expansions of mortar bars soaked in potassium formate deicer solutions with high-alkali and low-alkali cements, respectively. It is seen that the expansions of mortar bars containing reactive aggregate were significant (> 0.4% expansion for all aggregates at 14 days), irrespective of the alkali content of the cement used. However, it is observed that expansions in presence of the high-alkali cement were higher than those seen in the presence of low-alkali cement. Minor expansion (0.043% at 14 days) was observed in mortar bars containing the non-reactive Ottawa sand with both of the cements tested.

Comparing the expansions of mortar bars containing reactive aggregates soaked in potassium formate (see Figures 18 and 19) with mortar bars soaked in 1N sodium hydroxide solution (see Figures 10 and 11), it is evident that potassium formate deicer solution caused significantly more expansion than 1N sodium hydroxide soak solution. The mortar bars containing non-reactive Ottawa sand did not exhibit significant expansion (i.e. > 0.1% at 28 days) in either solution.

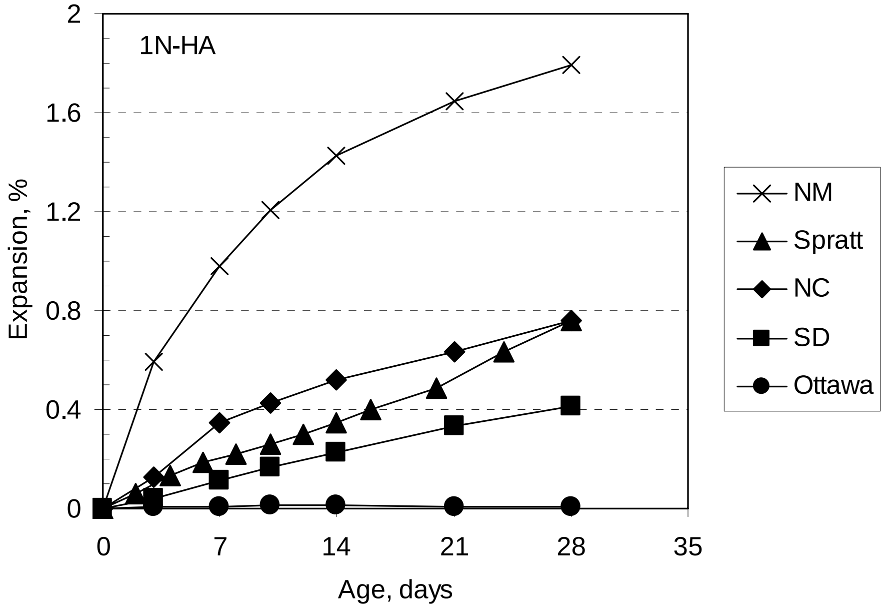


FIGURE 10. EXPANSION OF MORTAR BARS IN STANDARD ASTM C 1260 TEST WITH 1N NaOH SOLUTION AND HA CEMENT

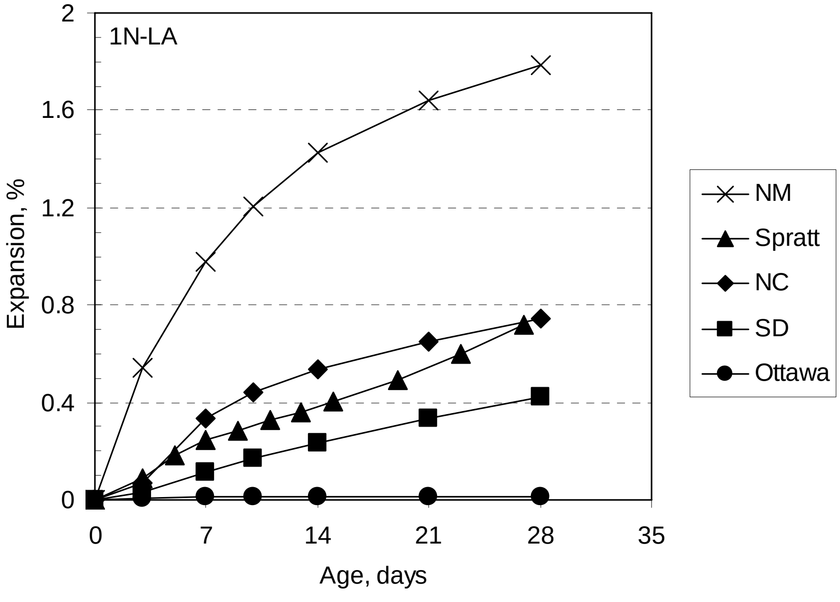


FIGURE 11. EXPANSION OF MORTAR BARS IN STANDARD ASTM C 1260 TEST WITH 1N NaOH SOLUTION AND LA CEMENT

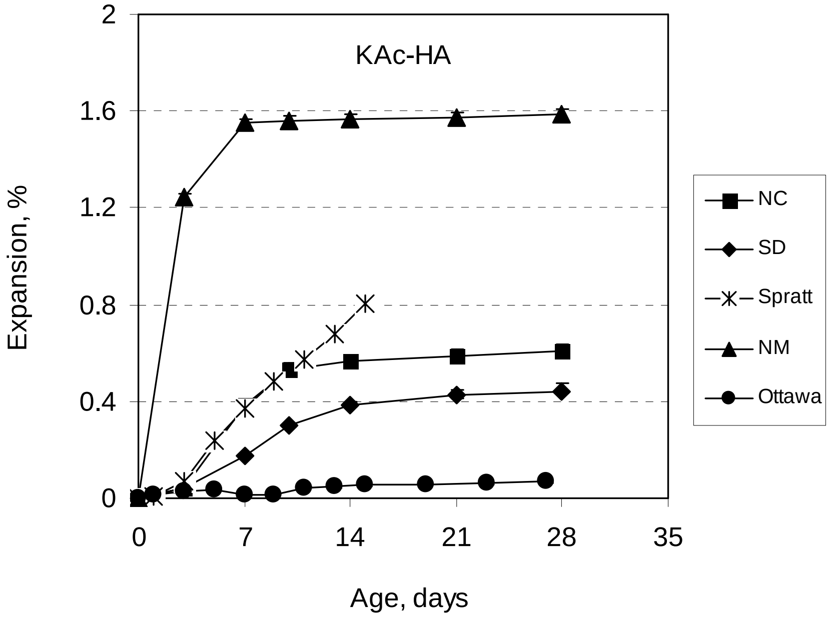


FIGURE 12. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH POTASSIUM ACETATE DEICER SOLUTION AND HA CEMENT

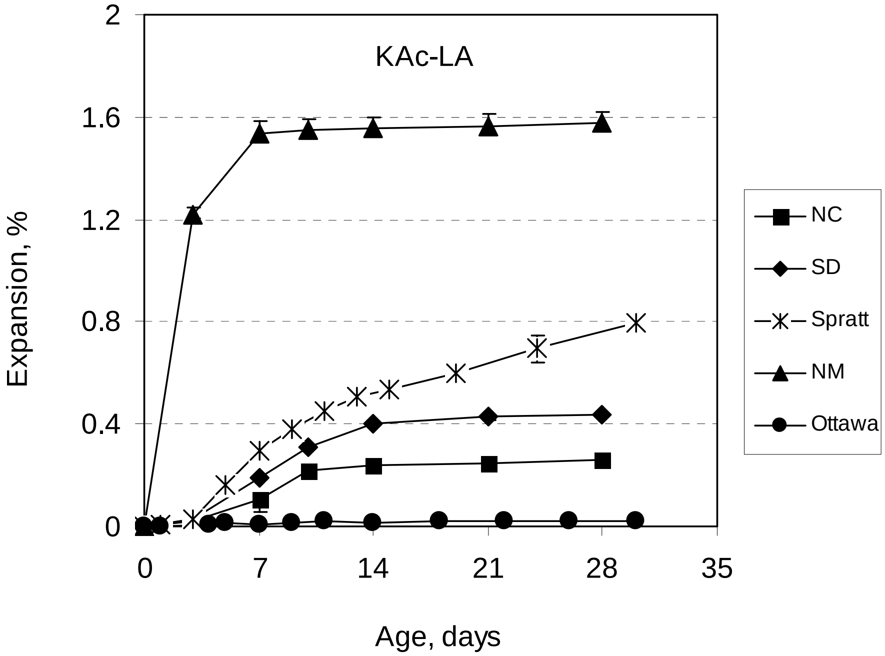


FIGURE 13. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH POTASSIUM ACETATE DEICER SOLUTION AND LA CEMENT

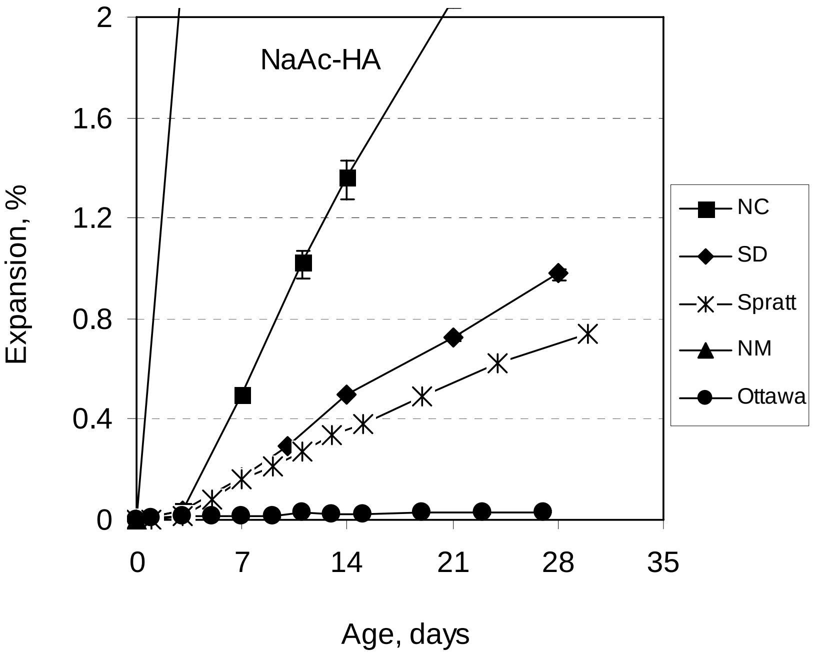


FIGURE 14. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH SODIUM ACETATE DEICER SOLUTION AND HA CEMENT

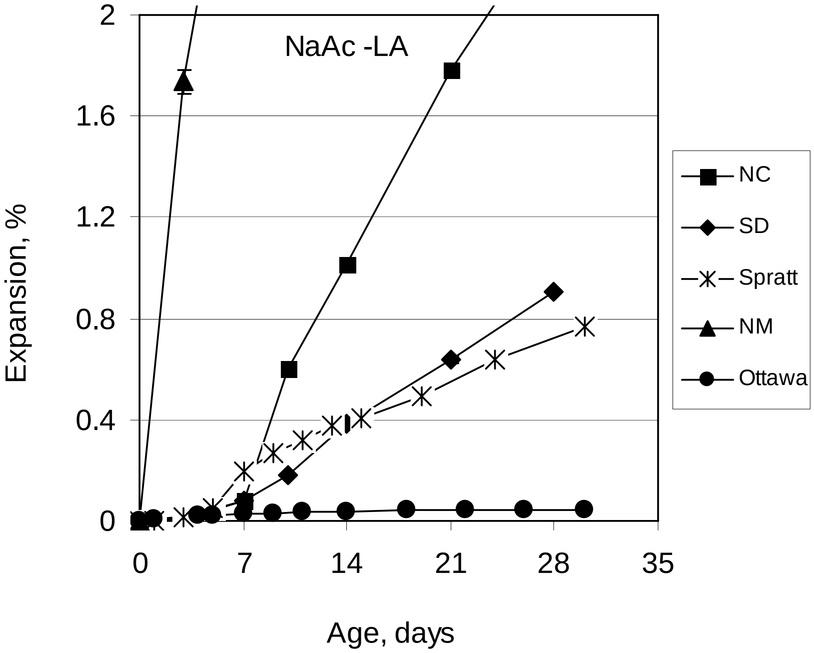


FIGURE 15. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH SODIUM ACETATE DEICER SOLUTION AND LA CEMENT

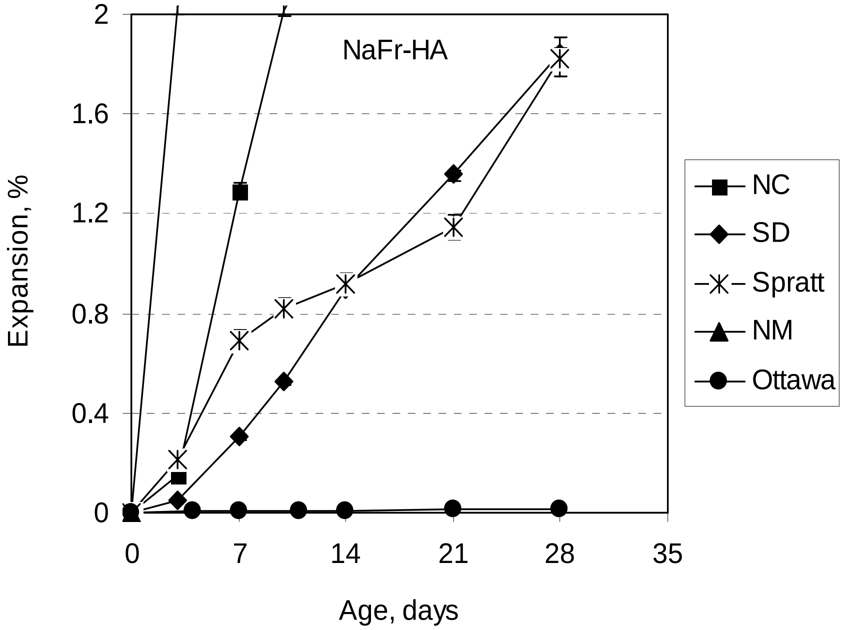


FIGURE 16. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH SODIUM FORMATE DEICER SOLUTION AND HA CEMENT

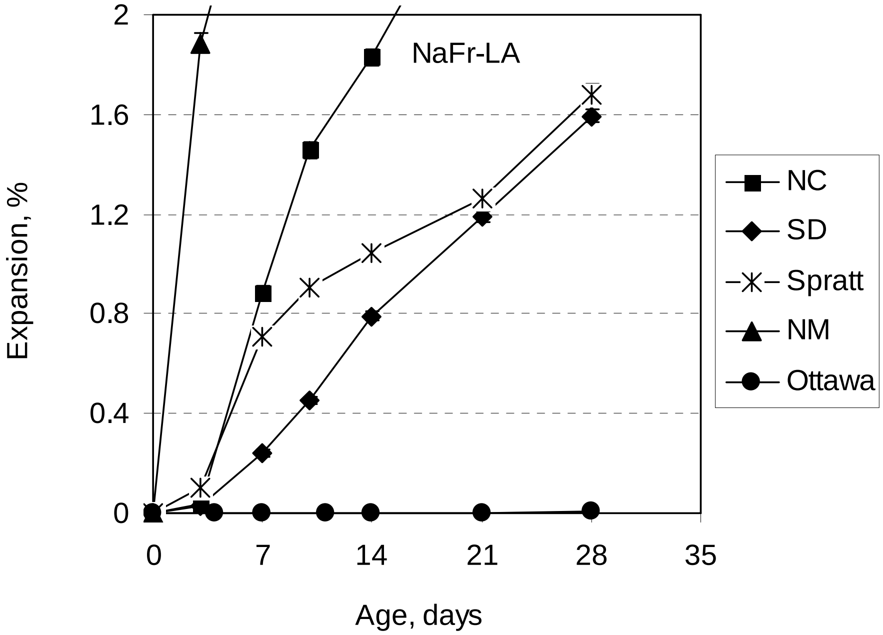


FIGURE 17. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH SODIUM FORMATE DEICER SOLUTION AND LA CEMENT

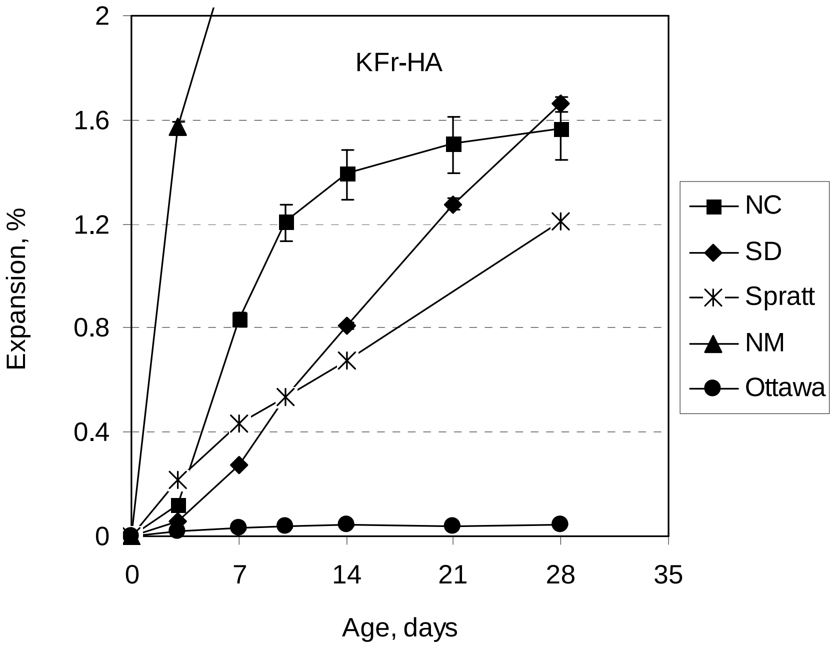


FIGURE 18. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH POTASSIUM FORMATE DEICER SOLUTION AND HA CEMENT

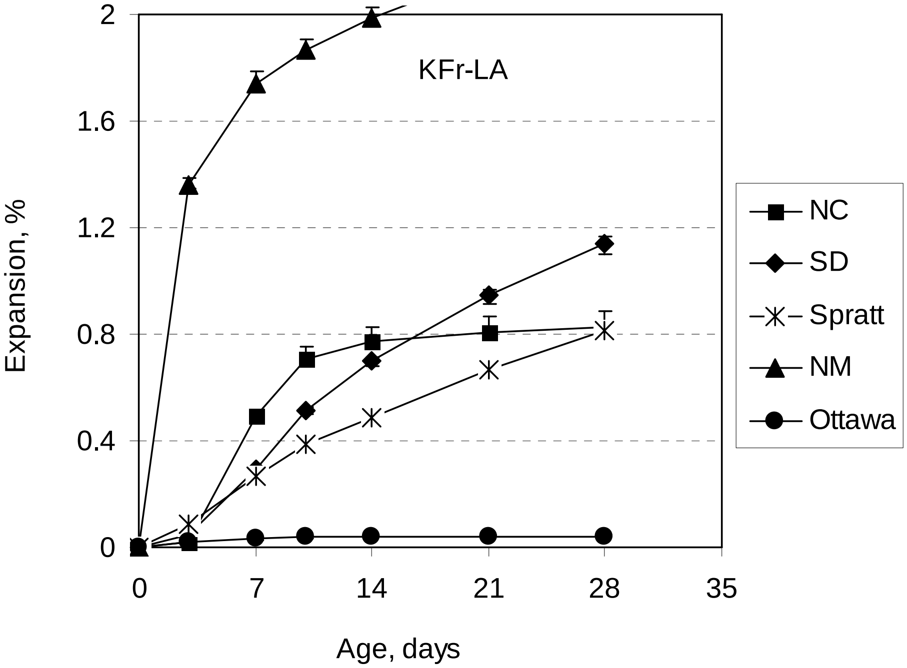


FIGURE 19. EXPANSION OF MORTAR BARS IN MODIFIED ASTM C 1260 TEST WITH POTASSIUM FORMATE DEICER SOLUTION AND LA CEMENT

5.2. DYNAMIC MODULUS OF ELASTICITY OF MORTAR BARS

Figures 20, 21, 22, 23 and 24 show the changes in dynamic modulus of elasticity (DME) of mortar bars containing reactive aggregates after being immersed in 1N sodium hydroxide, potassium acetate, sodium acetate, sodium formate and potassium formate deicer solutions, respectively. Also, the influence of the alkali content of the cement on the changes in DME is presented. Corresponding changes in DME, if any, of non-reactive Ottawa sand mortar bars could not be measured due to the failure of the resonant frequency probe at the time of testing.

It is seen that mortar bars made from reactive aggregates showed significant loss in DME within the first 7 to 14 days in the presence of all the soak solutions. However, the rates of loss in the DME of mortar bars in deicer solutions were more rapid than 1N sodium hydroxide solution. This observation is consistent with the relative mortar bar expansions observed in 1N sodium hydroxide solution compared with the deicer solutions. The rate of loss in DME was found to vary with the type of the aggregate and with the specific soak solution involved in the test.

For example, mortar bars prepared with Spratt limestone showed slower reduction in DME at early ages in 1N sodium hydroxide, sodium formate and potassium formate deicer solutions than in potassium acetate or sodium acetate deicer solutions. At later ages (after 14 days), mortar bars soaked in 1N sodium hydroxide solution and other alkali-formate deicer solutions also showed appreciable reductions in their DME.

Based on the visual and SEM examination of mortar bars stored in 1N sodium hydroxide and alkali-formate deicer soak solutions, it appears that at early ages the ASR gel product tended to fill the cracks within aggregates and in the adjoining cement paste. This appeared to confer some degree of rigidity, which was reflected in lack of any significant drop in DME. However at later ages, the cracks become larger and more widespread and are not completely filled with the ASR gel, thus leading to the observed gradual drop in the DME values.

However, for the Spratt limestone mortar bars soaked in potassium acetate and sodium acetate deicer solutions, the degree of deterioration is significant even at early ages (7 -14 days) and the cracks on the surface of the mortar bars appeared to be devoid of any reaction product. Presumably, the reaction product formed has moved out of the cracks thus weakening the structure and consequently reducing the DME of the mortar bars.

The alkali content of the cement used in the mortar bars did not show an influence on the changes in DME of mortar bars in the standard or modified ASTM C 1260 tests. However, the changes in DME of mortar bars corresponded well with the expansions observed in test specimens.

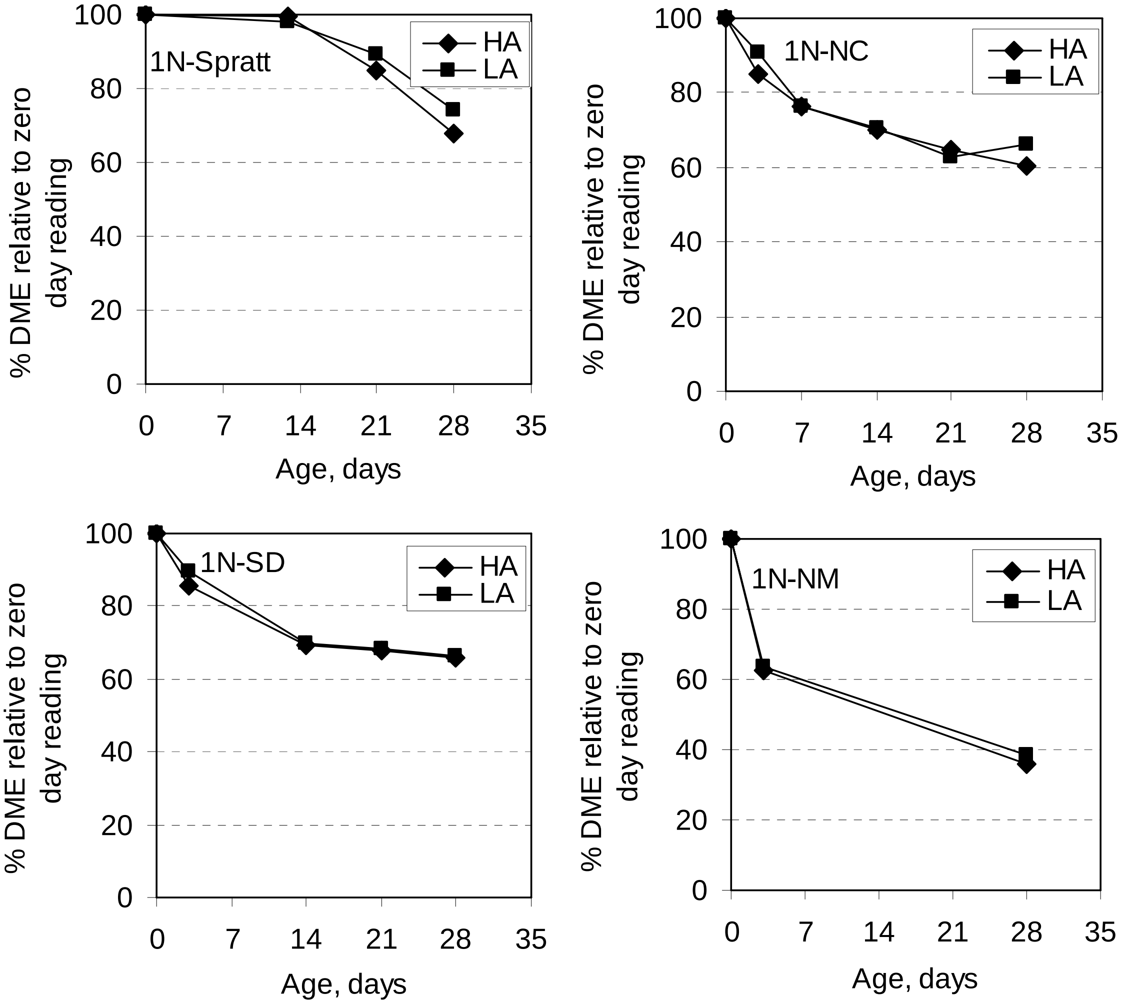


FIGURE 20. CHANGES IN DYNAMIC MODULUS OF MORTAR BARS EXPOSED TO 1 N NaOH SOLUTION IN THE STANDARD ASTM C 1260 TEST

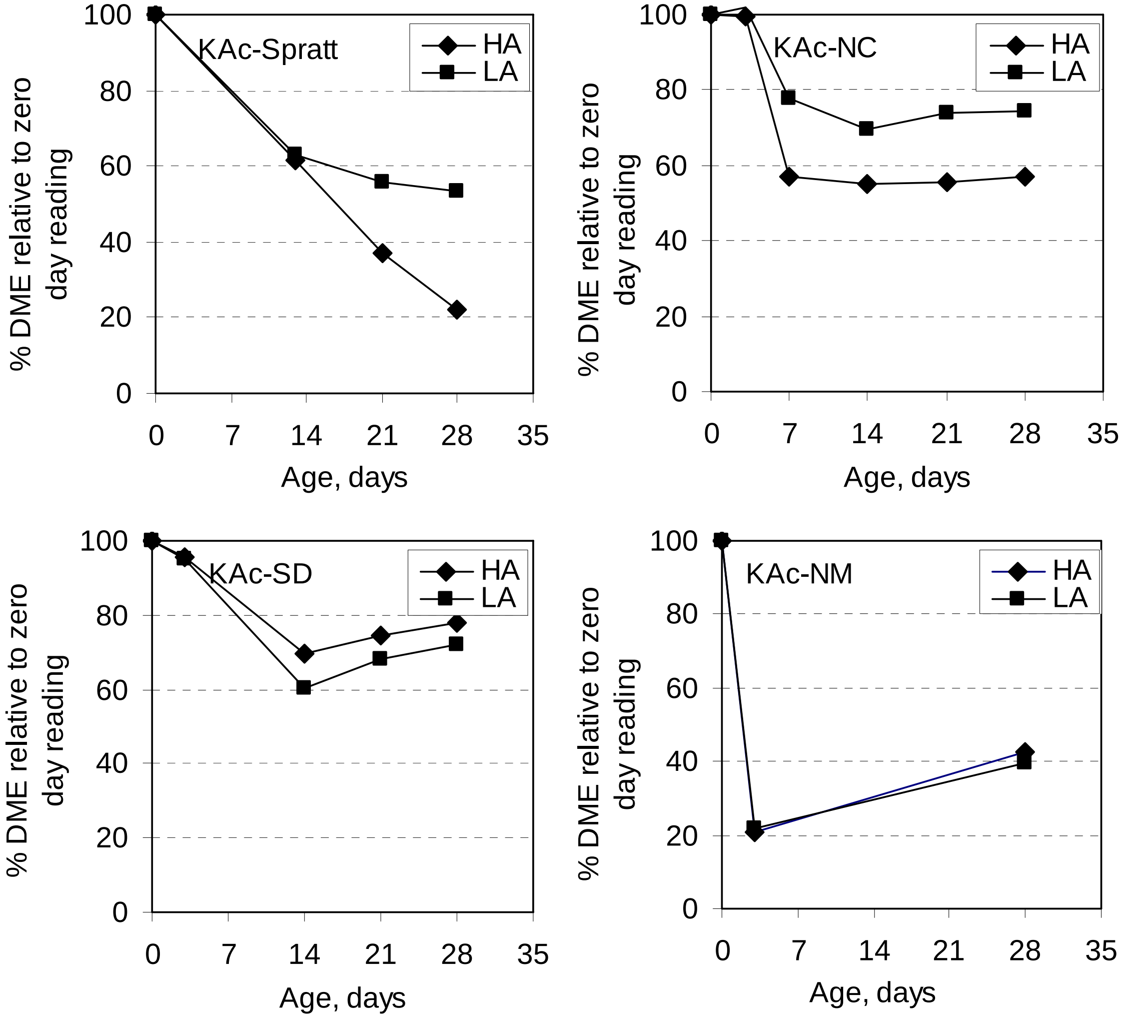


FIGURE 21. CHANGES IN DYNAMIC MODULUS OF MORTAR BARS EXPOSED TO POTASSIUM ACETATE DEICER SOLUTION IN THE MODIFIED ASTM C 1260 TEST

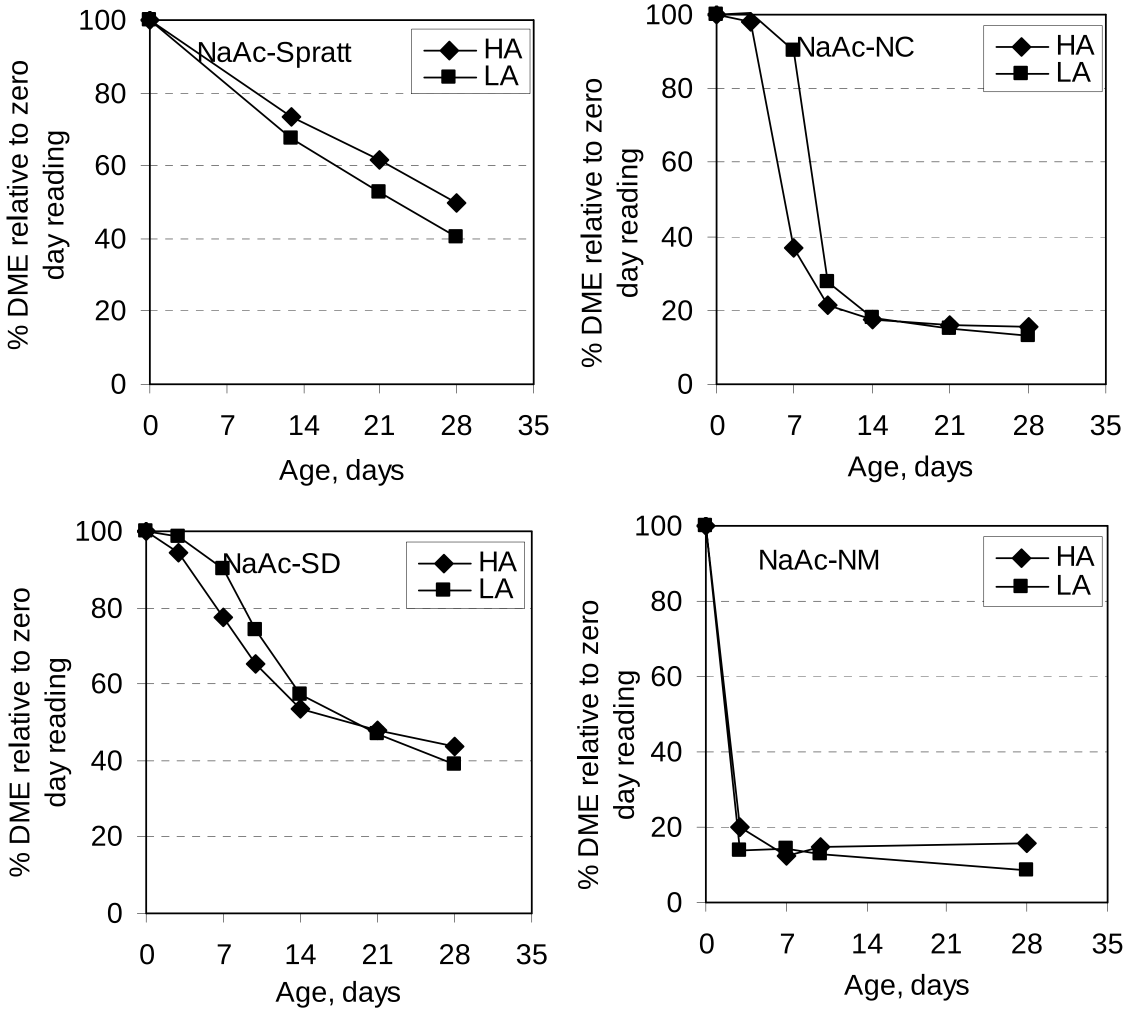


FIGURE 22. CHANGES IN DYNAMIC MODULUS OF MORTAR BARS EXPOSED TO SODIUM ACETATE DEICER SOLUTION IN THE MODIFIED ASTM C 1260 TEST

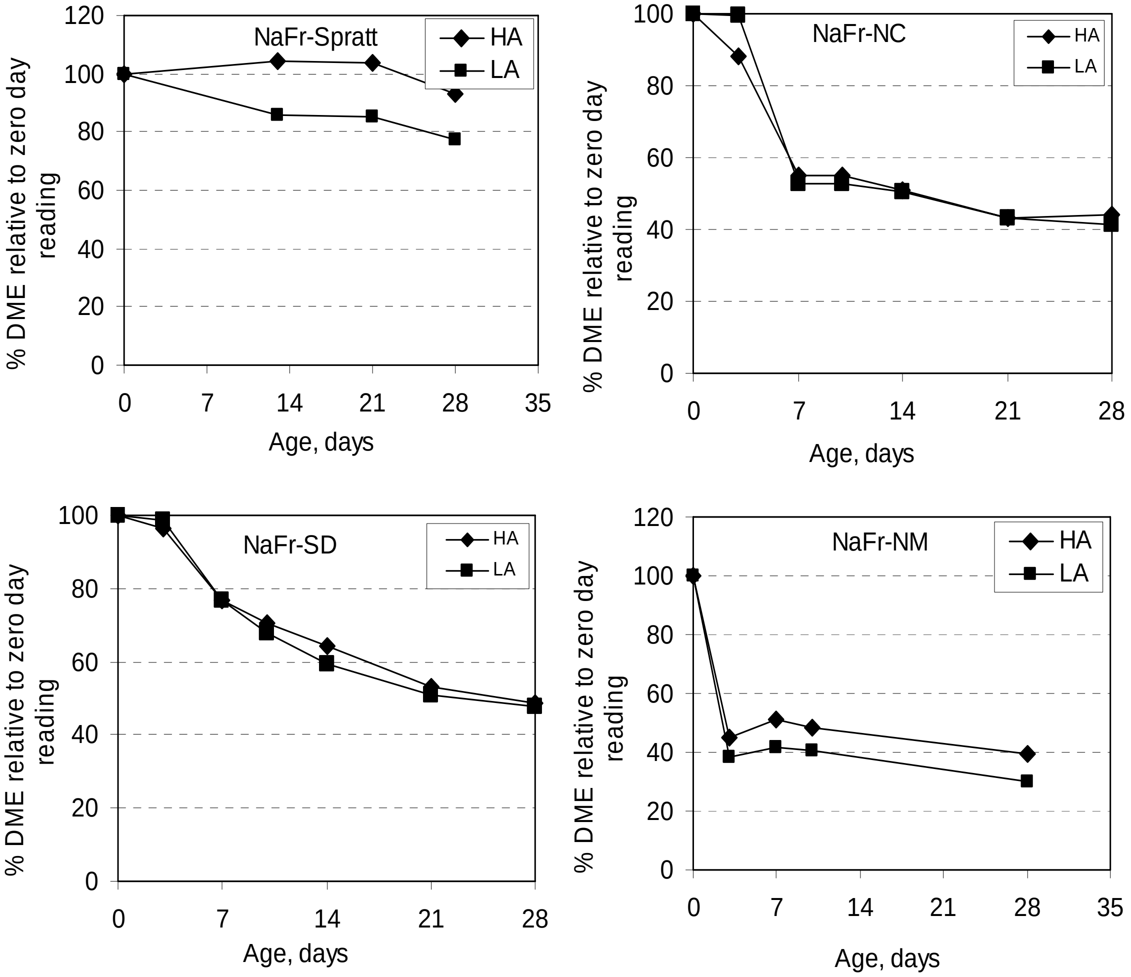


FIGURE 23. CHANGES IN DYNAMIC MODULUS OF MORTAR BARS EXPOSED TO SODIUM FORMATE DEICER SOLUTION IN THE MODIFIED ASTM C 1260 TEST

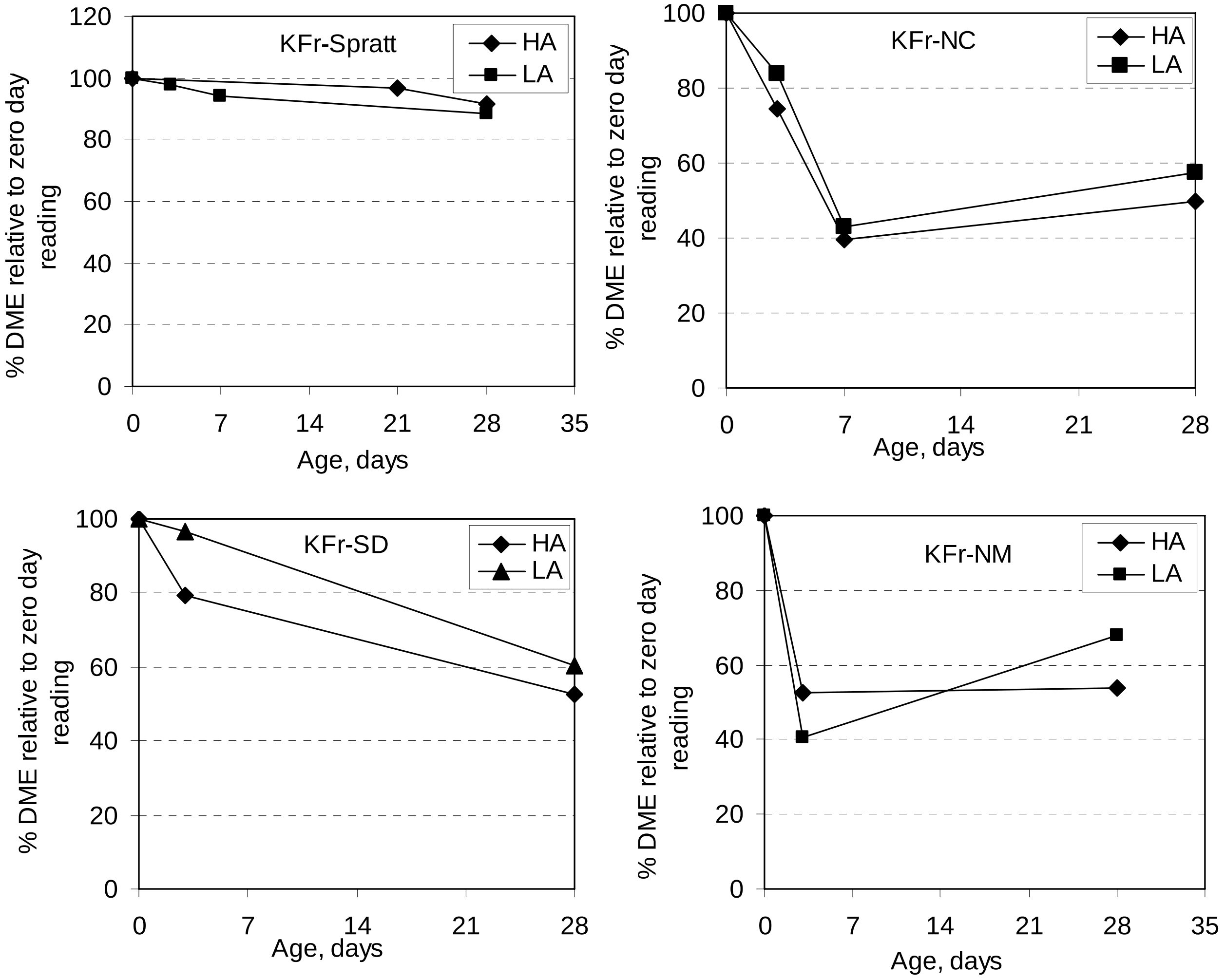


FIGURE 24. CHANGES IN DYNAMIC MODULUS OF MORTAR BARS EXPOSED TO POTASSIUM FORMATE DEICER SOLUTION IN THE MODIFIED ASTM C 1260 TEST

5.3. pH CHANGES IN SOAK SOLUTIONS

Figure 25 shows the measured pH values of all the soak solutions recovered from the standard and modified ASTM C 1260 tests in which high-alkali cement was used. The "plain solution" entries indicate the pH values of the solutions that have undergone the same regimen in terms of storage and temperature as the soak solution in ASTM C 1260 test procedure (i.e. 14 days at 80ºC), but within which no mortar bars were stored. This test was conducted to establish a base line measurement for each of the different soaking environments. The other pH values indicated in the Figure for each type of soak solution correspond to the pH values of solutions in which mortar bars prepared with specific aggregates were soaked. All the pH measurements were taken on samples of soak solutions that were retrieved from the storage container at 14 days and cooled to room temperature in sealed containers. Limited testing on changes in pH of soak solutions in which mortar bars prepared with low-alkali cement was also conducted. No specific differences were observed between the results of tests with high-alkali cement and low-alkali cement systems.

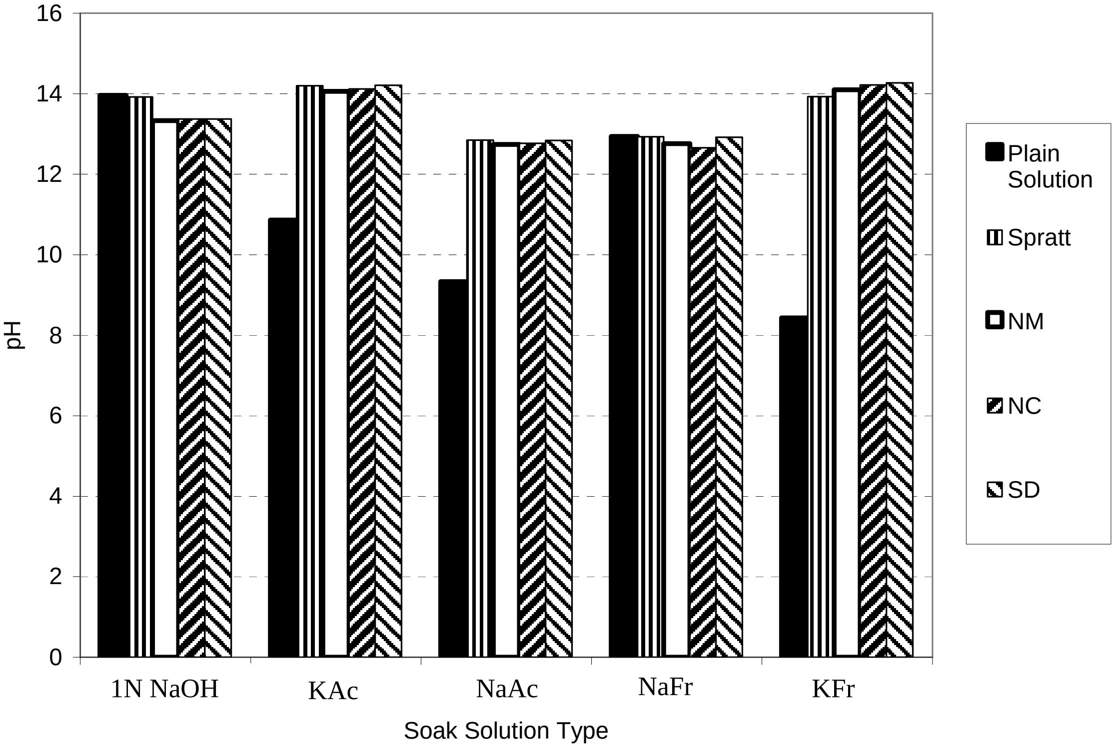


FIGURE 25. pH VALUES OF SOAK SOLUTIONS FROM STANDARD AND MODIFIED ASTM C 1260 TESTS FOR ALL AGGREGATES EVALUATED IN THIS STUDY (MEASURED AT ROOM TEMPERATURE)

5.3.1. 1N Sodium Hydroxide Soak Solution

It is apparent from the data presented in Figure 25 that the pH of 1N sodium hydroxide solution did not significantly differ between the plain solution and the solutions in which mortar bars prepared with different aggregates were soaked. This suggests that the soak solution was acting simply as an additional reservoir to the pore solution to maintain the high pH environment needed to accelerate ASR process.

5.3.2. Potassium Acetate Soak Solution

The pH value measured for the plain potassium acetate deicer solution was 11.04, which is well within the limits of manufacturer's specification of 11 ± 0.5. However, the pH values measured for the potassium acetate deicer solution in which mortar bars were soaked ranged between 14.02 and 14.23 for the 4 different reactive aggregates.

Limited investigations were carried out to establish the cause of the increase in the pH of the potassium acetate deicer solutions that had been exposed to the mortar bars, by studying interactions between reagent grade calcium hydroxide and potassium acetate deicer solutions. In these studies, small quantities of calcium hydroxide (ranging between 0.2 grams and 2.0 grams) were added to 50 ml volumes of potassium acetate deicer solution at room temperature, and the pH of the solution was monitored at close intervals. Figure 26 shows the influence of addition of reagent calcium hydroxide on pH of potassium acetate deicer solution.

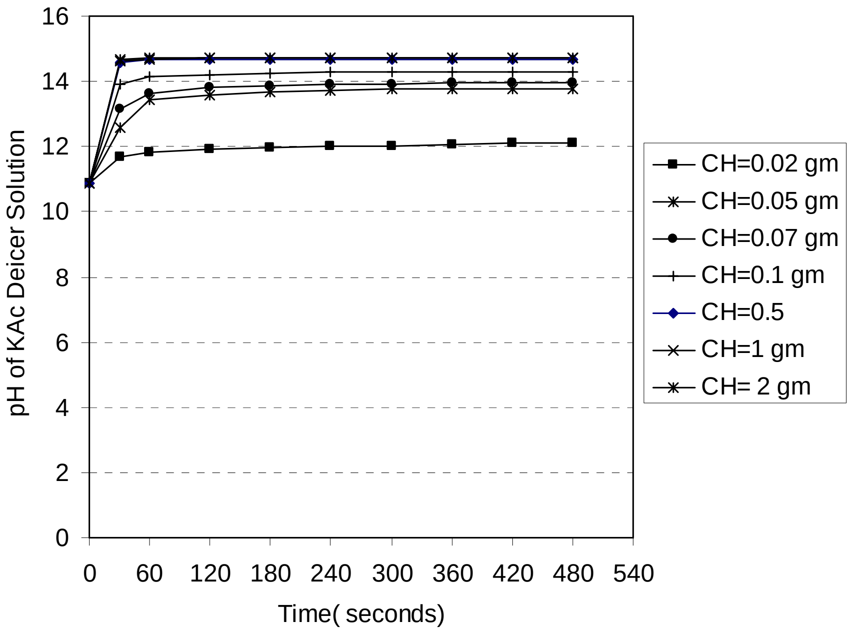


FIGURE 26. INFLUENCE OF ADDITION OF REAGENT GRADE CALCIUM HYDROXIDE (IN GRAMS) ON pH OF THE POTASSIUM ACETATE DEICER SOLUTION (50% Wt. SOLUTION) AT ROOM TEMPERATURE.

It is evident from Figure 26 that the pH of the plain potassium acetate deicer solution (10.86) increased rapidly upon addition of small amounts of calcium hydroxide, reaching a maximum pH value of 14.71 at a dosage of 0.5 grams. Incremental additions of calcium hydroxide beyond 0.5 grams did not influence the pH of the deicer solution any further. These findings suggest that the pH increase observed in the potassium acetate deicer solution depended on the amount of calcium hydroxide that went into solution at lower levels of addition (i.e. < 0.5 grams). Beyond 0.5 grams, it appears that the pH of the potassium acetate deicer remained unchanged, suggesting that a saturation limit for calcium hydroxide in the potassium acetate deicer solution had been reached. From these results, it is concluded that the calcium hydroxide that is normally present in hydrated portland cement (~ 20 - 25% by mass), is responsible for the observed increase in pH of the potassium acetate deicer soak solution in the modified ASTM C 1260 tests. The underlying chemistry involved in these hydrolysis reactions remains to be investigated in future studies.

5.3.3. Sodium Acetate Soak Solution

It is evident from Figure 25 that the measured pH of the saturated solution of sodium acetate at room temperature is 9.33. However, the pH of the solutions in which mortar bars were soaked ranged between 12.74 and 12.85, for the 4 aggregates evaluated in the study. Figure 27 shows the influence of addition of reagent grade calcium hydroxide on pH of saturated solution of sodium acetate deicer solution.

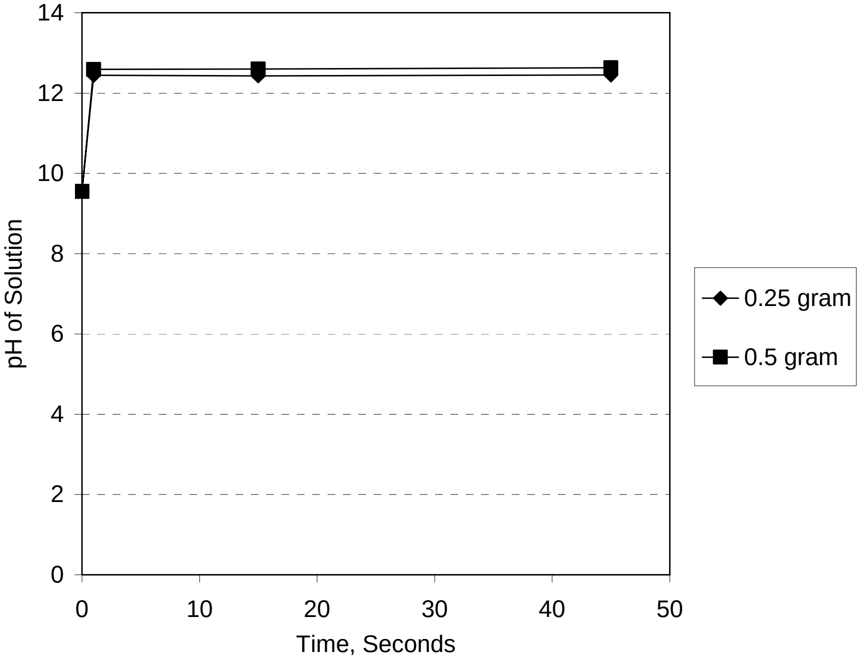


FIGURE 27. INFLUENCE OF ADDITION OF REAGENT GRADE CALCIUM HYDROXIDE (IN GRAMS) ON THE PH OF THE SATURATED SODIUM ACETATE DEICER SOLUTION AT ROOM TEMPERATURE.

It is evident from the results that a rapid and significant increase in pH of the saturated solution of sodium acetate deicer was observed upon addition of small quantities of reagent grade calcium hydroxide, similar to potassium acetate deicer solution, except that this increase was limited to slightly above the pH of a saturated calcium hydroxide in water solution. It is not yet evident as to the nature of the reaction that is leading to this rise in pH. It is suspected that this higher pH environment triggered by interactions between cement paste and deicer solution is likely to be responsible for alkali-silica reactions in the test specimens.

5.3.4. Sodium Formate Soak Solution

The change in pH of sodium acetate deicer solution exposed to mortar bars prepared with reactive and non-reactive aggregates is also shown in Figure 25. The results indicate that that the pH of the plain solution of sodium formate deicer at room temperature did not significantly differ from the pH of the sodium formate deicer solution in which mortar bars were soaked. Figure 28 shows the influence of addition of reagent grade calcium hydroxide on the pH of the saturated sodium formate deicer solution. Although, addition of calcium hydroxide caused an increase in the pH of the sodium formate deicer solution, the "pH jump" effect is subdued compared to other deicer solutions. It is not evident yet, as to the reasons behind such departure of behavior of sodium formate deicer from other deicers such as sodium acetate, potassium acetate and potassium formate.

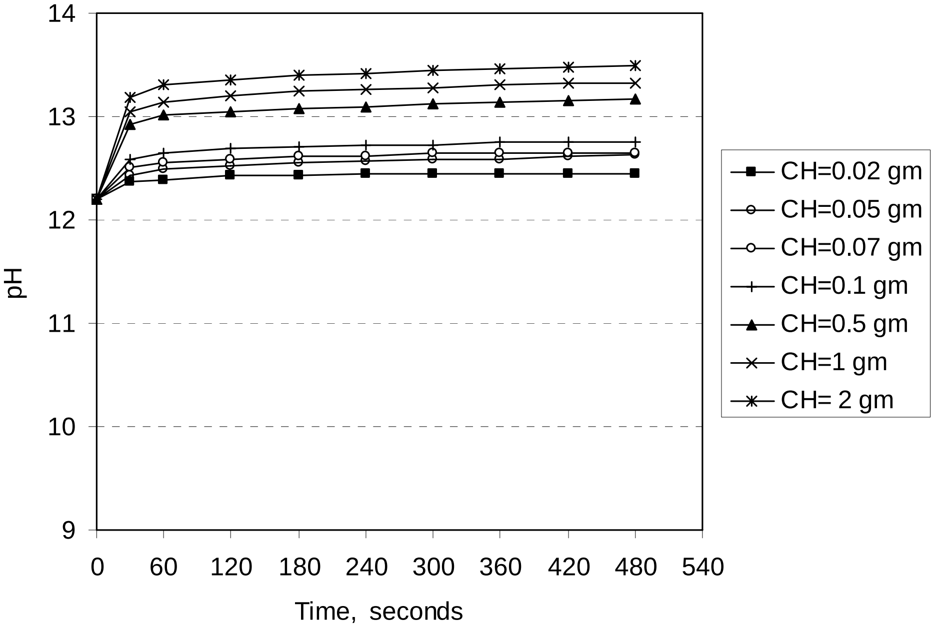


FIGURE 28. INFLUENCE OF ADDITION OF REAGENT GRADE CALCIUM HYDROXIDE (IN GRAMS) ON THE PH OF THE SATURATED SODIUM FORMATE DEICER SOLUTION AT ROOM TEMPERATURE.

5.3.5. Potassium Formate Soak Solution

Figure 25 shows the changes in pH of the potassium formate deicer soak solutions upon exposure to mortar bars. It is evident from the data that the behavior of potassium formate deicer solutions is very similar to that of potassium acetate and sodium acetate. However, it is to be noted that the difference between pH of the plain solution of potassium formate deicer (8.43) and solutions in which mortar bars were soaked (ranging between 13.97 – 14.27), is greater than either potassium acetate or sodium acetate deicer solutions, and substantially greater than that experienced with sodium formate deicer solution. Figure 29 shows the influence of addition of reagent grade calcium hydroxide on the pH of the potassium formate deicer solution. It is evident that even small additions of calcium hydroxide to potassium formate deicer solutions caused significant increase in the pH. The results shown in Figure 29 are comparable to those shown with potassium acetate solution in Figures 26.

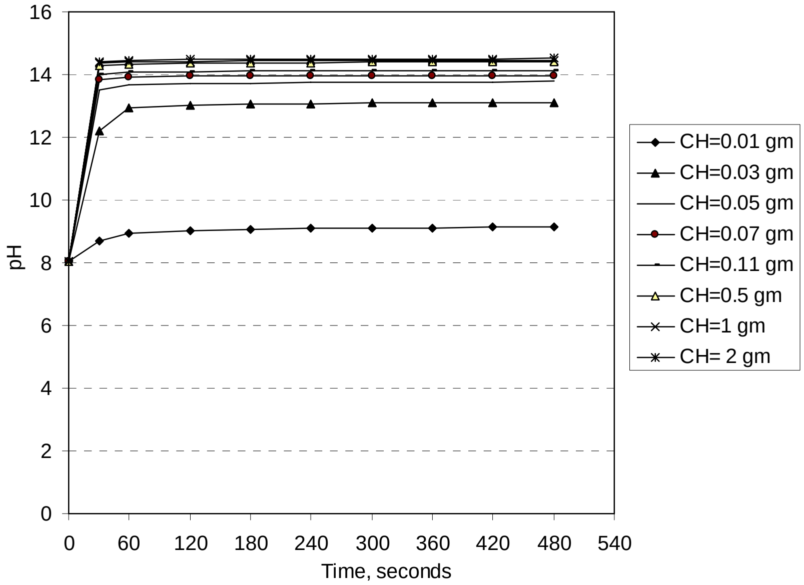


FIGURE 29. INFLUENCE OF ADDITION OF REAGENT GRADE CALCIUM HYDROXIDE (IN GRAMS) ON THE pH OF POTASSIUM FORMATE DEICER SOLUTION (50% Wt. SOLUTION) AT ROOM TEMPERATURE.

5.4. MICROSTRUCTURE INVESTIGATION OF MORTAR BARS FROM STANDARD AND MODIFIED ASTM C 1260 TESTS

This section of the report summarizes the main features observed during the SEM examination of mortar specimens tested using either standard or modified ASTM C1260 protocol as described in sections 3.2.1 and 3.2.2 of the report.

All SEM specimens were prepared following the procedure described in Section 3.2.7 of this report. In total, 25 different specimens including test specimens for each of the five aggregates in the standard and modified ASTM C 1260 tests prepared with HA cement were examined, as listed in Table 6. Since the expansion results in the modified ASTM C 1260 tests for all the mortars prepared with LA cement were similar to those with HA cement, mortar bars prepared with the former cement were not examined. The symbols shown in Table 6 represent the name designations in the Appendix that contains the SEM micrographs collected for those individual specimens. For example, the series of micrographs collected for North Carolina argillite exposed to sodium acetate solution can be found in the Appendix **A-III-3**. On average about 10 micrographs were collected from each specimen, but only a smaller group were selected to be included in the Appendix in order to limit the overall size of the report.

TABLE 6. TEST MATRIX FOR SEM/EDX ANALYSIS OF MORTAR SPECIMENS

Specimen Type	Soak Solution	Non-Reactive Aggregate	Reactive Aggregate			
		Standard Ottawa Sand	Spratt Limestone	NC Argillite	NM Rhyolite/Andesite	SD Sioux Quartzite
Reference	1N Sodium Hydroxide	**A-I-1**	**A-I-2**	**A-I-3**	**A-I-4**	**A-I-5**
Test	Potassim Acetate	**A-II-1**	**A-II-2**	**A-II-3**	**A-II-4**	**A-II-5**
	Sodium Accetate	**A-III-1**	**A-III-2**	**A-III-3**	**A-III-4**	**A-III-5**
	Sodium Formate	**A-IV-1**	**A-IV-2**	**A-IV-3**	**A-IV-4**	**A-IV-5**
	Potassium Formate	**A-V-1**	**A-V-2**	**A-V-3**	**A-V-4**	**A-V-5**

Due to the large number of images involved, it was impractical to analyze each of them individually. Instead, the authors of the report adopted an approach in which the effects of the deicers on the microstructure of mortars were evaluated in three broad categories: *presence and location of cracks*, *presence and location of gel*, and *alteration of paste composition* (see Tables for the individual deicers in the next section). For each of these categories, the severity of the effect was assigned a relative rating (ranging from light to severe) as shown in Table 7. The discussion presented in the remaining part of this chapter constitutes the author's attempt to generalize the main changes in the characteristics of microstructure resulting from exposure to the different deicers.

TABLE 7. RELATIVE RANKINGS OF SEVERITY OF MICROSTRUCTURAL CHANGES OBSERVED DURING THE SEM/EDX ANALYSIS OF MORTAR SPECIMENS

Relative Ranking of Severity	Description
"no"	The feature of interest not observed
"+"	The feature of interest present but the intensity was *light*
"++"	*Moderate* intensity of the feature of interest
"+++"	*Severe* intensity of the feature of interest
"-"	Not possible to confirm if the feature of interest was present due to lack of supporting evidence (e.g. no EDX in the paste)

5.4.1. Mortar Specimens Exposed to 1N Sodium Hydroxide Soak Solution

Table 8 summarizes the main features observed during the SEM observations of mortar specimens exposed to 1N sodium hydroxide solution during the standard ASTM C1260 test.

TABLE 8. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF MORTAR SPECIMENS EXPOSED TO 1N SODIUM HYDROXIDE SOLUTION (STANDARD ASTM C1260 TEST).

Main Features of the Microstucture		**Sodium Hydroxide (NaOH)**				
		Ottawa	Spratt	NC	NM*	SD
Cracking - general appearance		+	+	+	+	+
	within the aggregate	no	++	+	+	++
	within the paste	+	+	+	+	+
	at the interfaces	no	no	no	no	no
gel presence		no	+	+	+	+
	within the aggregate	no	+	+	+	+
	within the paste	no	+ (pores)'	+ (pores)'	no	no
	at the interfaces	no	no	no	+	no
paste alteration						
	increased level of K	no	no	no	no	no
	increased level of Na	+	+	no	-	no
	increased level of S	no	no	no	no	no
	increased level of Al	no	no	no	no	no
	presence of Na-Ca-S	no	no	no	no	no
	presence of K-Ca-S	no	no	no	no	no
	presence of monosulfate	-	-	+	-	-

**Presence of gel observed in pockets and cracks of the NM rhyolite*

In general, only occasional cracking was observed in the paste of mortar bars containing the reference, non-reactive aggregate (Ottawa sand) but there were no cracks seen in the aggregates themselves. A typical example is presented in Figure 30. The composition of paste for this mortar was not altered and no gel was observed.

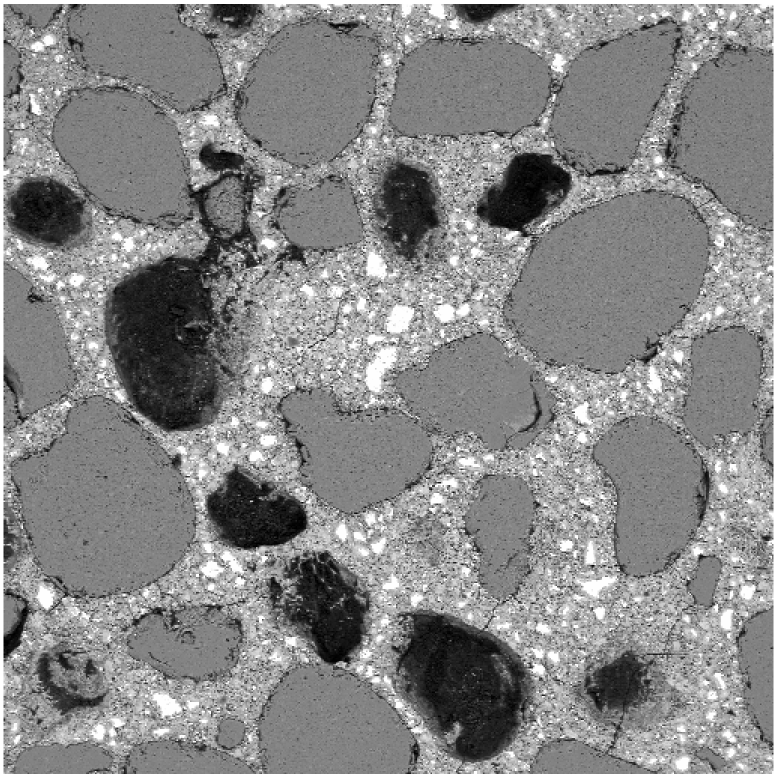


FIGURE 30. TYPICAL MICROSTRUCTURE OF OTTAWA SAND MORTAR EXPOSED TO 1N NaOH SOLUTION

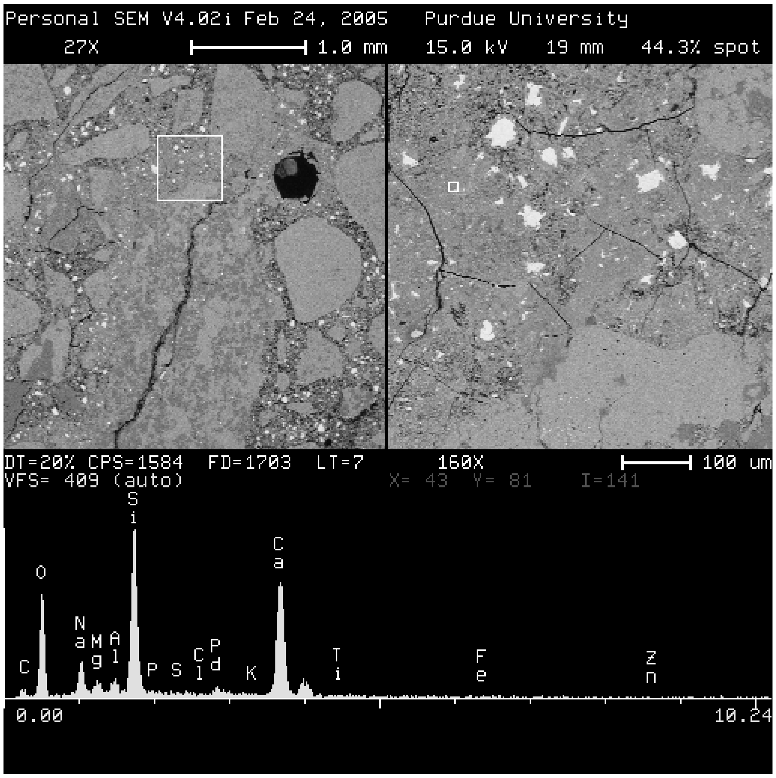


FIGURE 31. MICROSTRUCTURE OF SPRATT LIMESTONE MORTAR EXPOSED TO 1N NaOH SOLUTION

In contrast, a fair amount of cracking was observed both within the aggregates and in the paste components of mortars prepared with the Spratt aggregate. A typical example is shown in Figure 31. For these mortars, dense regions of paste containing deposits of gel (Ca-Si-Na) were also observed (see Figure 31). As seen in the same figure, the paste in the vicinity of these dense regions contained short cracks. In general, the cracks in paste appear to be mostly empty, in contrast the cracks in aggregate are partially or totally in-filled with gel. Occasional deposits of gel were also observed in the air voids (in the form of thin layer deposited around the perimeter of the void) as illustrated in Figure 32.

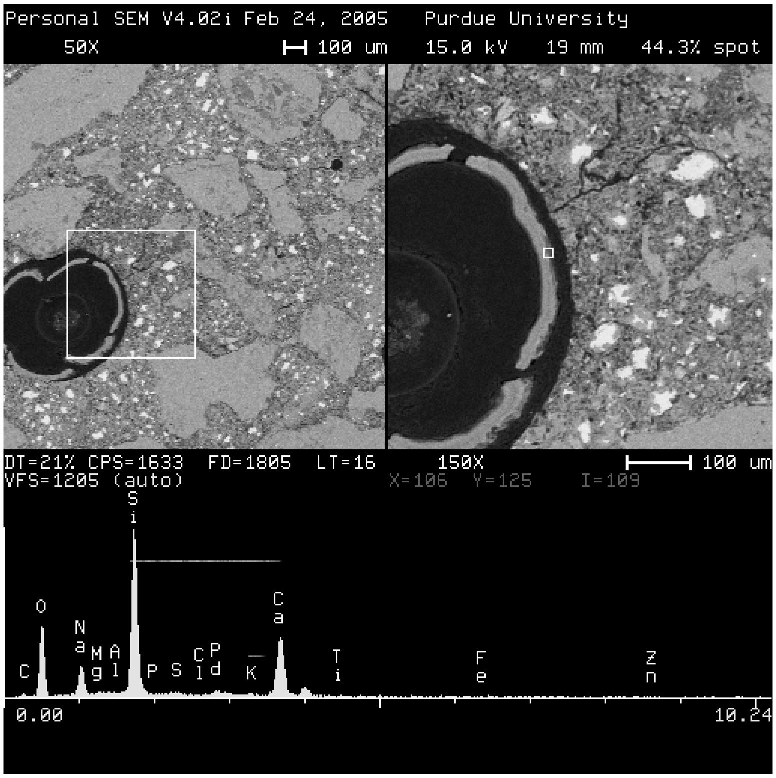


FIGURE 32. ROUND VOID WITH LINING OF Ca-Si-Na GEL IN SPRATT LIMESTONE MORTAR

Similarly, a fair level of cracking was also observed in mortars containing the NM rhyolite and the SD quartzite aggregates. However, in both sets of mortar the aggregate grains were cracked more than the paste (see Figures 33 and 34). Many of the aggregate cracks were in-filled with Ca-Si-Na gel.

For mortars containing the NC argillite aggregate only few cracks were observed in the paste, but the aggregate particles themselves were moderately cracked.

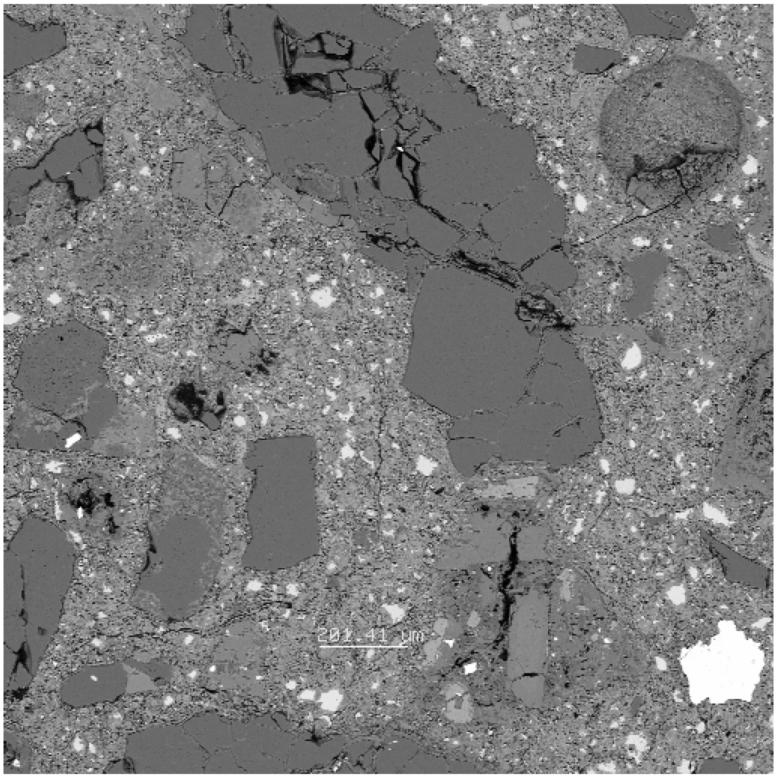


FIGURE 33. MICROSTRUCTURE OF NM RHYOLITE MORTAR EXPOSED TO 1N NaOH SOLUTION

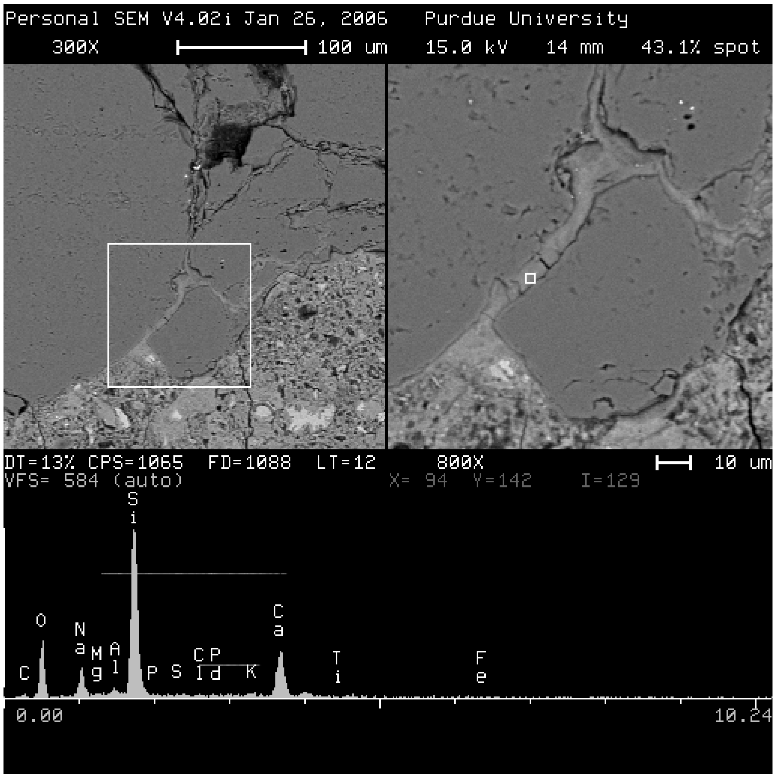


FIGURE 34. Ca-Si-Na GEL IN THE PARTICLE OF SD QUARTZITE EXPOSED TO 1N NaOH SOLUTION

5.4.2. Mortar Specimens Exposed to Potassium Acetate Deicer Soak Solution

Table 9 summarizes the main features observed during the SEM observations of mortar specimens exposed to potassium acetate solution in the modified ASTM C1260 test.

TABLE 9. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF MORTAR SPECIMENS EXPOSED TO POTASSIUM ACETATE SOLUTION (MODIFIED ASTM C1260 TEST).

Main Features of the Microstucture		**Potassium Acetate (KAc)**				
		Ottawa	Spratt	NC	NM	SD
Cracking - general appearance		no	++	++	+++	++
	within the aggregate	no	++	++	++	++
	within the paste	no	++	+	+++	+
	at the interfaces	no	++	+	+++	+
gel presence		no	++	++	-	+
	within the aggregate	no	++	+++	-	+
	within the paste	no	++	+	-	no
	at the interfaces	no	no	no	-	no
paste alteration						
	increased level of K	+	-	-	+	++
	increased level of Na	no	-	-	no	no
	increased level of S	no	-	-	+	no
	increased level of Al	no	-	-	no	no
	presence of Na-Ca-S	no	-	-	no	no
	presence of K-Ca-S	no	+	-	++	no
	presence of monosulfate	-	-	-	-	-

In general, neither paste nor aggregate grains suffered visible damage in mortar bars containing the reference non-reactive aggregate (Ottawa sand). The composition of paste for this mortar was not altered and no gel was observed.

On the other hand, extensive cracking was observed in mortar specimens prepared with the New Mexico rhyolite and Spratt limestone aggregates. In both cases, open (and mostly empty) cracks were prominently observed in the paste and at the interfaces with aggregate particles, as illustrated in Figure 35 (for the Spratt limestone) and Figure 36 (for the NM rhyolite). The presence of gaps around the aggregate implies the possibility of overall paste expansion, in addition to the expansion of the aggregate grains themselves.

The paste expansion may account for the majority of the expansion observed in the NM specimens as, in general, no cracks were observed within the aggregate grains themselves. Rather, the paste in the vicinity of the aggregate was morphologically changed and “infused” with Si-K-Ca gel, as shown in Figure 37. Due to very reactive nature of the NM rhyolite aggregate, it is likely that most of the reaction occurred on the aggregate surface, rather than within the aggregate grain. This mode of reaction is also supported by the rapid expansions observed in the NM rhyolite mortar bars exposed to potassium acetate deicer solution (see Figure

10). In contrast, some cracks were present in the Spratt aggregate particles, but these were typically in-filled with gel (see Figure 38).

The mortar specimens containing SD quartzite and exposed to the potassium acetate solution developed network of cracks both in the aggregate particles (Figure 39) and in the paste (Figure 40). In these mortars the cracks within the aggregate grains were between the detrital quartz grains of the quartzite, with the preferential site for the reaction being the secondary quartz cement. Most of these cracks are filled with Si-K-rich gel (see Figure 41). In contrast, the cracking of the paste is not very extensive and most cracks appear to be empty. In general, the paste contains increased levels of K (see Figure 40).

The cracking observed in the NC argillite mortar was not as extensive as cracking in either the Spratt limestone or the NM rhyolite mortars. An illustration is provided in Figure 42. The bigger cracks were predominantly present either in the aggregate itself or at the paste-aggregate interface. The cracks present in the aggregate were often filled with gel. The larger cracks in the paste itself were mostly empty. They often appeared to be an extension of the cracks that originated in the aggregate (Figure 43). Smaller empty paste cracks were often seen as accompanying the larger crack and were typically oriented perpendicular to them (see Figure 43).

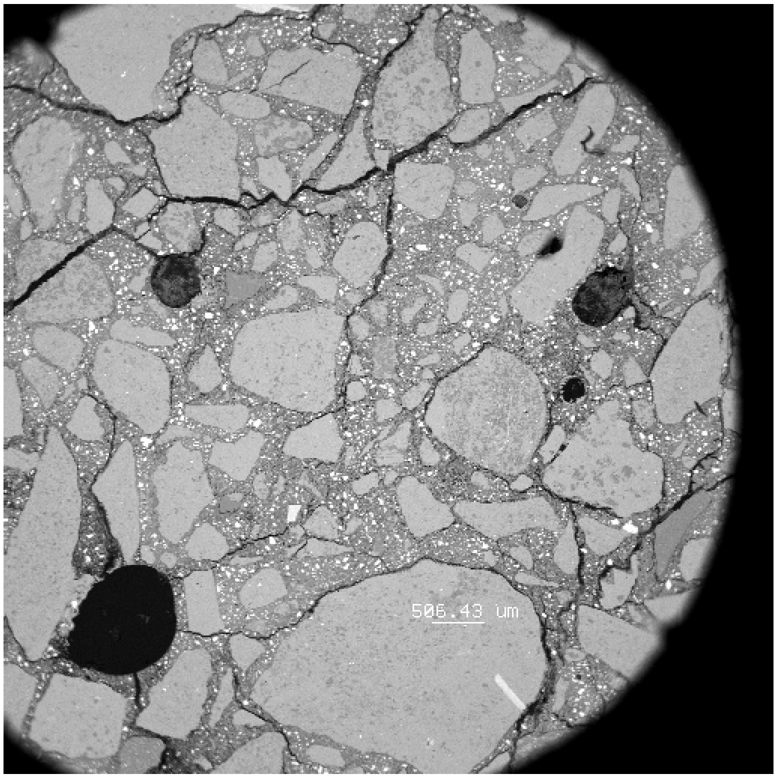


FIGURE 35. EXTENSIVE CRACKING OF THE SPRATT LIMESTONE MORTAR EXPOSED TO KAc SOLUTION

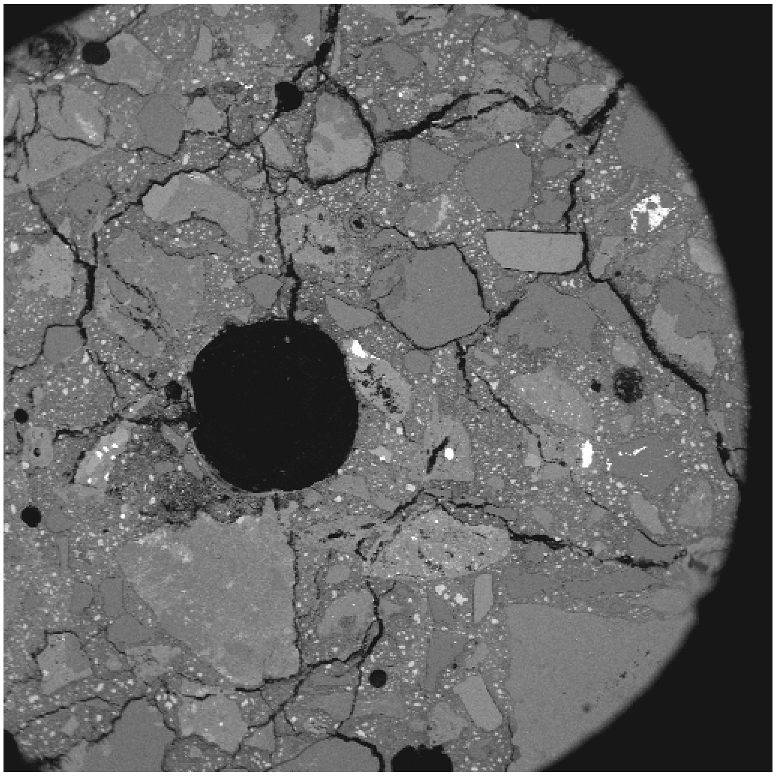


FIGURE 36. CRACKING OF THE NM RHYOLITE MORTAR EXPOSED TO KAc SOLUTION

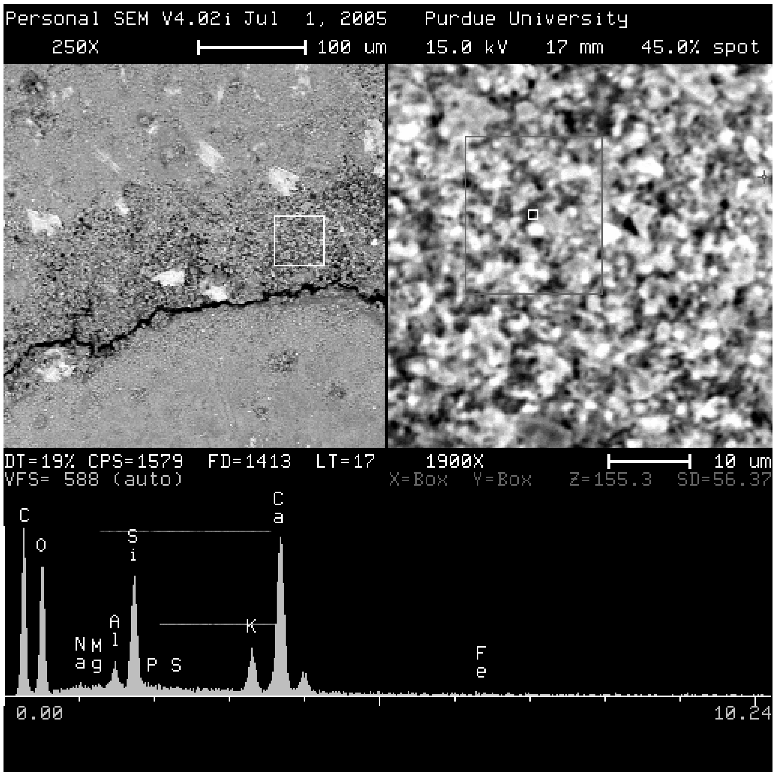


FIGURE 37. Si-K-Ca GEL IN THE INTERFACIAL ZONE OF NM RHYOLITE MORTAR EXPOSED TO KAc SOLUTION

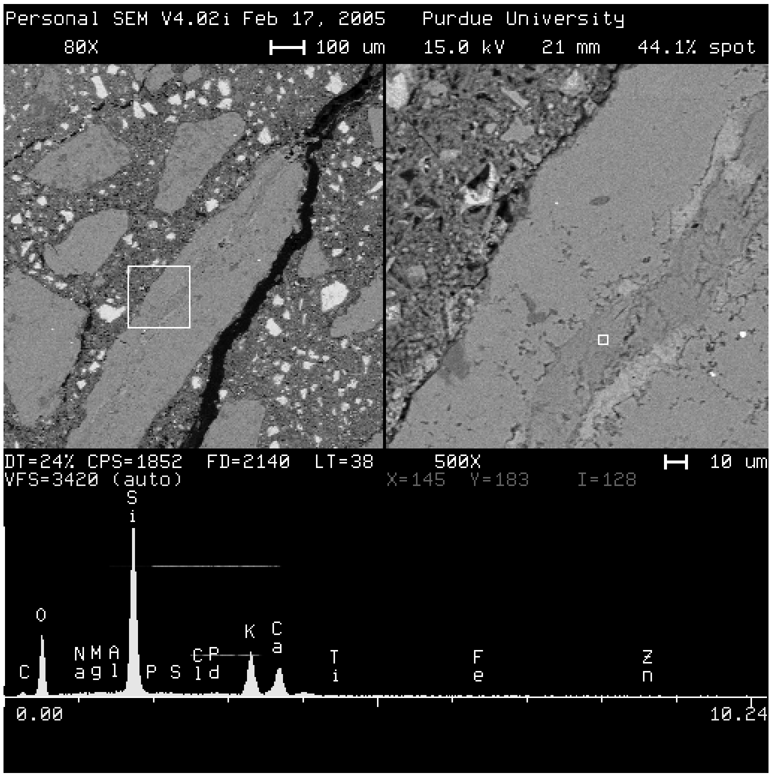


FIGURE 38. Si-K-Ca GEL-FILLED CRACK IN THE PARTICLE OF SPRATT LIMESTONE MORTAR EXPOSED TO KAc SOLUTION

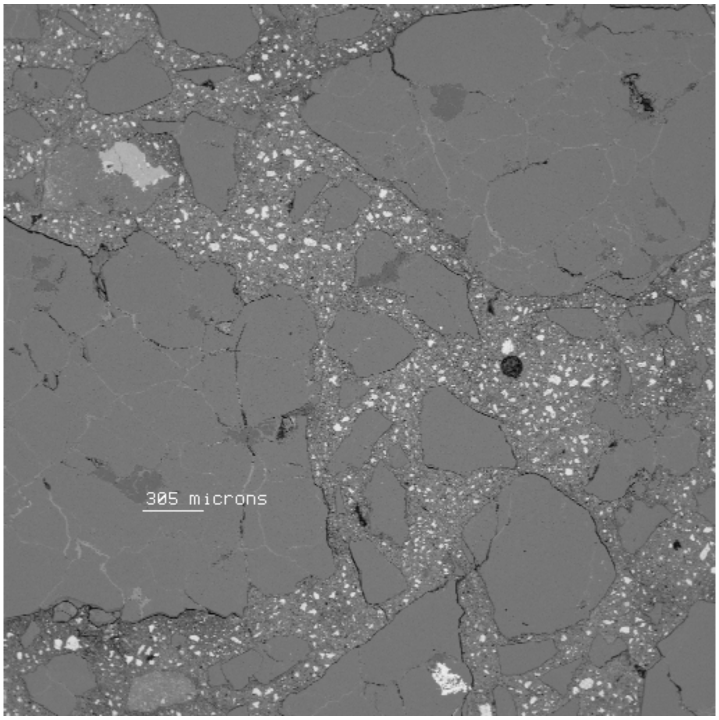


FIGURE 39. SD QUARTZITE MORTAR EXPOSED TO KAc SOLUTION WITH VISIBLE NETWORK OF GEL-FILLED CRACKS WITHIN THE AGGREGATE PARTICLES

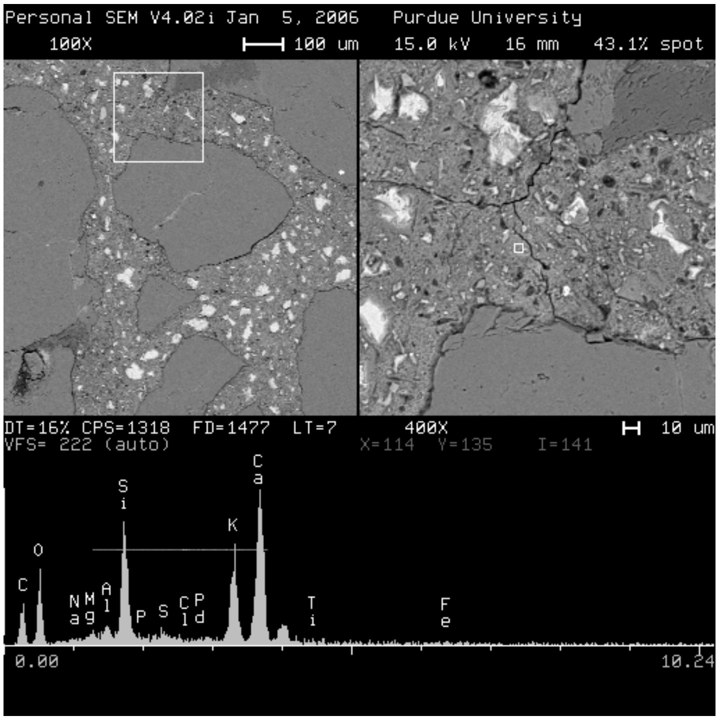


FIGURE 40. GEL-CONTAINING NETWORK OF FINE CRACKS IN THE PASTE FRACTION OF MORTAR SPECIMEN WITH SD QUARTZITE EXPOSED TO KAc SOAK SOLUTION.

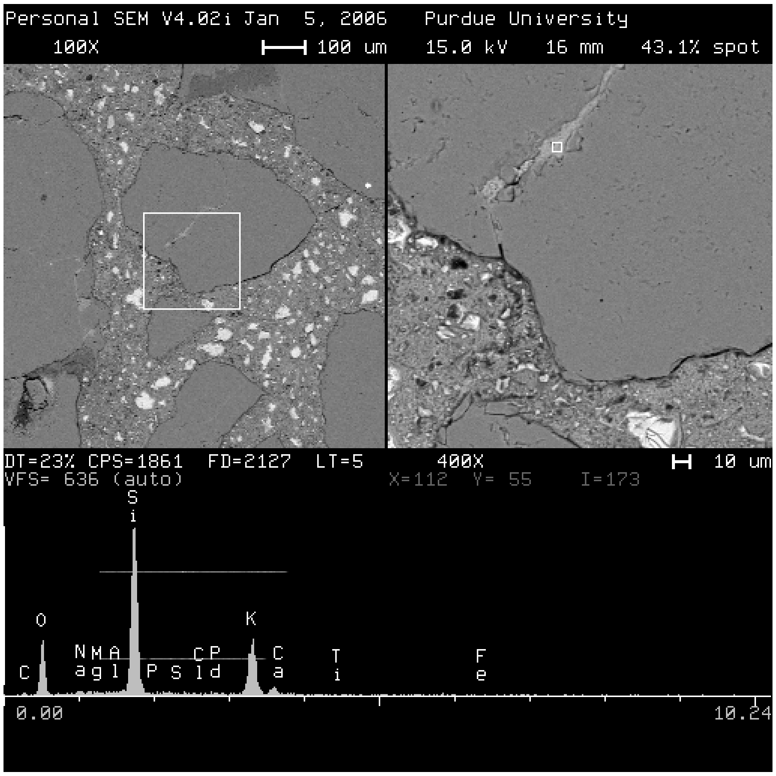


FIGURE 41. Si-K RICH GEL IN THE CRACKS OF MORTAR SPECIMENS CONTAINING SD QUARTZITE EXPOSED TO KAc DEICER

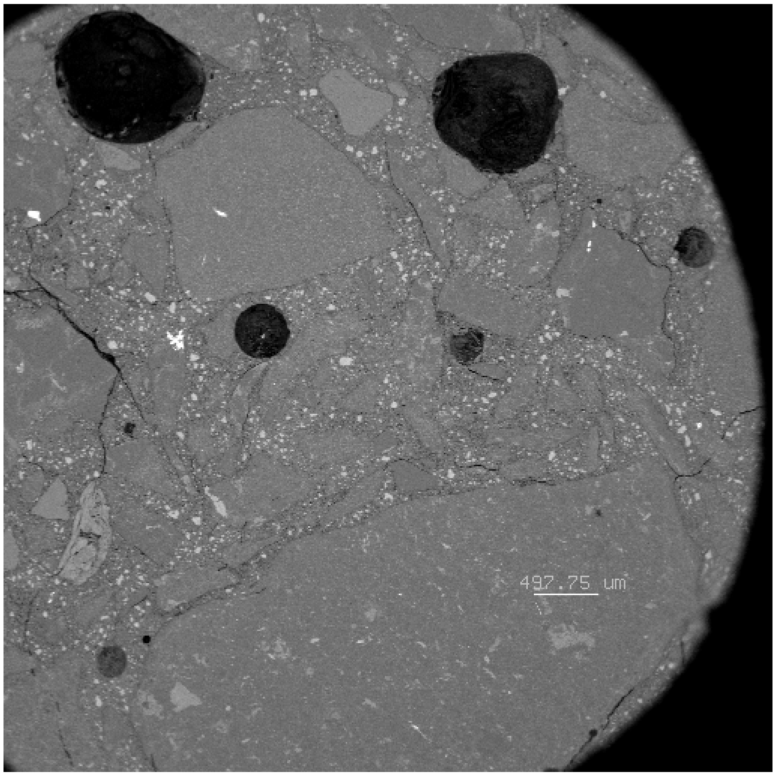


FIGURE 42. NETWORK OF CRACKS IN THE NC ARGILLITE MORTAR SPECIMEN EXPOSED TO POTASSIUM ACETATE DEICER

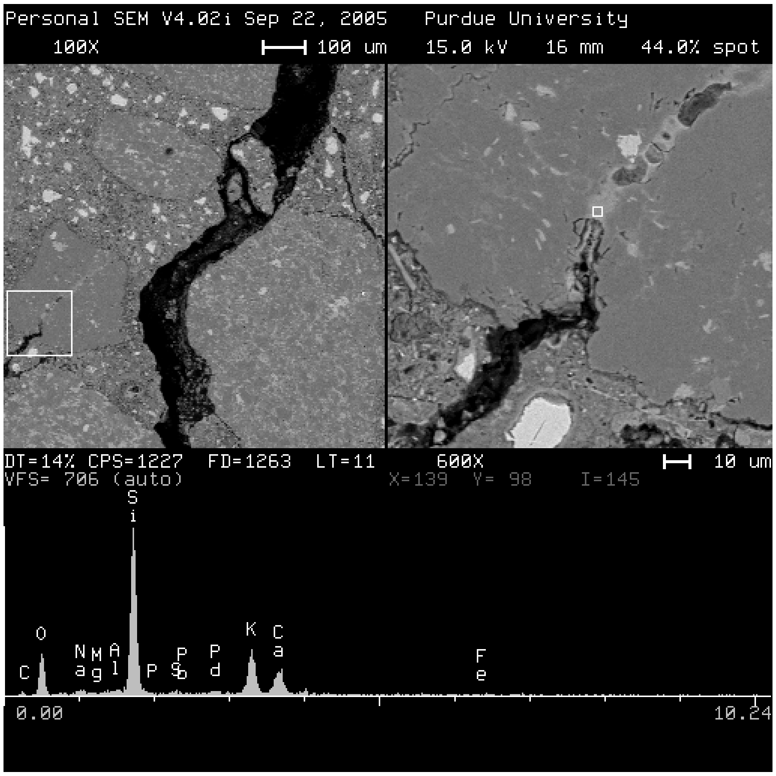


FIGURE 43. LARGE CRACKS IN PASTE (WITH SMALLER CRACKS ORIENTED PERPENDICULAR TO THE LARGER CRACK) IN THE NC ARGILLITE MORTAR SPECIMEN EXPOSED TO KAc DEICER

5.4.3. Mortar Specimens Exposed to Sodium Acetate Deicer Soak Solution

Table 10 summarizes the main features observed during the SEM observations of mortar specimens exposed to sodium acetate solution in the modified ASTM C1260 test.

TABLE 10. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF MORTAR SPECIMENS EXPOSED TO SODIUM ACETATE SOLUTION

Main Features of the Microstucture		**Sodium Acetate (NaAc)**				
		Ottawa	Spratt	NC	NM	SD
Cracking - general appearance		no	+	+++	+++	+++
	within the aggregate	no	+	+++	+++	++
	within the paste	no	+	+++	+++	+++
	at the interfaces	no	+	++	+++	+++
gel presence		no	+	++	++	+
	within the aggregate	no	+	+	+	+
	within the paste	no	+	+	+	no
	at the interfaces	no	+	no	+	no
paste alteration						
	increased level of K	no	no	no	-	no
	increased level of Na	+	+	+	-	+
	increased level of S	+	no	+	-	-
	increased level of Al	no	no	+	-	-
	presence of Na-Ca-S	+	no	-	-	-
	presence of K-Ca-S	no	no	-	-	-
	presence of monosulfate	-	+	+	-	+

Similarly to what has been reported for other deicers, no signs of significant damage were observed in the paste or the aggregates grains of mortar bars containing the reference non-reactive aggregate (Ottawa sand) that was exposed to sodium acetate deicer. However, some areas of the paste showed increased levels of sulfur (S) and sodium (Na), as well as the presence of material with Na-S-Ca composition.

All mortars prepared with reactive aggregates showed some degree of cracking when exposed to the sodium acetate deicer. Particularly, extensive cracking was observed for NM rhyolite, NC argillite and SD quartzite mortars. The paste cracks in NM rhyolite specimens were generally quite wide (some approaching 100 µm in width), in contrast in these mortars the cracks in the aggregate particles were mostly much narrower (see Figure 44). The wide paste cracks were generally empty, in contrast the generally narrow cracks in the aggregate were often filled with Ca-Si-Na gel (see Figure 45). Very similar features (broad mostly empty cracks within the paste and presence of gel in the cracks of aggregate) were also observed in the SD quartzite mortars (Figures 46 and 47) and NC argillite mortars (Figures 48 and 49).

In contrast to mortars made with these aggregates, much less cracking was observed in mortars made with Spratt limestone. A few cracks in the aggregate contained gel that was “outflowing” into the paste (see Figure 50). Several locations within the paste contained monosulfate (see Figure 51).

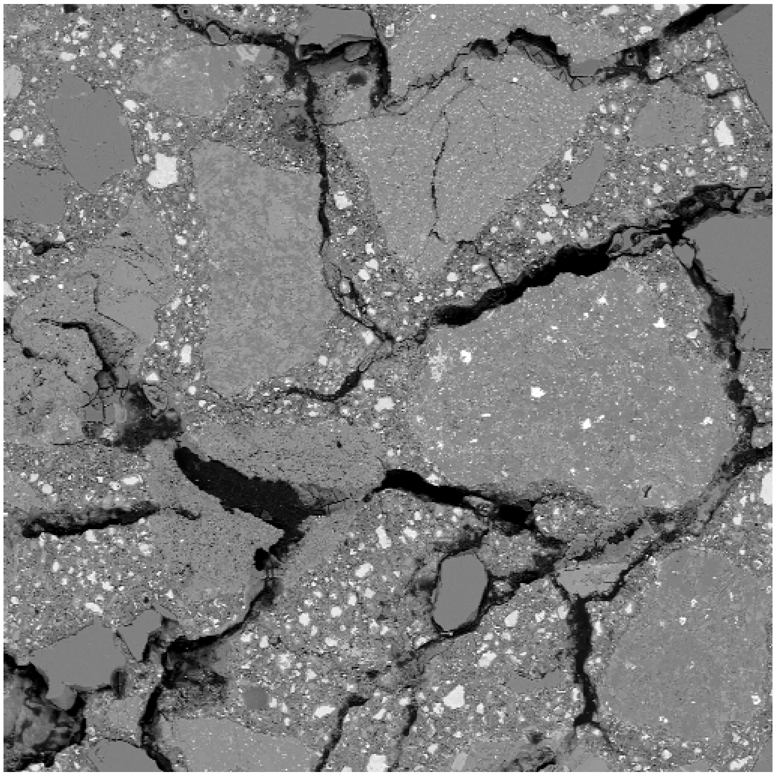


FIGURE 44. GENERAL APPEARANCE OF THE NM RHYOLITE MORTAR SPECIMEN EXPOSED TO THE SODIUM ACETATE DEICER. EXTENSIVE CRACKS IN THE PASTE AND IN THE AGGREGATE.

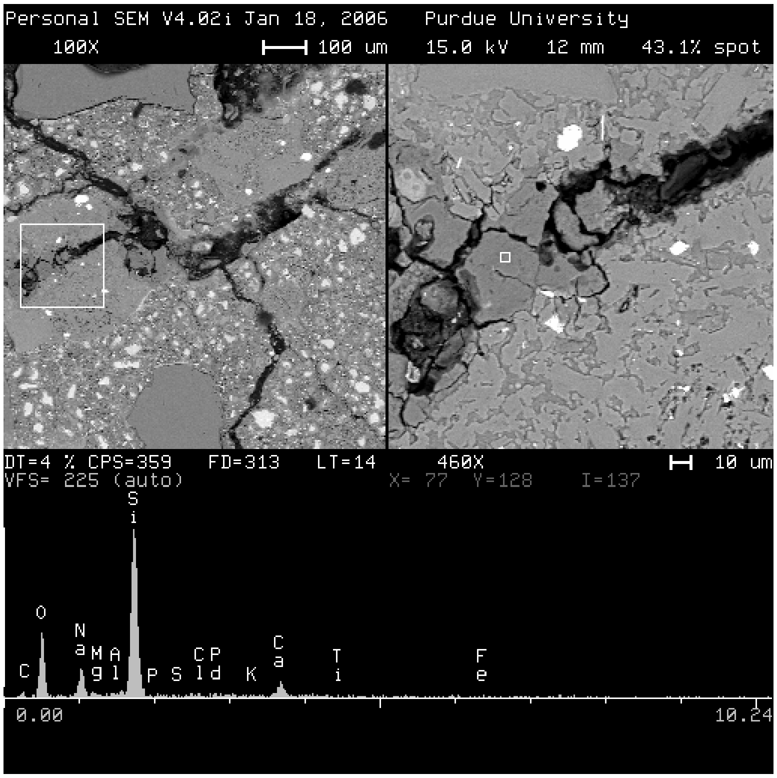


FIGURE 45. Na-Si-Ca GEL IN THE CRACK OF NM RHYOLITE EXPOSED TO SODIUM ACETATE DEICER

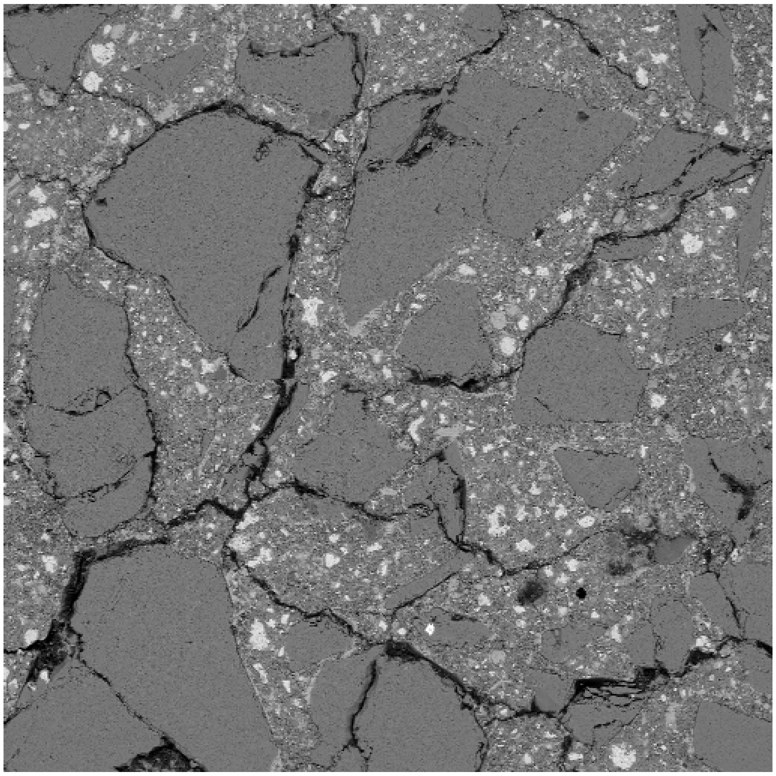


FIGURE 46. EXTENSIVE CRACKING OF THE SD QUARTZITE MORTAR EXPOSED TO THE SODIUM ACETATE DEICER

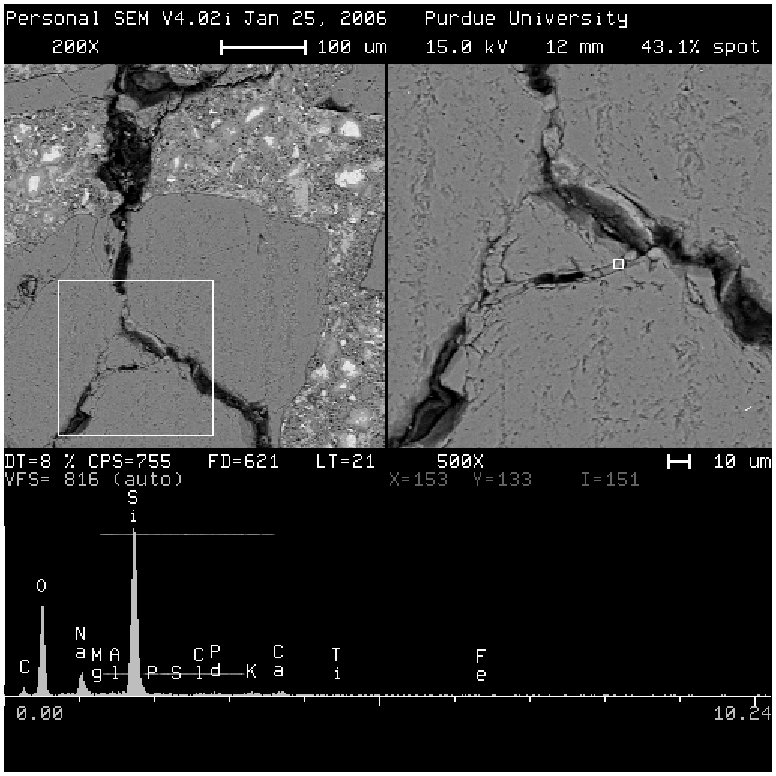


FIGURE 47. CRACK FILLED WITH Na-Si GEL IN THE GRAIN OF SD QUARTZITE EXPOSED TO THE SODIUM ACETATE DEICER

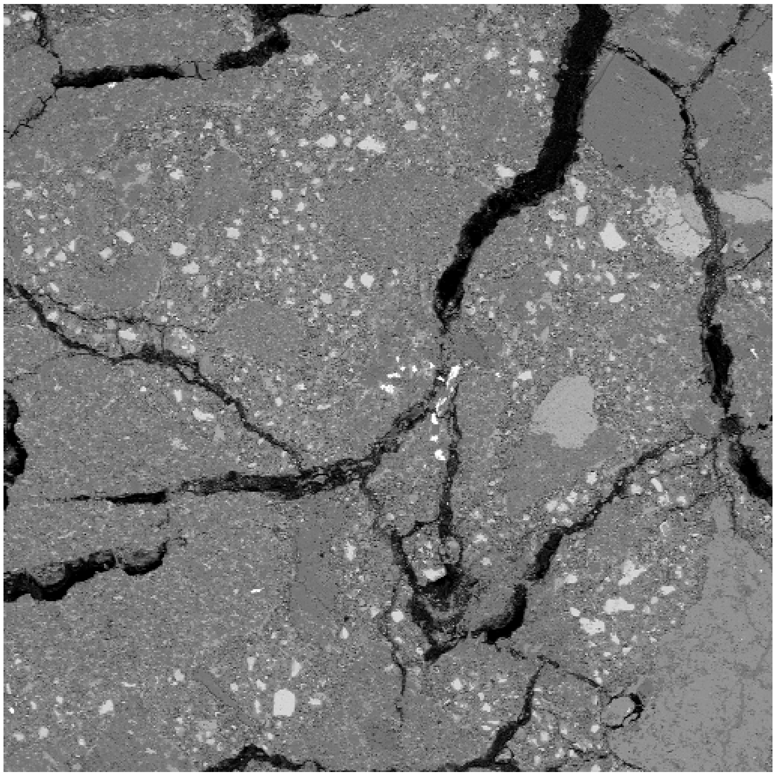
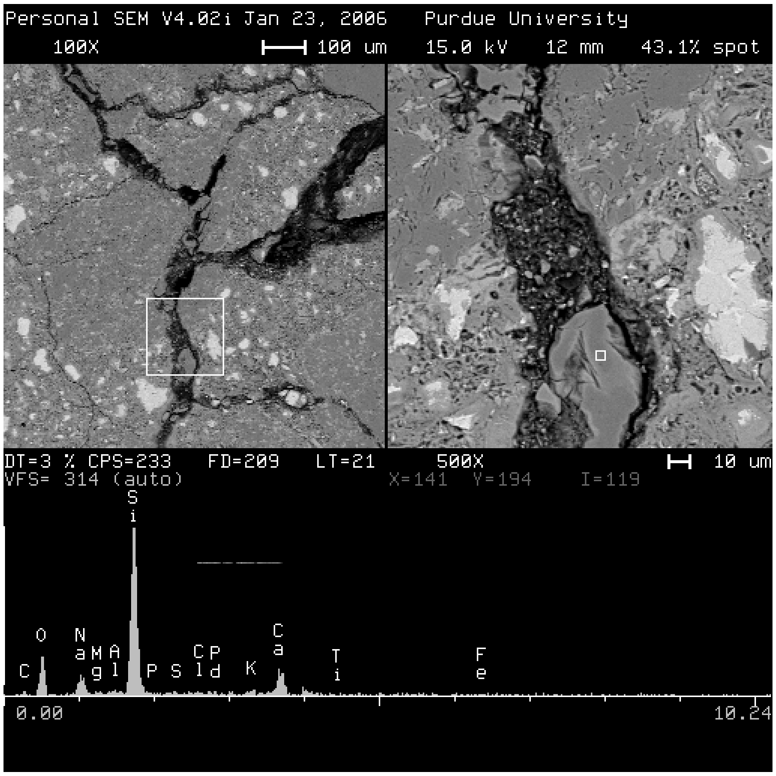


FIGURE 48. CRACKED NC ARGILLITE MORTAR EXPOSED TO SODIUM ACETATE DEICER



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Personal SEM V4.02i Jan 23, 2006    Purdue University
    100X            100 um   15.0 kV    12 mm    43.1% spot
DT=3 % CPS=233    FD=209    LT=21      500X          10 um
VFS= 314 (auto)                    X=141  Y=194     I=119
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FIGURE 49. Na-Si GEL INSIDE THE CRACK OF NC ARGILLITE SPECIMEN EXPOSED TO SODIUM ACETATE DEICER

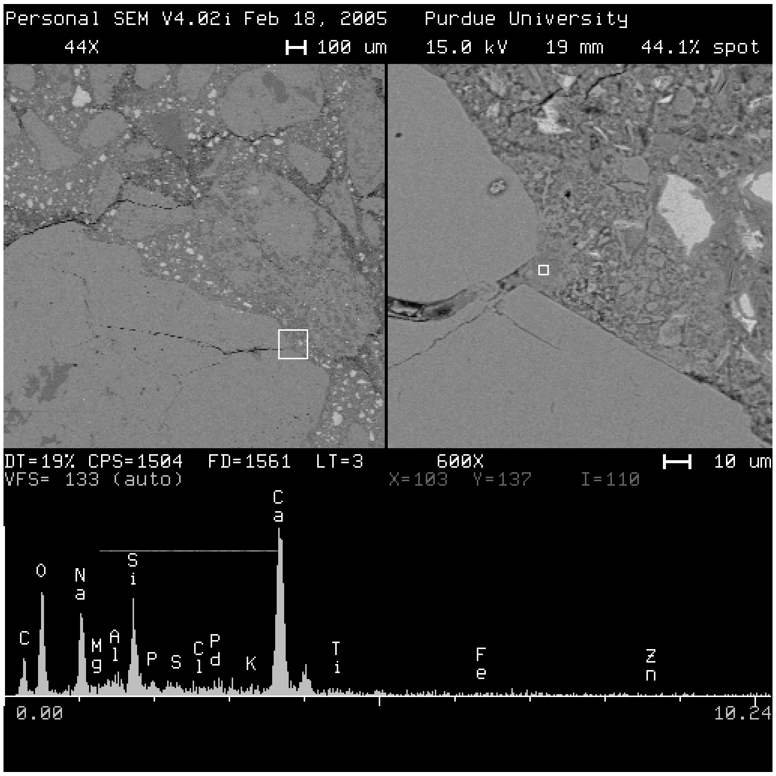

FIGURE 50. RIVER OF GEL IN THE SPRATT LIMESTONE AGGREGATE EXPOSED TO SODIUM ACETATE DEICER

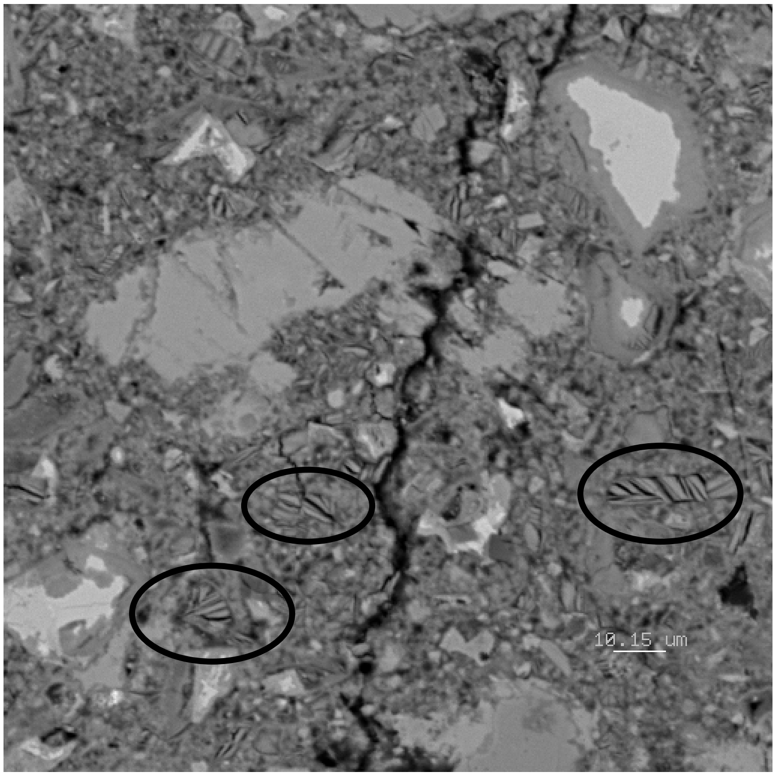

FIGURE 51. MONOSULFATE IN THE PASTE OF SPRATT LIMESTONE MORTAR EXPOSED TO SODIUM ACETATE SOLUTION

5.4.4. Mortar Specimens Exposed to Sodium Formate Deicer Soak Solution

Table 11 summarizes the main features observed during the SEM observations of mortar specimens exposed to sodium formate solution in the modified ASTM C1260 test.

TABLE 11. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF MORTAR SPECIMENS EXPOSED TO SODIUM FORMATE SOLUTION (MODIFIED ASTM C1260 TEST)

Main Features of the Microstucture		**Sodium Formate (NaFr)**				
		Ottawa	Spratt	NC	NM	SD
Cracking - general appearance		++	+	++	++	++
	within the aggregate	++	+	++	++	+++
	within the paste	+	+ (pores)'	+	+	+
	at the interfaces	no	+	no	++	no
gel presence		+	+	++	++	+
	within the aggregate	+	+	++	++	+
	within the paste	no	+	+	++	++
	at the interfaces	no	+	no	++	no
paste alteration						
	increased level of K	no	-	-	-	-
	increased level of Na	+	+	-	-	-
	increased level of S	no	-	-	-	-
	increased level of Al	no	-	-	-	-
	presence of Na-Ca-S	no	-	+	-	-
	presence of K-Ca-S	no	-	-	-	-
	presence of monosulfate	-	+	-	-	+

**Rivers of gel observed in the NC argillite, NM rhyolite and SD quartzite aggregates*

In contrast to what was observed for previously discussed deicers, the sodium formate solution seems to have initiated the ASR reaction within the grains of Ottawa sand, which was used as a control (i.e. non-reactive) aggregate in this study. The affected grains were seen to be partially dissolved and cracked, with cracks extending to the paste (see Figure 52). Closer examination of the cracks in the grains indicated that they contain Ca-Si-Na gel (see Figure 53).

Massive amount of cracking was observed in the paste of the NM rhyolite mortars exposed to sodium formate deicer solution with the widest cracks typically present at the interface between the aggregate and the surrounding paste matrix (see Figure 54). Some of the severely distressed rhyolite grains were surrounded by layers of Na-Si-Ca gel, as shown in Figure 55. In contrast to these observations, the damage observed in the NC argillite mortars exposed to sodium formate was typically confined to the grains of the aggregate themselves (see Figure 56). The affected grains were severely eroded and cracked, with parts of the cracks being filled with Na-Si-Ca gel that was out-flowing into the surrounding paste (see Figure 57). Very similar observations were recorded for sodium formate-exposed mortars containing Spratt aggregate (see Figures 60 and 61). Signs of severe erosion were also noted in grains of SD quartzite exposed to sodium formate (Figure 60), with rivers of Ca-Si-Na gel protruding into the adjacent paste (Figure 61).

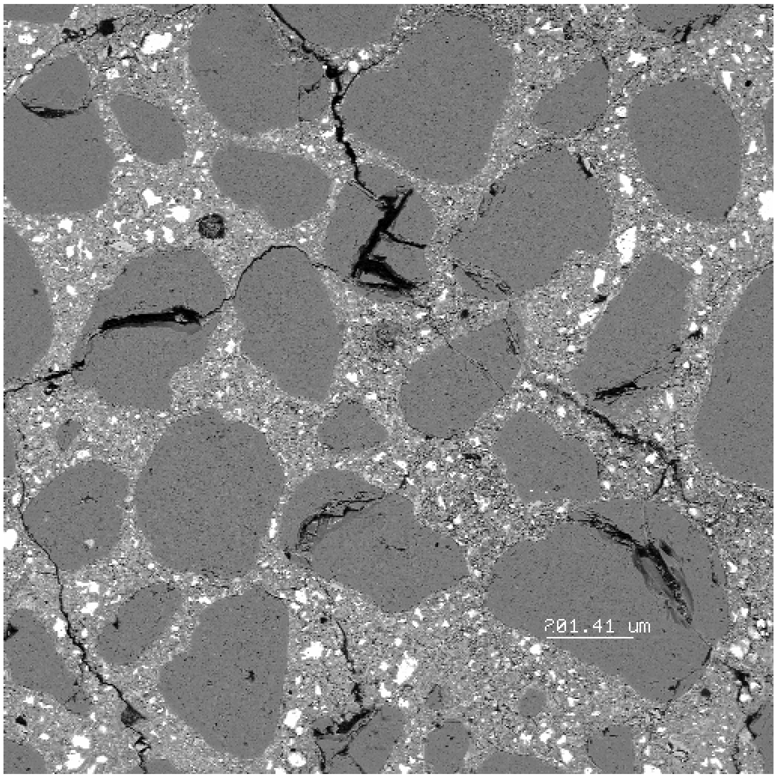

FIGURE 52. AGGREGATE AND PASTE CRACKS IN THE OTTAWA SAND MORTAR SOAKED IN SODIUM FORMATE SOLUTION

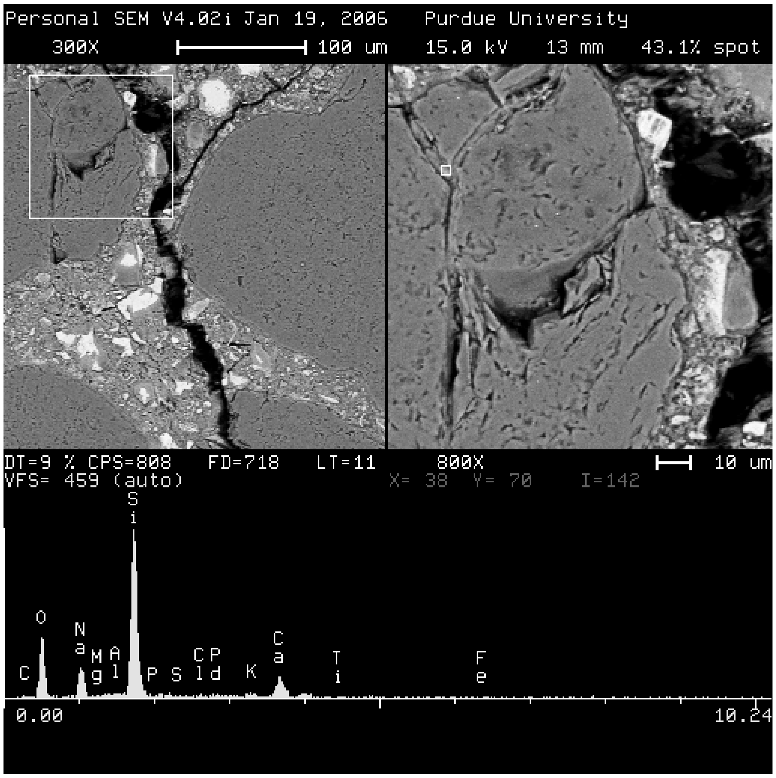

FIGURE 53. Ca-Si-Na GEL IN THE SEVERELY DISTRESSED GRAIN OF OTTAWA SAND (MORTAR SOAKED IN SODIUM FORMATE SOLUTION).

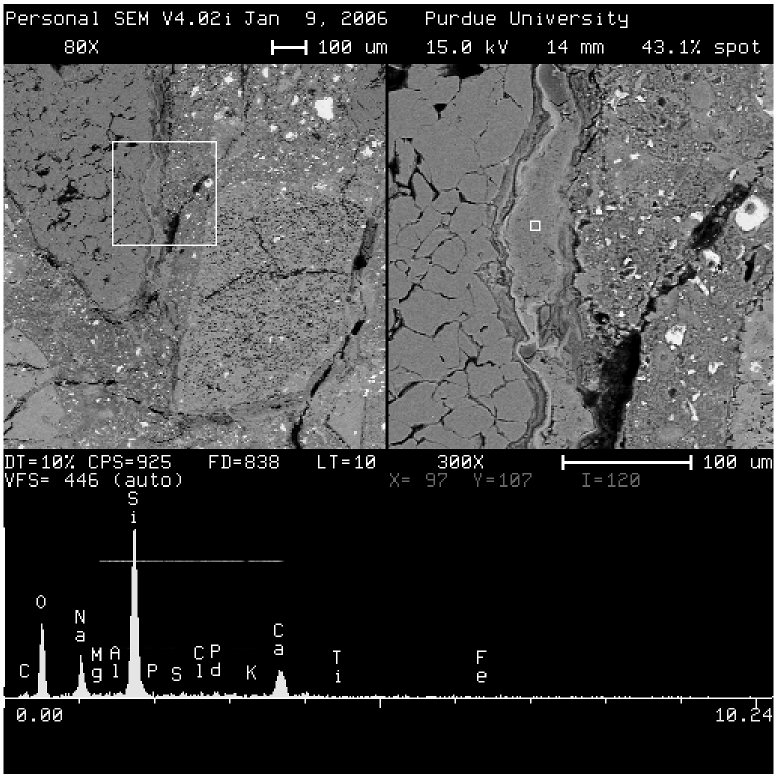

FIGURE 54. MASSIVE CRACKS IN THE PASTE OF NM RHYOLITE MORTARS SOAKED IN SODIUM FORMATE SOLUTION. LAYER OF GEL IN THE AIR VOID

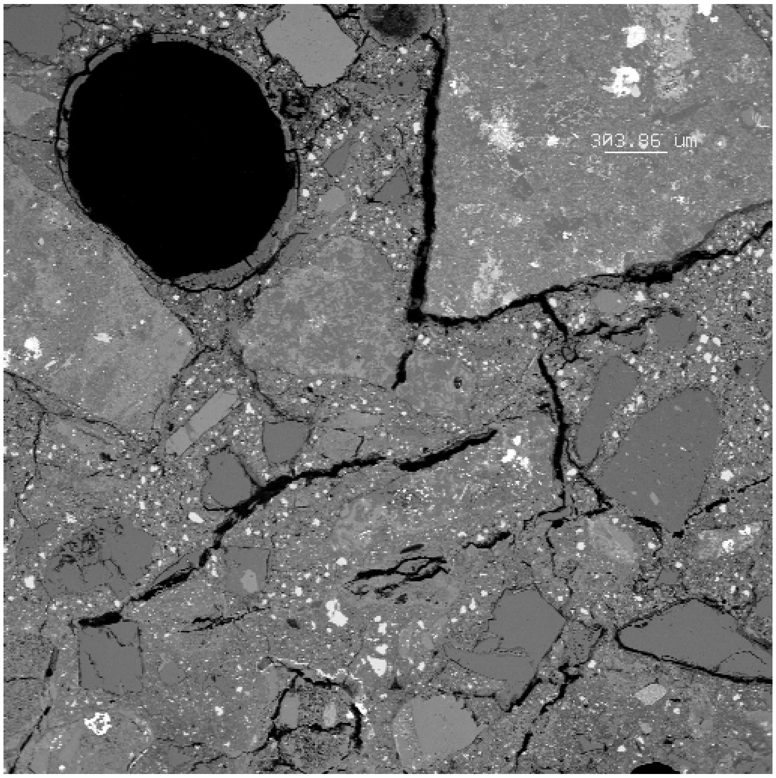

FIGURE 55. LAYER OF GEL AT THE INTERFACE BETWEEN PASTE AND SEVERELY DISTRESSED GRAIN OF NM RHYOLITE IN MORTAR SOAKED IN SODIUM FORMATE SOLUTION.

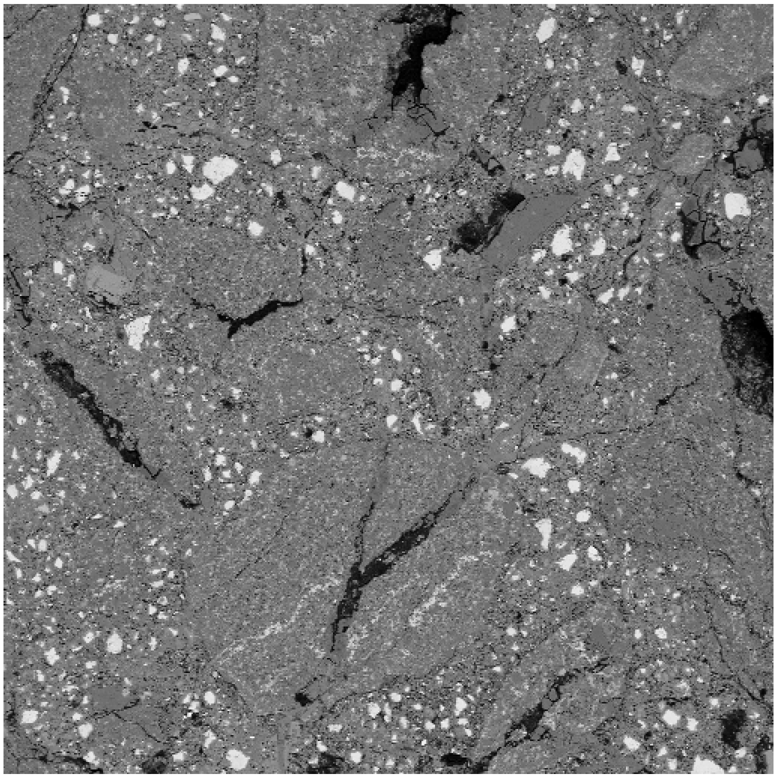

FIGURE 56. EXTENSIVE DAMAGE (CRACKING AND EROSION) IN THE GRAINS OF THE NC ARGILLITE FROM MORTAR SOAKED IN SODIUM FORMATE SOLUTION.

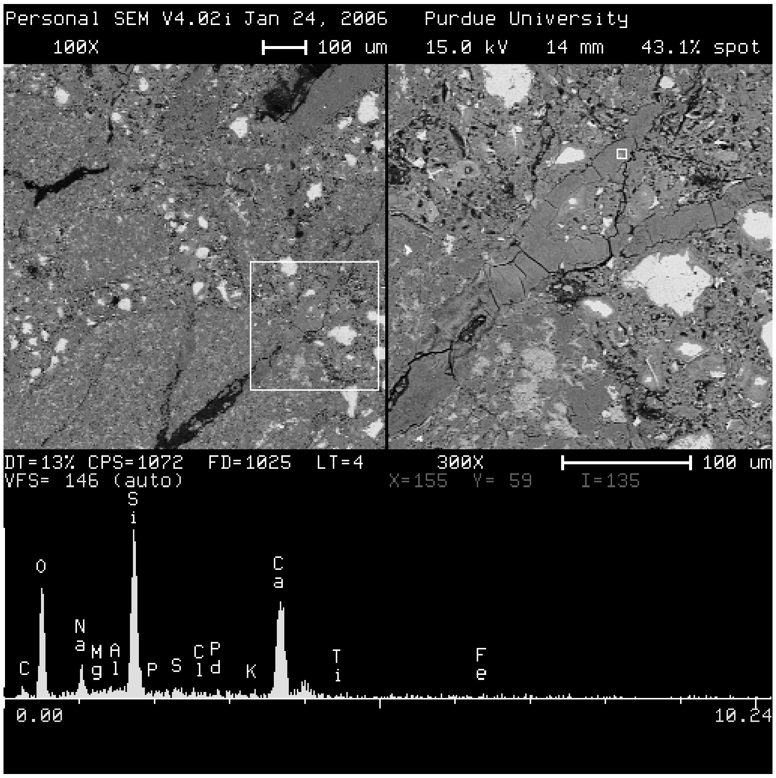

FIGURE 57. GEL OUT-FLOWING INTO THE PASTE FROM THE GRAIN OF THE NC ARGILITE IN MORTAR SOAKED IN SODIUM FORMATE SOLUTION.

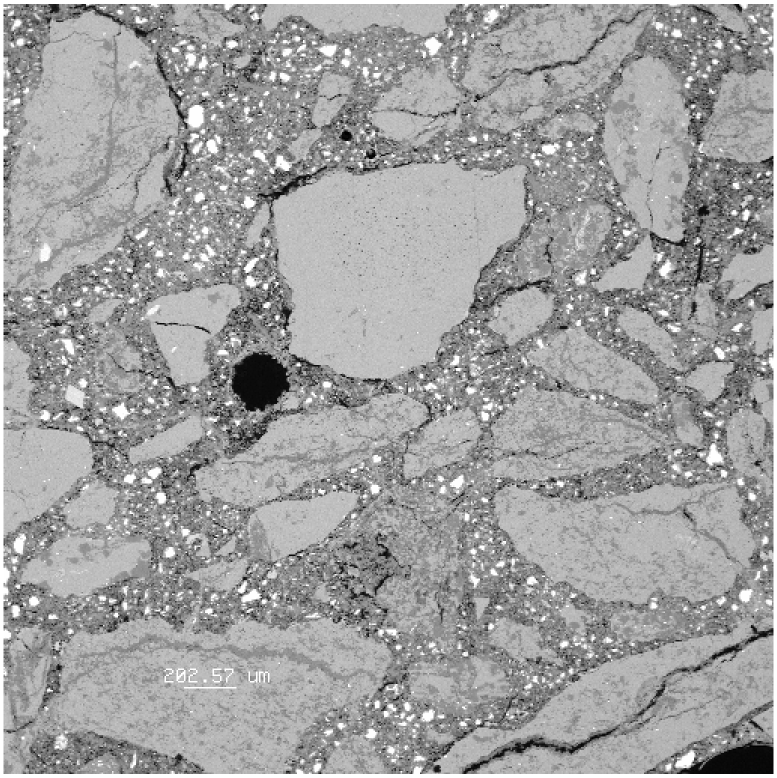

FIGURE 58. NUMEROUS CRACKS IN THE GRAINS OF THE SPRATT LIMESTONE IN MORTAR SOAKED IN SODIUM FORMATE SOLUTION

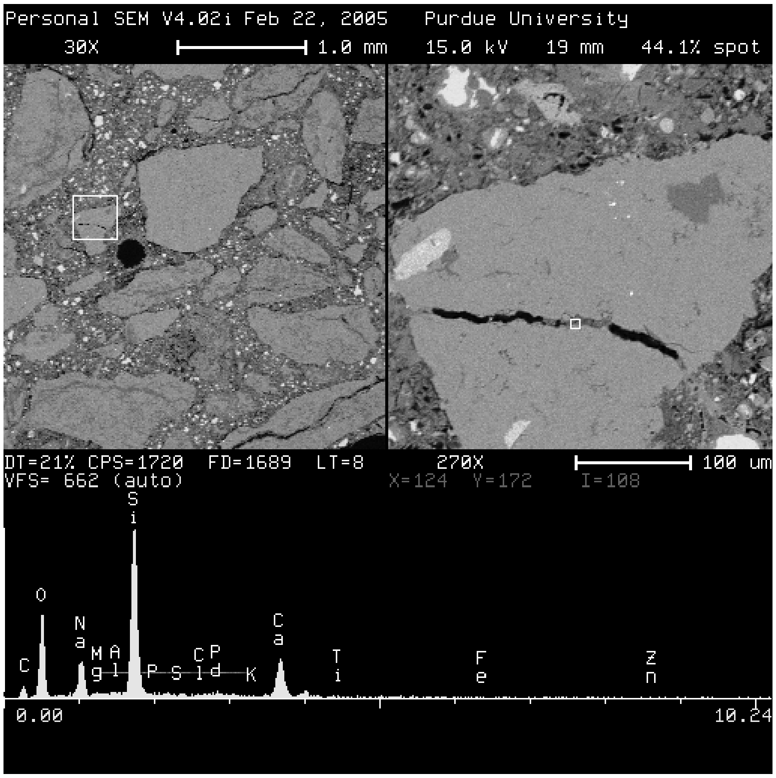

FIGURE 59. Ca-Si-Na GEL IN THE GRAIN OF SPRATT LIMESTONE FROM MORTAR SPECIMEN SOAKED IN SODIUM FORMATE SOLUTION

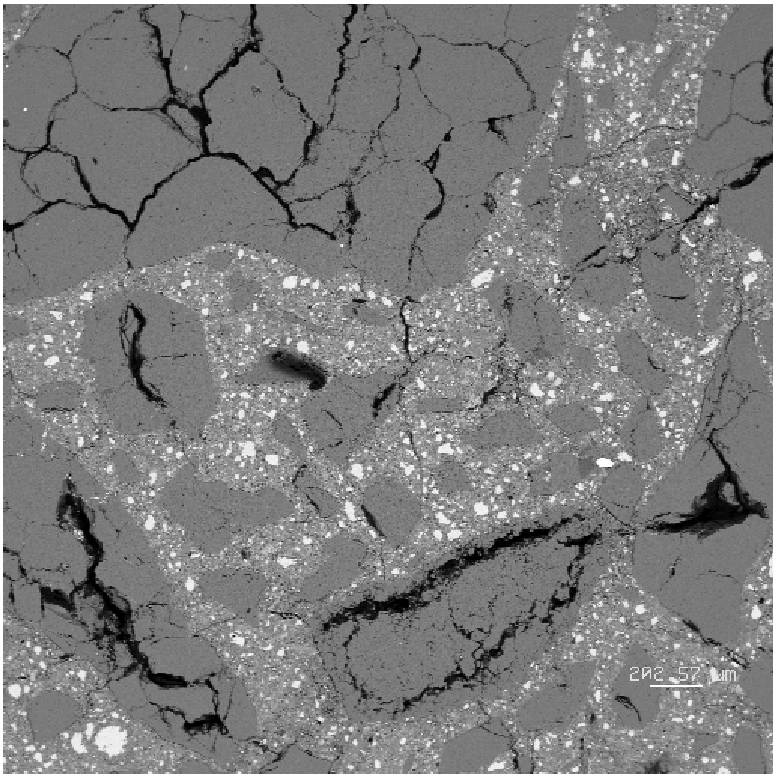

FIGURE 60. CRACKED AND ERODED GRAINS OF SD QUARTZITE AND PASTE CRACKS IN THE MORTAR SPECIMEN SOAKED IN SODIUM FORMATE SOLUTION

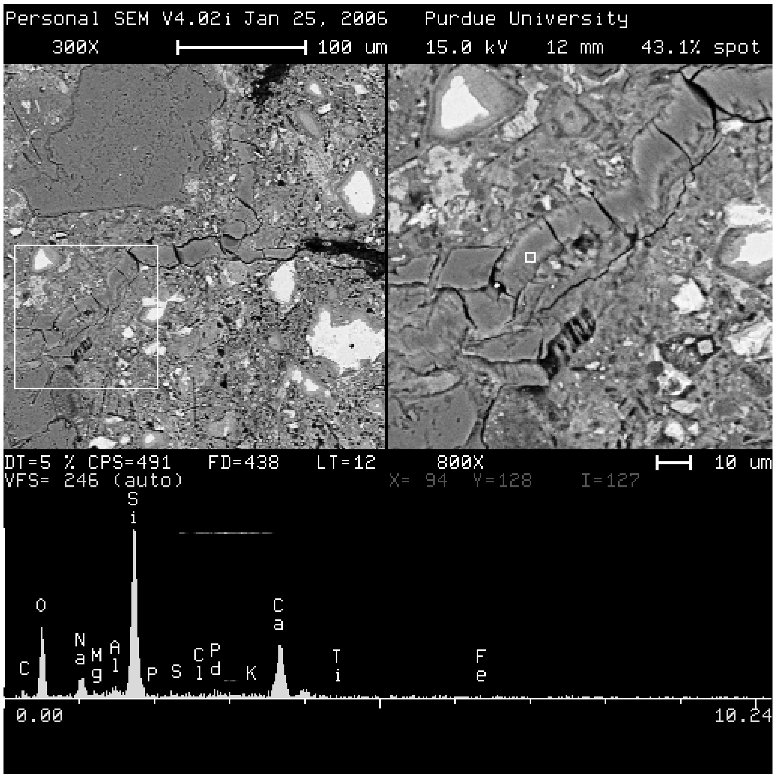

FIGURE 61. RIVER OF Ca-Si-Na GEL IN THE SD QUARTZITE MORTAR SOAKED IN SODIUM FORMATE SOLUTION

5.4.5. Mortar Specimens Exposed to Potassium Formate Deicer Soak Solution

Table 12 summarizes the main features observed during the SEM observations of mortar specimens exposed to potassium formate solution in the modified ASTM C1260 test.

TABLE 12. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF MORTAR SPECIMENS EXPOSED TO POTASSIUM FORMATE SOLUTION

Main Features of the Microstucture		**Potassium Formate (KFr)**				
		Ottawa	Spratt	NC	NM	SD
Cracking - general appearance		+	+	+++	+	+++
	within the aggregate	no	++	+++	no	+++
	within the paste	+	+	++	+	+
	at the interfaces	no	+	+	no	+++
gel presence		no	+	+	+	+
	within the aggregate	no	+	+	-	+
	within the paste	no		+	no	+
	at the interfaces	no	+	no	+	no
paste alteration						
	increased level of K	++	+	+	+	+
	increased level of Na	no	no	no	no	no
	increased level of S	no	no	no	no	no
	increased level of Al	no	+	+	+	+
	presence of Na-Ca-S	no	no	no	no	no
	presence of K-Ca-S	no	+	+	+	no
	presence of monosulfate	-	-	-	-	-

In general, the Ottawa sand mortar exposed to the potassium formate solution shows only modest signs of distress, with some grain erosion and limited cracking of paste visible in the SEM micrographs (see Figure 62). However, many locations within the paste contain bands and pockets of Ca-Si-K gel, as shown in Figure 63.

Some of the NM rhyolite grains in mortars exposed to potassium formate show signs of extensive erosion (Figure 64) and are surrounded by a thin layers of Ca-Si-K gel located at the grain-paste interface (see Figure 65). The microstructural damage in the NC argillite specimens exposed to potassium formate solution was primarily visible in the paste portion (Figure 66) which contained many deposits of Ca-Si-K gel (Figure 67). On the other hand, the damage in the mortar made with SD quartzite and exposed to potassium formate is primarily visible within the aggregate grains, which are highly eroded and cracked (see Figure 68). The cracks extend into the paste and the parts of the paste cracks immediately adjacent to the aggregate grain were typically filled with Ca-Si-K gel (see Figure 69).

Although the dominant mode of failure observed in mortars with Spratt limestone was also the cracking of the aggregate grains, the cracks appeared to be finer than those seen with NM rhyolite and SD quartzite (Figure 70). In close-up views, the grain cracks were filled with Ca-Si-K gel (see Figure 71). In addition, Ca-Al-rich deposits we observed at various locations within the paste (see Figure 72).

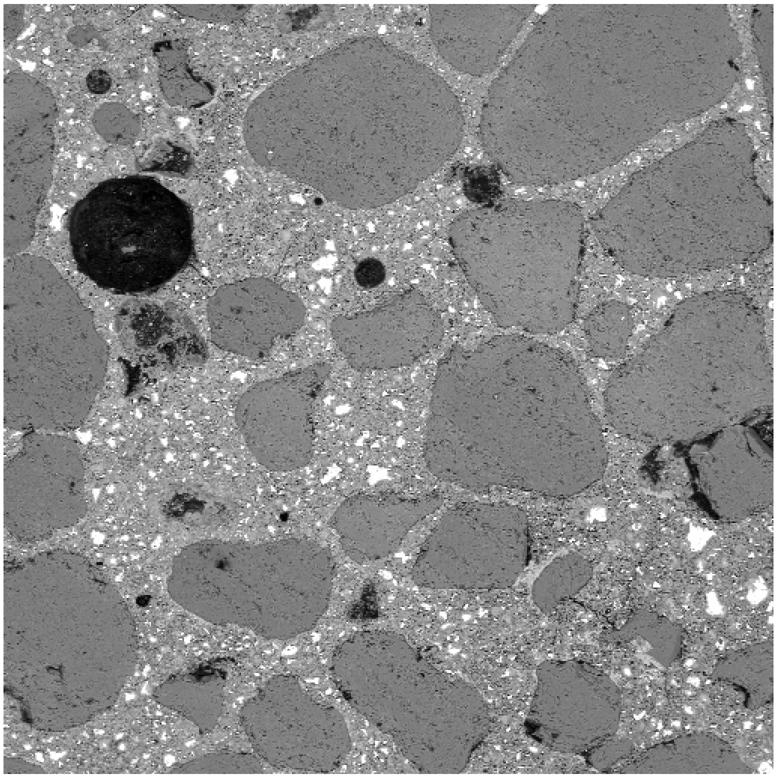

FIGURE 62. GENERAL VIEW OF THE OTTAWA SAND MORTAR EXPOSED TO THE POTASSIUM FORMATE DEICER (SOME GRAIN EROSION AND LIMITED CRACKING OF PASTE).

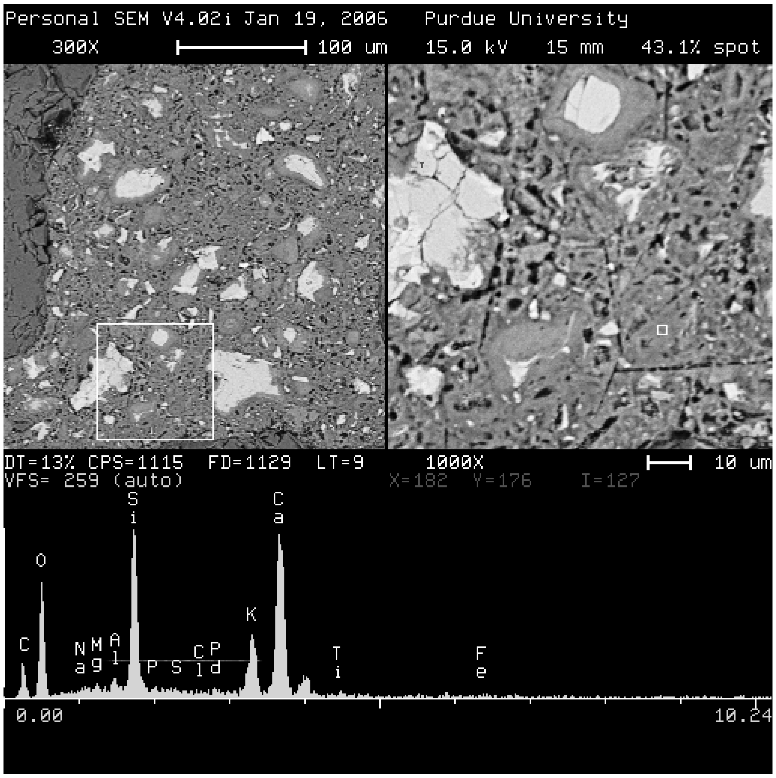

FIGURE 63. DEPOSIT OF Ca-Si-K GEL IN THE PASTE COMPONENT OF THE OTTAWA SAND MORTAR SPECIMEN SOAKED IN POTASSIUM FORMATE SOLUTION

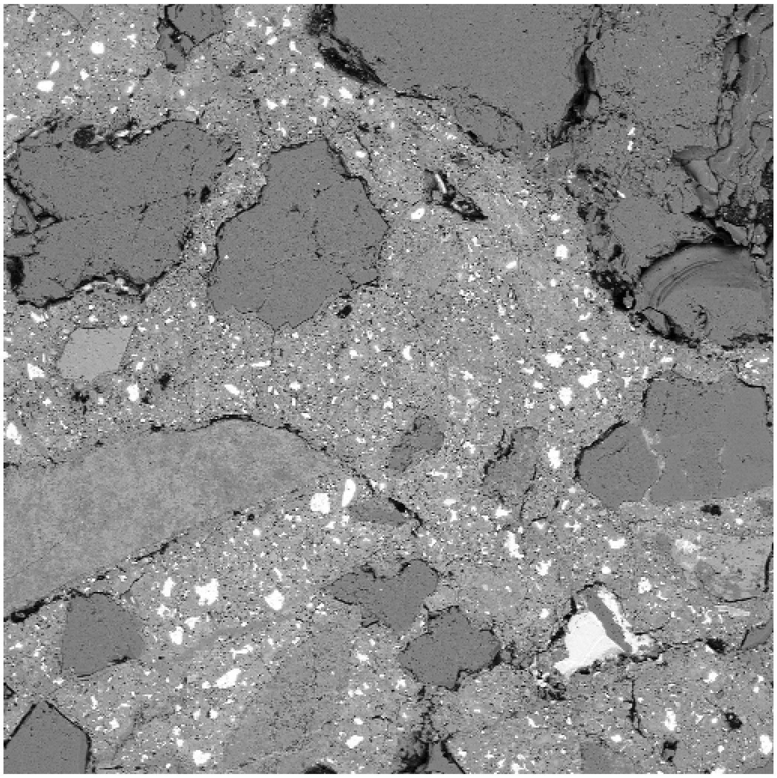

FIGURE 64. GENERAL VIEW OF THE NM RHYOLITE MORTAR EXPOSED TO THE POTASSIUM FORMATE DEICER (SOME GRAIN EROSION AND LIMITED CRACKING OF PASTE).

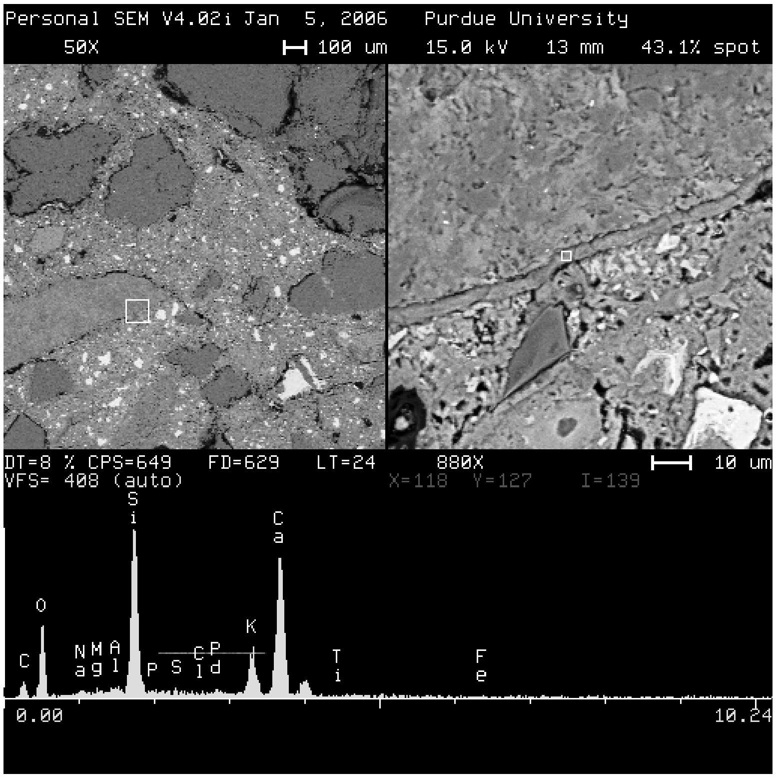

FIGURE 65. DEPOSIT OF Ca-Si-K GEL AT THE NM RHYOLITE GRAIN/PASTE INTERFACE IN THE MORTAR SPECIMEN SOAKED IN KFr SOLUTION

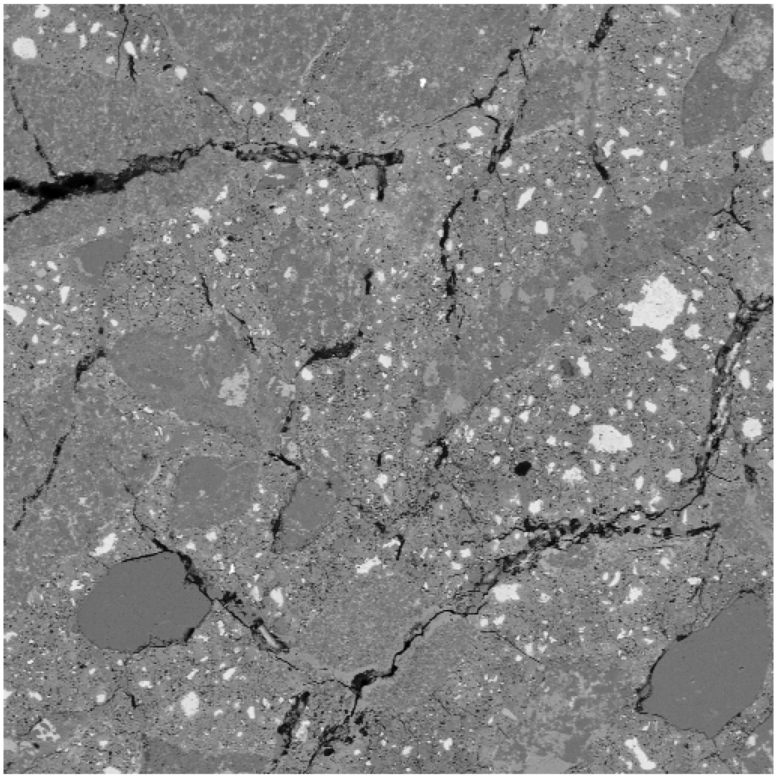

FIGURE 66. GENERAL VIEW OF THE NC ARGILLITE MORTAR EXPOSED TO THE POTASSIUM FORMATE DEICER (EXTENSIVE CRACKING OF PASTE AND AGGREGATE).

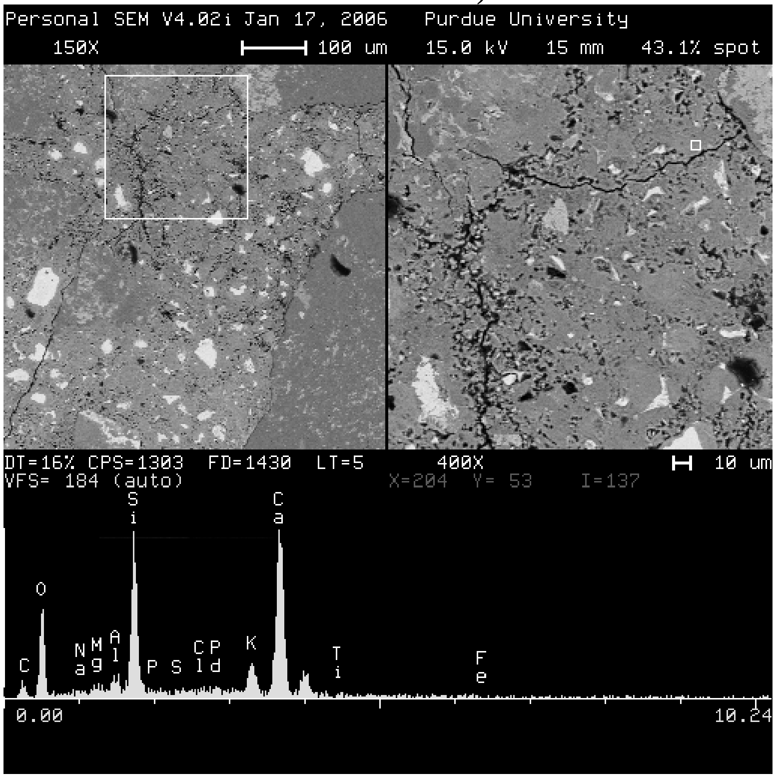

FIGURE 67. DEPOSIT OF Ca-Si-K GEL IN THE PASTE OF NC ARGILLITE MORTAR SPECIMEN SOAKED IN POTASSIUM FORMATE SOLUTION

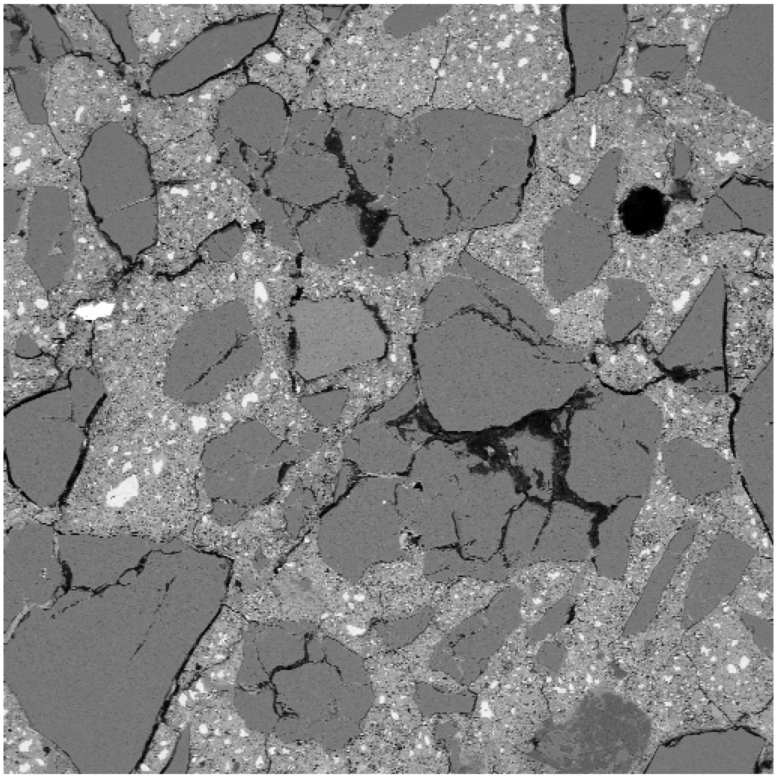

FIGURE 68. GENERAL VIEW OF THE MICROSTRUCTURE OF THE SD QUARTZITE MORTAR EXPOSED TO THE POTASSIUM FORMATE DEICER (EXTENSIVE CRACKING OF AGGREGATE EXTENDING INTO THE PASTE).

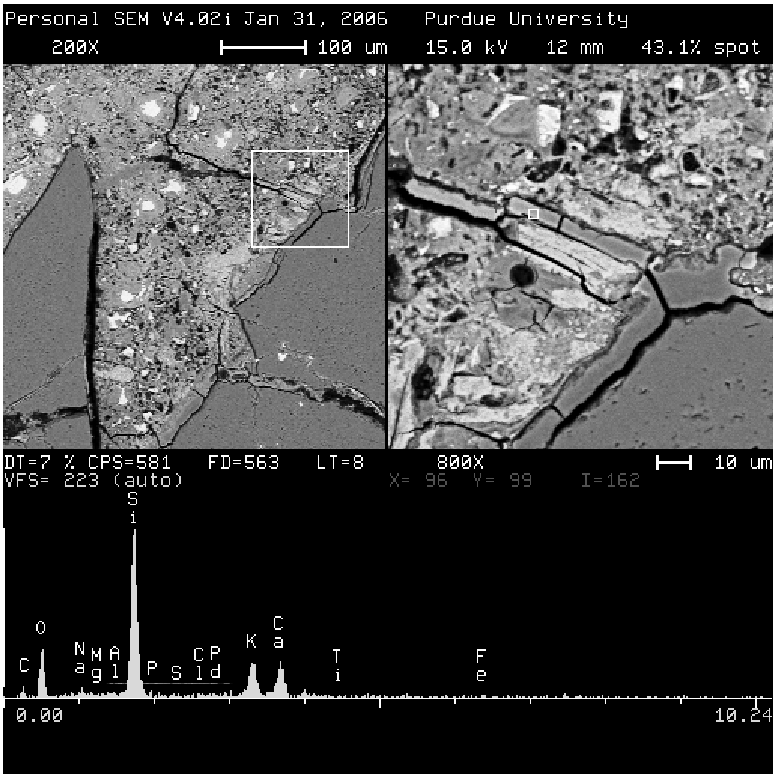

FIGURE 69. CRACK IN THE PASTE OF SD GUARTZITE MORTAR SPECIMEN SOAKED IN POTASSIUM FORMATE SOLUTION FILLED WITH THE Ca-Si-K GEL.

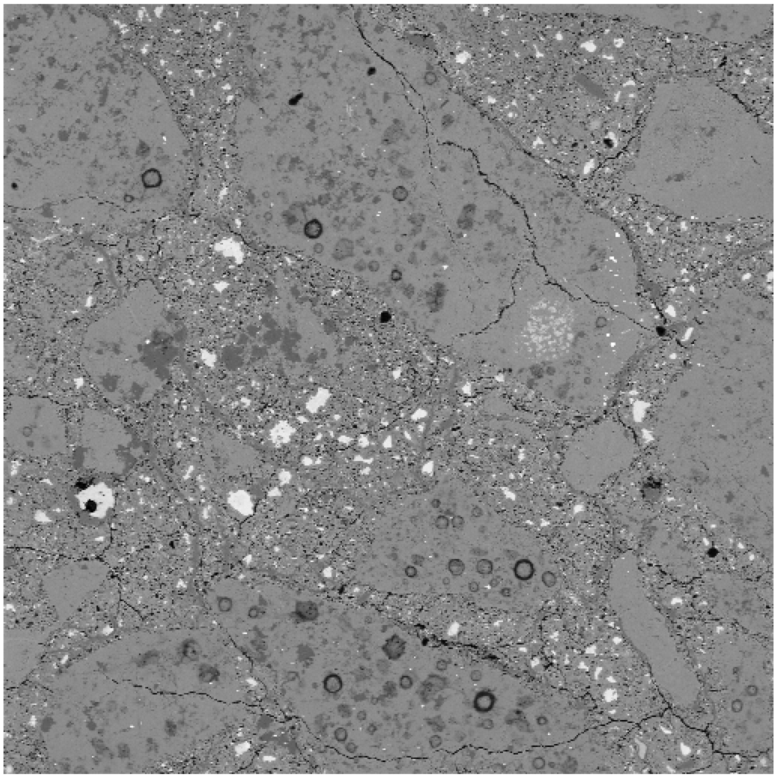

FIGURE 70. GENERAL VIEW OF THE MICROSTRUCTURE OF THE SPRATT LIMESTONE MORTAR EXPOSED TO THE POTASSIUM FORMATE DEICER (FINE AGGREGATE CRACKS EXTEND INTO THE PASTE).

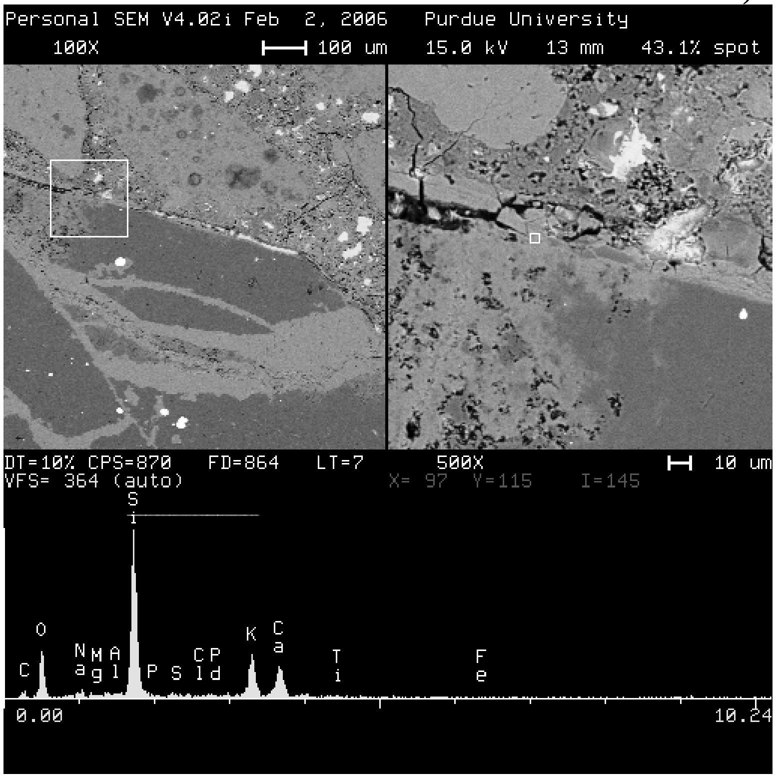

FIGURE 71. Ca-Si-K GEL IN THE CRACK OF SPRATT LIMESTONE GRAIN FROM THE MORTAR SPECIMEN SOAKED IN POTASSIUM FORMATE SOLUTION

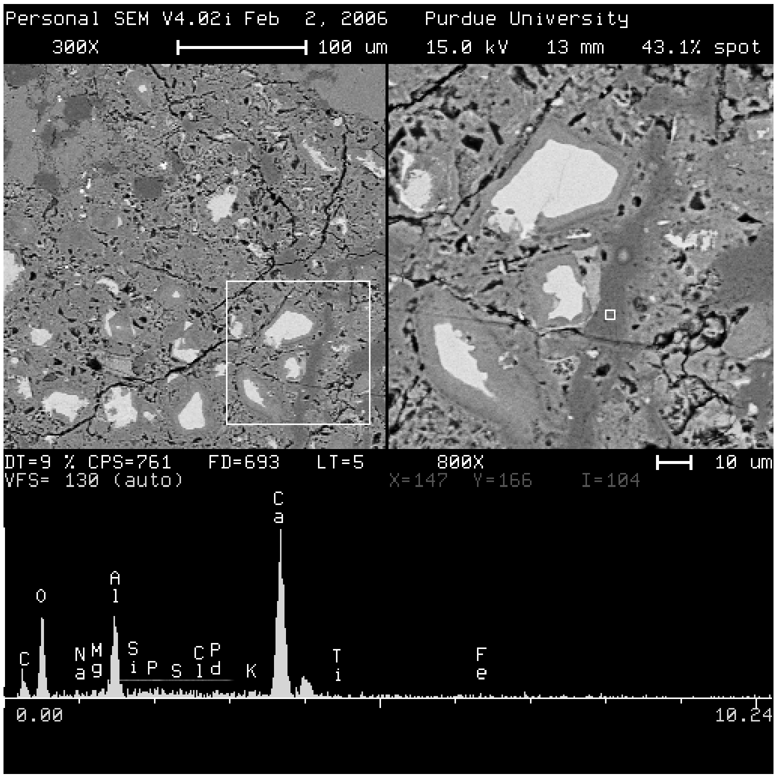

FIGURE 72. Ca-Al RICH DEPOSIT WITHIN THE PASTE OF THE SPRATT LIMESTONE MORTAR SPECIMEN SOAKED IN POTASSIUM FORMATE SOLUTION.

5.4.6. Summary of the Deicers Effects on the Microstructure of Mortars

The discussions presented in sections 5.4.1 to 5.4.5 of this report clearly indicates that while the individual effects varied, all of the deicers investigated in this research program had induced major effects in microstructure of the mortars. The degree of changes observed in the microstructure (severity of the attack) varied as a function of both the type of the deicer and the type of the aggregate. These effects are briefly summarized below.

5.4.6.1. Presence and Location of Cracks

In the various mortars, cracks induced by ASR were observed in the individual grains of the aggregates, within the paste and at the interfaces between the paste and the aggregate. Cracks in aggregates were most frequently encountered in mortars made with NC argillite, SD quartzite and Spratt limestone, and were most severe when the mortars containing these aggregates were exposed to sodium formate, sodium acetate and potassium formate. Sodium formate deicer was the only deicer that initiated ASR reaction in the grains of Ottawa sand, an aggregate that has been assumed to be non-reactive and therefore used as a control aggregate in this study. With respect to cracks in the paste, most severe cracking seemed to occur with the NC argillite and NM rhyolite, especially when mortars containing these aggregates were exposed to sodium acetate and potassium acetate deicers. Finally, interface cracks were found most prominently in mortars with NM rhyolite and SD quartzite aggregates and exposed to potassium acetate and sodium acetate deicers. Very high overall levels of cracking were found with mortars made with NC argillite, NM rhyolite and SD quartzite exposed to either potassium acetate, potassium formate or sodium acetate deicer solutions.

5.4.6.2. Presence and Location of Gel

In most cases, the presence of gel was strongly linked to the presence of cracks. As a result, the analyses of the gel were differentiated with respect to location in the grains of aggregate, in the paste or at the interface. Gel found within the aggregate grains were most commonly encountered within mortars made with Spratt limestone and NC argillite aggregates and exposed to potassium acetate and sodium formate deicers. Gel within the paste was most frequently encountered in mortars made with Spratt limestone and NC argillite and exposed to sodium formate deicer. Gel at interfaces was most frequently found in mortars made with Spratt limestone and NM rhyolite aggregates and exposed to sodium formate deicer. In general, ASR gel presence was most abundantly observed in mortars made with NC argillite, Spratt limestone and NM rhyolite exposed to potassium acetate, sodium acetate or sodium formate deicers.

5.4.6.3. Alteration of Paste Composition

Extensive signs of alteration of paste composition were associated with Spratt limestone and NC argillite aggregates and with potassium acetate, sodium acetate and potassium formate deicers.

6. RESULTS AND ANALYSIS OF DATA FROM CONCRETE PRISM TESTS

This section presents results from the standard and modified ASTM C 1293 tests conducted on concrete prisms at 38ºC. Tests were conducted on concrete prisms made with both reactive and non-reactive aggregates; see Table 4 for test matrix. The specific results presented in this section include:

1. Length change measurements of concrete prisms
2. Dynamic modulus of elasticity of concrete prisms
3. pH changes observed in soak solutions of modified ASTM C 1293 tests
4. Microstructure of concrete prisms

6.1. LENGTH-CHANGE MEASUREMENTS OF CONCRETE PRISMS

6.1.1. Standard ASTM C 1293 Test

Figure 73 shows the expansion behavior of concrete prisms prepared using different aggregates with high alkali cement in the standard ASTM C 1293 test. Figure 73 also shows the influence of prism orientation in the storage container on the expansion observed during the course of testing. The "control-vertical" samples refer to prisms that were stored in 5-gallon pails as recommended in the standard test procedure; the "control-horizontal" samples refer to prisms that were stored in shoe-box type containers. It is seen that at the end of one year the expansions of all prisms containing reactive aggregates are well above 0.04%, the expansion limit above which an aggregate is considered reactive. The one-year expansion of the concrete prisms made with IL dolomite aggregate is only 0.025%, which shows the non-reactive nature of the aggregate. At the end of 1 year, among all the remaining aggregates, concrete prisms made with NC aggregate showed the greatest expansion of 0.230 %, followed by concrete prisms made with NM, Spratt and SD aggregates, which showed expansions of 0.196%, 0.150% and 0.109% respectively.

The expansions of prisms stored horizontally were somewhat greater than the prisms stored vertically. It is likely that the self-weight of the prism may have had a restraining effect on the expansion observed in the prisms stored in vertical orientation compared to those stored in horizontal orientation. The expansions of prisms stored horizontally made with Spratt, NM, SD, NC and IL aggregates were 21%, 28%, 18%, 6.4% and 29% greater than those of the corresponding prisms made with same aggregates but stored vertically.

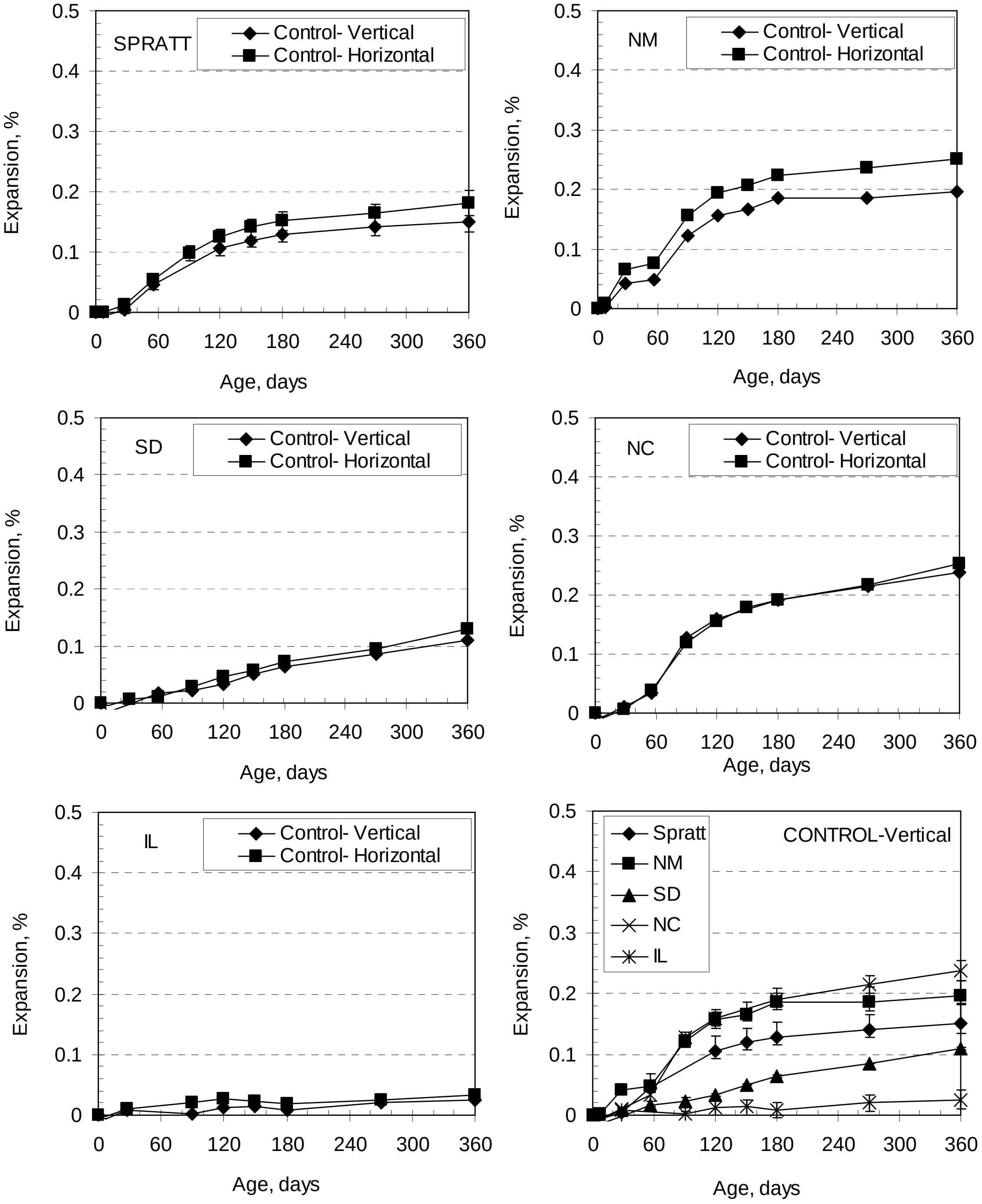

FIGURE 73. EXPANSION OF CONCRETE PRISMS IN STANDARD ASTM C 1293 TESTS WITH HORIZONTAL AND VERTICAL ORIENTATION OF CONCRETE PRISMS IN STORAGE CONTAINERS

6.1.2. Modified ASTM C 1293 Tests

6.1.2.1. 1N Sodium Hydroxide Soak Solution

Figures 74 and 75 show the expansion behavior of concrete prisms prepared with each of the four reactive aggregates and the one non-reactive aggregate using high-alkali and low-alkali cements, respectively. In these tests, the concrete prisms were soaked in 1N sodium hydroxide solution at 38ºC. These results serve as a reference against which to compare the expansion behavior of corresponding concrete prisms soaked in deicer solutions.

It is seen from Figure 74 and 75 that at the end of one year the expansions of prisms prepared with reactive aggregates were all significantly higher (> 0.04% at one year) compared to those of prisms prepared with non-reactive IL aggregate. However, it is apparent that the alkali content of cement has a significant influence on the rate of expansions of all the prisms, particularly at early ages. For prisms prepared with reactive aggregates, those with high-alkali cement showed higher rates of expansion up to 180 days than corresponding prisms prepared with low-alkali cement. The specific rate of expansion however varied with the individual aggregate. At later ages (> 180 days), prisms prepared with low-alkali cements showed considerably higher rates of expansion compared to those prepared with high-alkali cement.

This difference in expansion behavior of prisms prepared with different cements appears to be due both to nature and source of alkalis involved in the reaction and to the dimension of the test specimens. For prisms prepared with high-alkali cement, the alkalis are readily available within the matrix of concrete to trigger ASR in the prisms. As a result, rapid expansions were observed at early ages. As the degree of reaction progressed, i.e. beyond about 180 days, the rate of expansion gradually slowed down. It appears that the alkalis supplied by the external 1N sodium hydroxide soak solution did not play a significant role other than to provide a moist environment to sustain the reaction.

In comparison, the prisms prepared with low-alkali cement do not have adequate alkali levels within the matrix of concrete at early ages to trigger ASR. Instead, the alkalis from the external soak solution (1N sodium hydroxide solution) had to permeate into the prism to reach adequate levels to initiate the reaction. At later ages when the threshold concentration of alkalis sufficient to trigger ASR was reached within the matrix of concrete, the rates of expansion increased substantially. Although the threshold levels of alkalis required to trigger ASR in different concrete prisms were not quantified in this study, it is apparent from Figures 74 and 75 that it is a function of the reactivity of the specific aggregate involved.

The results of the standard ASTM C 1293 test (see Figure 73) are comparable to those found in the modified ASTM C 1293 test with 1N NaOH soak solution (see Figure 74 for HA cement). It is evident that the expansions of prisms at 360 days in the two exposure conditions are very similar to each other for each of the reactive aggregates.

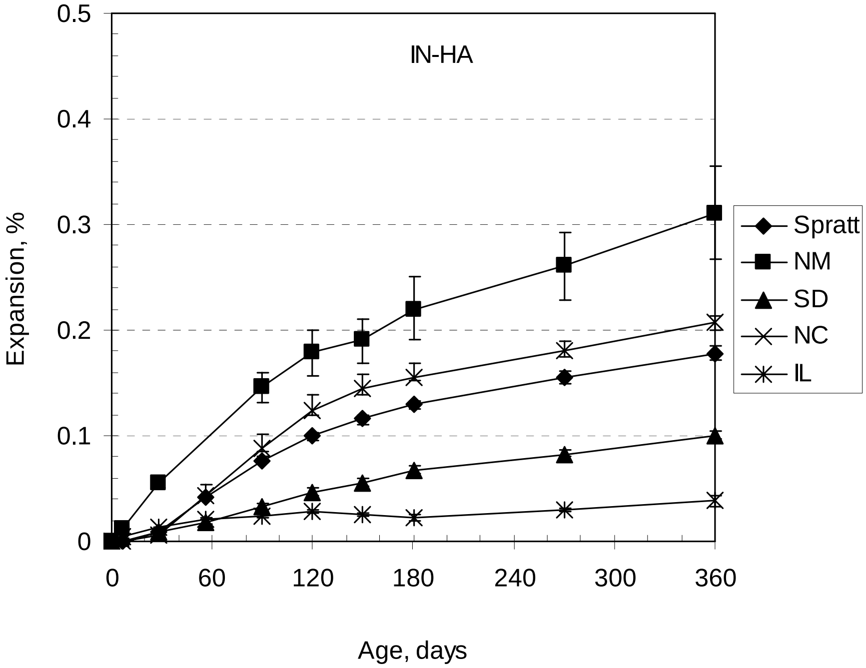

FIGURE 74. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH 1N NaOH SOLUTION AND HA CEMENT

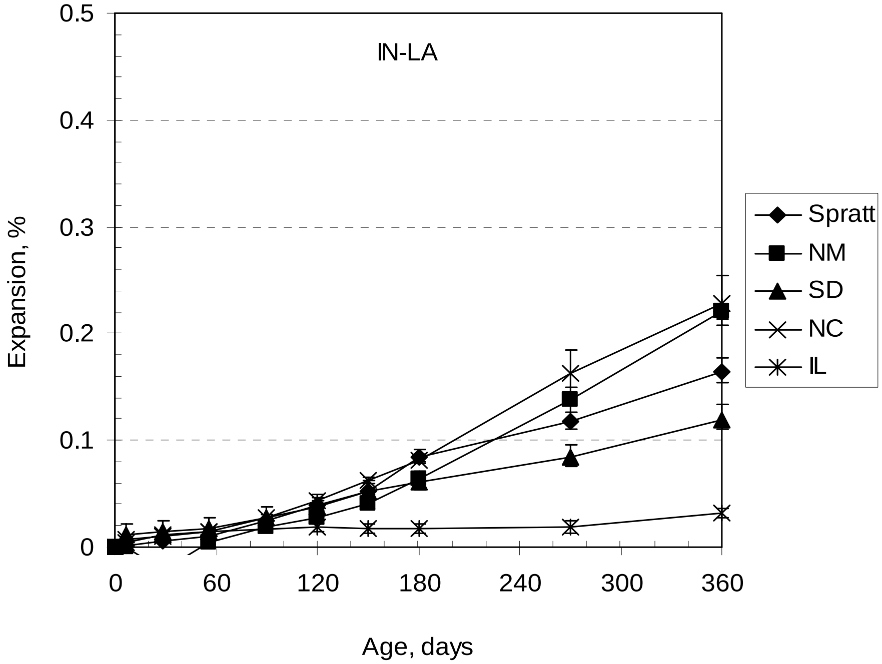

FIGURE 75. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH 1N NaOH SOLUTION AND LA CEMENT

6.1.2.2. Potassium Acetate Deicer Soak Solution

Figures 76 and 77 show the expansion behavior of concrete prisms prepared with each of the four reactive aggregates and the one non-reactive aggregate in the modified ASTM C 1293 test using high-alkali and low-alkali cements, respectively. In these tests the concrete prisms were soaked in potassium acetate deicer solution at 38ºC for one year. It is evident from the results that regardless of the alkali content of the cement used, prisms containing reactive aggregates showed significant expansions (i.e. greater than 0.04% at one year) when exposed to potassium acetate deicer solution. However, the rate of expansion and the magnitude of expansion at one year depended on the specific combination of aggregate and cement.

Prisms prepared with NM rhyolite aggregate using high-alkali cement and low-alkali cement that were exposed to potassium acetate deicer showed very high levels of expansion at early ages (>1.35% expansion at 120 days) and cracked extensively. Beyond 120 days of exposure, the NM aggregate-bearing prisms actually broke into several pieces. Expansions of concrete prisms prepared with NC and Spratt aggregates that were exposed to potassium acetate deicer solution were slower and much less severe, although they were significantly higher than 0.04% at the end of 1 year. This was true regardless of the alkali content of the cement used. These prisms only showed extensive surface cracking and they remained intact at the end of one year making it possible to take long-term length-change measurements.

For concrete prisms prepared with SD aggregate, although the expansions at one year were higher than 0.04% regardless of the alkali content of the cement used, prisms prepared with low-alkali cement showed considerably higher level of expansion (0.34% at one year) than those prepared with high-alkali cement (0.15% at one year). No explanation is yet available for this surprising behavior.

For the non-reactive IL dolomite aggregate, no significant expansions were observed in prisms prepared with high-alkali cement and exposed to KAc deicer solution. However, unanticipated levels of expansions (0.24% at one year) were observed in prisms prepared with low-alkali cement and exposed to KAc deicer solution. Considering that the IL dolomite and the Ottawa sand are non-reactive (Standard ASTM C 1260 expansions < 0.1% at 14 days; Standard ASTM C 1293 expansion < 0.04% at one year), the observed expansions were not believed to be due to ASR. Further investigation of microstructure of these prisms revealed that ASR was not the source of expansion. Instead, certain unanticipated phases rich in potassium sulfate were observed in cracks and voids in the paste matrix and as rim formations around aggregate particles. It appears likely that sulfoaluminate phases originally present in the hydrated cement paste may have been attacked by potassium acetate deicer, resulting in the formation of an expansive potassium sulfate phase. Further investigation was considered necessary to understand this behavior, but such investigation was beyond the scope of this project and was not pursued. Evidence of the potassium sulfate phase in the microstructure will be discussed in section 6.4.

In summary, exposure to potassium acetate deicer solution caused aggressive expansion in all concrete prisms containing reactive aggregates. The rate and magnitude of expansion appears to be a function of the specific aggregate type and the alkali content of the cement used. Additional investigation is necessary to study the abnormal expansion observed in prisms containing IL dolomite aggregate with low-alkali cement.

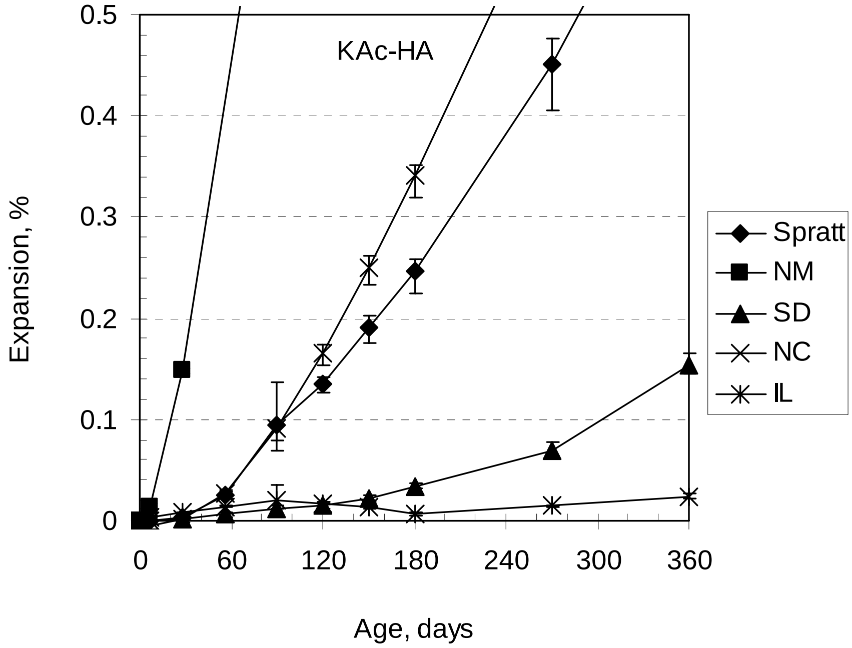

FIGURE 76. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH POTASSIUM ACETATE DEICER SOLUTION AND HA CEMENT

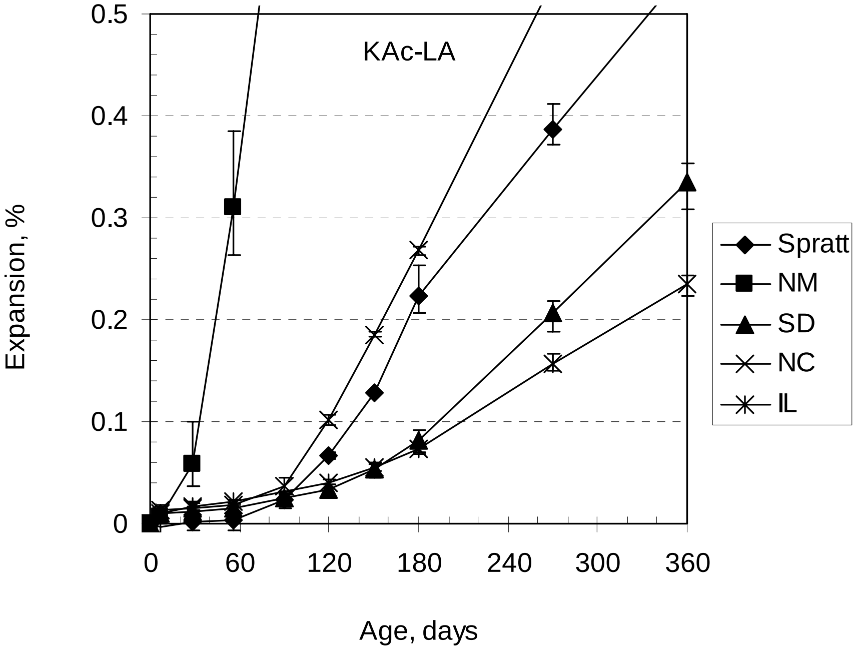

FIGURE 77. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH POTASSIUM ACETATE DEICER SOLUTION AND LA CEMENT

6.1.2.3. Sodium Acetate Deicer Soak Solution

Figures 78 and 79 show the expansion behavior of concrete prisms prepared with each of the four reactive aggregates and the one non-reactive aggregate in the modified ASTM C 1293 tests using high-alkali and low-alkali cements, respectively. In these tests, the prisms are soaked in sodium acetate deicer soak solution at 38ºC.

From these figures it is evident that prisms made with NM rhyolite, NC argillite and Spratt limestone aggregates showed significant expansion at one year (> 0.04% at one year), regardless of the alkali content of the cement used. However, with all the three aggregates the rate of expansion appears to be significantly higher at earlier ages (~ 60 days) with high-alkali cement than with low-alkali cement (where higher rates of expansion were evident at ~ 150 days). It is likely that the internal alkalis supplied by the high-alkali cement may have played a role in triggering the ASR at early ages. However, the rates of expansion in the prisms prepared with low-alkali cement at later ages suggest that the penetration of alkalis supplied from external NaAc deicing soak solution is responsible for the distress.

The SD quartzite aggregate behaved somewhat differently from other reactive aggregates in the presence of sodium acetate solution. Although this aggregate is considered to be reactive based on its performance in the standard ASR test methods, prisms prepared with this aggregate and soaked in sodium acetate deicer showed an expansion of only 0.049% at one year with high-alkali cement and 0.029% at one year with low-alkali cement. These expansions are significantly less than those observed on exposure to the other deicers or 1N sodium hydroxide soak solutions.

Prisms prepared with non-reactive IL dolomite aggregate exposed to sodium acetate deicer solution did not exhibit any significant level of expansion (i.e. < 0.04% at one year), with either high-alkali or low-alkali cements.

In summary, all the reactive aggregates except the SD quartzite, showed significant levels of expansion at one year upon exposure to sodium acetate deicer solution. These findings clearly indicate that sodium acetate deicer solution is capable of triggering ASR distress in concrete containing moderate to highly reactive aggregates. With aggregates such as SD quartzite, the alkali content of the cement appears to influence the magnitude of the expansion observed.

These findings collectively suggest that sodium acetate deicer solution may be highly aggressive towards aggregates that are moderately to highly reactive. However, no deleterious expansions were observed in prisms containing non-reactive aggregates.

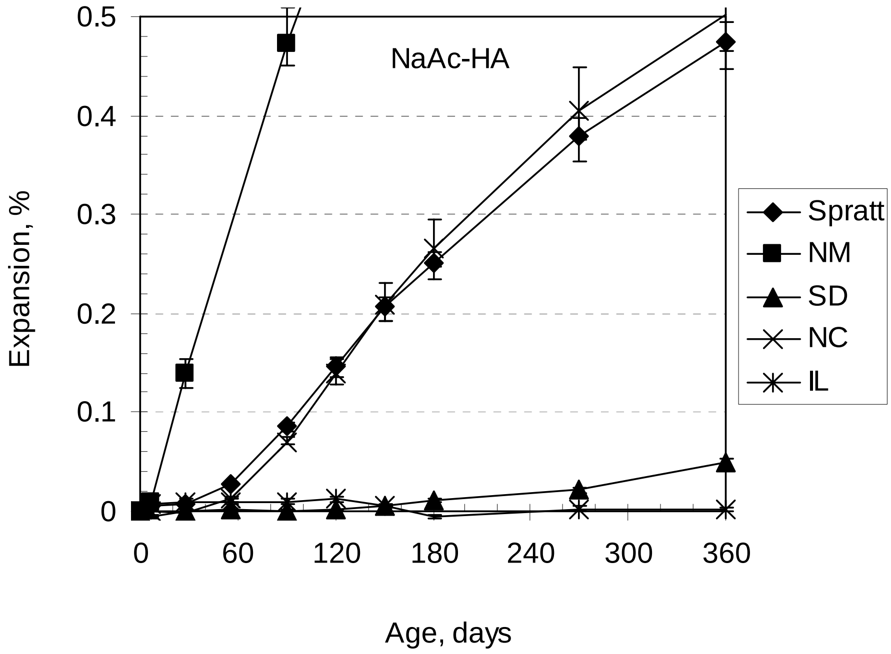

FIGURE 78. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH SODIUM ACETATE DEICER SOLUTION AND HA CEMENT

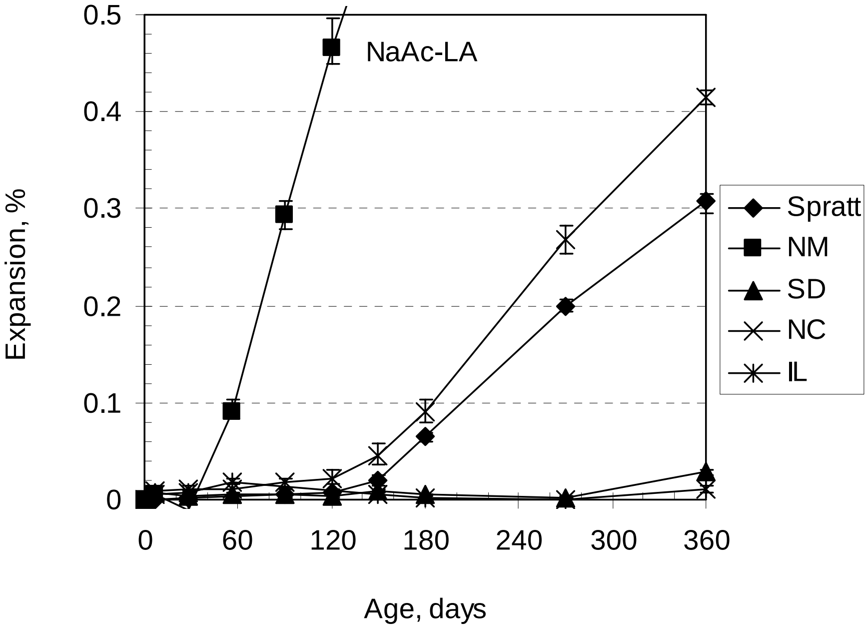

FIGURE 79. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH SODIUM ACETATE DEICER SOLUTION AND LA CEMENT

6.1.2.4. Sodium Formate Deicer Soak Solution

Figures 80 and 81 show the expansion behavior of concrete prisms made with each of the four reactive aggregates and the one non-reactive aggregate in the modified ASTM C 1293 test using high alkali and low alkali cements, respectively, on exposure to sodium formate deicer.

From figures 80 and 81 it is evident that concrete prisms prepared with NM aggregates showed significant expansion in presence of sodium formate deicer solution, regardless of the alkali content of the cement used. However, the prisms prepared with low-alkali cement showed a delay (~ 60 days) in their expansion at early ages compared to prisms prepared with high-alkali cement. However, at later ages low-alkali cement prisms exhibited higher expansion level than those with high-alkali cement.

In contrast, prisms prepared with NC argillite and Spratt limestone aggregates exhibited relatively moderate expansions at one year. The expansion levels were over 0.04%; however the magnitude of expansion was distinctly influenced by the alkali content of the cement. Prisms made with high-alkali content cement showed rapid expansions as early as 60 days. In contrast, prisms with low-alkali cement showed significant expansion only after 180 days. This again indicates the time lag involved in the permeation of external deicing solution into the concrete prisms and consequent triggering of deleterious expansions in concrete prisms.

The behavior of prisms made with the SD quartzite aggregate exposed to sodium formate deicer was substantially different from prisms made with the other reactive aggregates. While this aggregate was characterized as moderately reactive based on standard ASR test methods (see Figures 11 and 73) and field performance, prisms prepared with this aggregate and soaked in sodium formate deicer showed expansions of only 0.012% at one year with high-alkali cement, and 0.002% at one year with low-alkali cement. These expansions are significantly less than those observed on exposure to other deicers or 1N sodium hydroxide solutions.

For prisms prepared with the non-reactive IL dolomite aggregate and exposed to sodium formate deicer solution, no expansion was observed regardless of the alkali content of the cement used.

In summary, it appears that sodium formate deicer solution caused very severe distress in prisms prepared with NM rhyolite aggregate and somewhat less severe distress in those made with NC argillite and Spratt limestone aggregates. With all three aggregates, the high-alkali cement caused higher rates of expansion at early ages. For SD quartzite aggregates, surprisingly, the sodium formate deicer caused no apparent distress on prisms made with either high alkali cement or low alkali cement at one year. With the non-reactive aggregate, sodium formate did not cause any distress in the test specimens regardless of the alkali content of the cement used. Based on these findings, it appears that sodium formate deicer solution is more aggressive towards concretes containing moderately and highly reactive aggregate such as NM rhyolite, NC argillite and Spratt limestone aggregates.

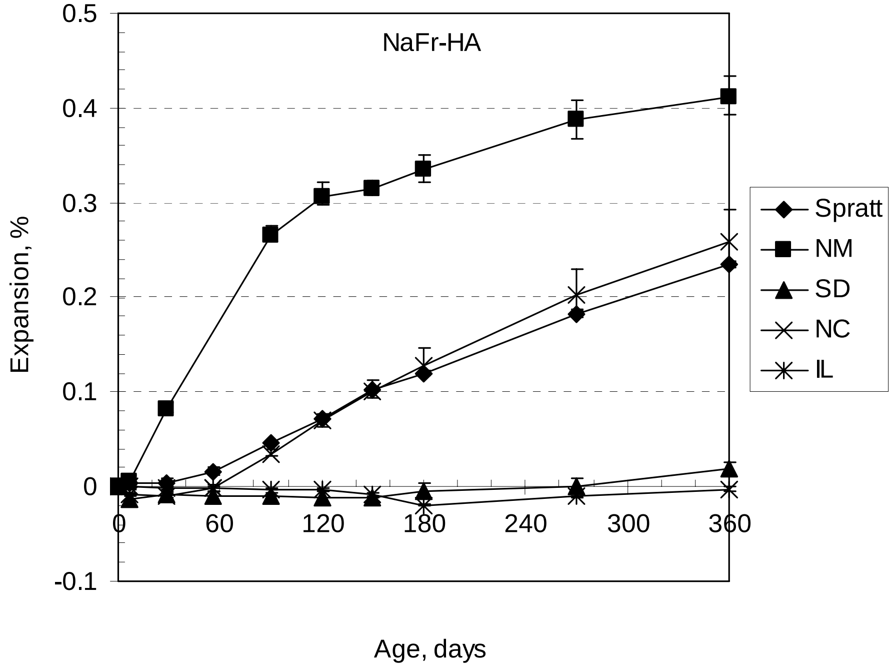

FIGURE 80. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH SODIUM FORMATE DEICER SOLUTION AND HA CEMENT

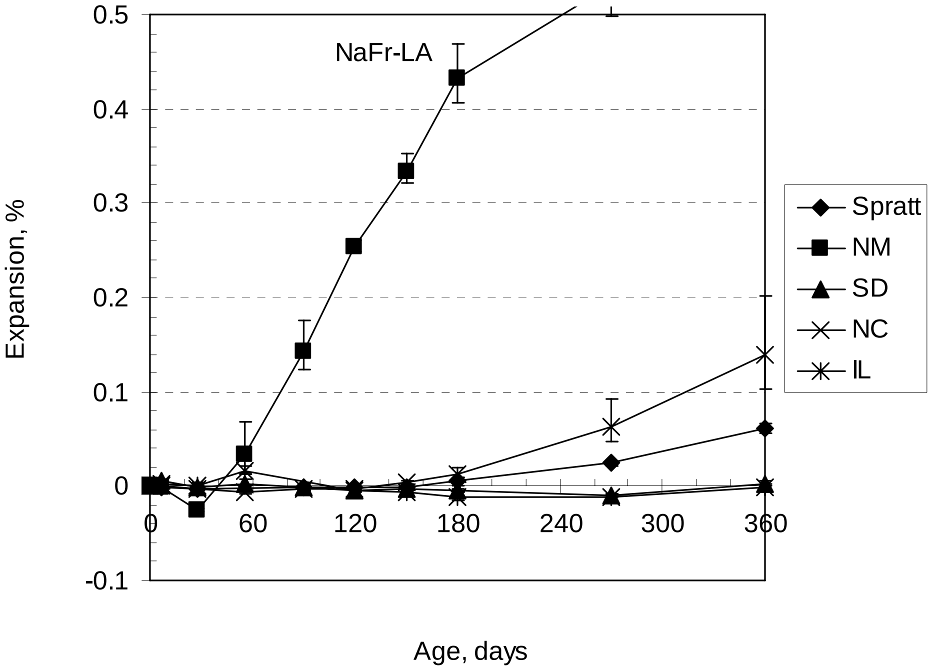

FIGURE 81. EXPANSION OF CONCRETE PRISMS IN MODIFIED ASTM C 1293 TESTS WITH SODIUM FORMATE DEICER SOLUTION AND LA CEMENT

6.2. DYNAMIC MODULUS OF ELASTICITY OF CONCRETE PRISMS

6.2.1. Changes in DME of Prisms in the Standard ASTM C 1293 Test

Figure 82 shows the changes in the DME observed in the standard ASTM C 1293 tests for each of the four reactive aggregates and the one non-reactive aggregate. The figure shows the comparisons of the changes in DME for concrete prisms stored vertically in 5 gallon pails (as per the standard ASTM C 1293 test) and those prisms horizontally in shoe box containers (modified ASTM C 1293 tests). From these results it is evident that prisms containing reactive aggregates such as NM rhyolite, Spratt limestone, NC argillite, SD quartzite showed substantial reduction in DME at one year in the standard ASTM C 1293 test, compared to their initial DME. Prisms made with the non-reactive IL dolomite aggregate showed a net increase in DME at end of one year, although some reduction in the DME was observed at intermediate ages.

In summary, the changes in DME of the concrete prisms containing reactive aggregates corresponded well with the expansion behavior discussed in the previous section.

6.2.2. Changes in DME of Prisms in the Modified ASTM C 1293 Test

Figures 83 through 86 show the changes in the DME of concrete prisms prepared with each of the five aggregates and exposed to 1N sodium hydroxide, potassium acetate, sodium acetate and sodium formate deicer solutions, respectively, in the modified ASTM C 1293 tests. In these tests, the influence of the alkali content of the cement on the changes in DME of the concrete prisms was also evaluated.

Except for prisms containing NM rhyolite aggregate, concrete prisms with the other aggregates showed an increase in DME up to 2 months and then subsequently decreased. Prisms containing NM rhyolite aggregate showed a rapid deterioration in DME soon after exposing to external soak solutions. While the alkali content of the cement did not have a significant influence on the changes in DME for concrete made with Spratt limestone, NC argillite and SD quartzite aggregates, it showed a distinct influence with those containing NM rhyolite aggregate. Prisms containing high-alkali cement deteriorated at a faster pace than prisms containing low-alkali cement. Prisms with non-reactive IL dolomite aggregate showed a gradual increase or a stable DME values up to 180 days in presence of all the soak solutions. Beyond 180 days, a drop in DME was observed. The DME values of concrete prisms containing IL aggregates were all at or near 100% at the conclusion of the test, with exception of the low-alkali prisms in KAc deicer solution.

The initial increase in the DME values observed for most of the prisms is due to continued hydration of cement and the consequent gain in stiffness. However, the subsequent drop in DME is associated with deleterious reactions with soak solutions involving expansion and cracking effects. For prisms made with NM rhyolite aggregate, due to the rapid rate of ASR reactions the matrix started to deteriorate at early ages. Among the three deicers, potassium acetate deicer had the most disastrous influence on the DME of concrete prisms for the reactive aggregates followed closely by sodium acetate, sodium formate and the 1N sodium hydroxide solution.

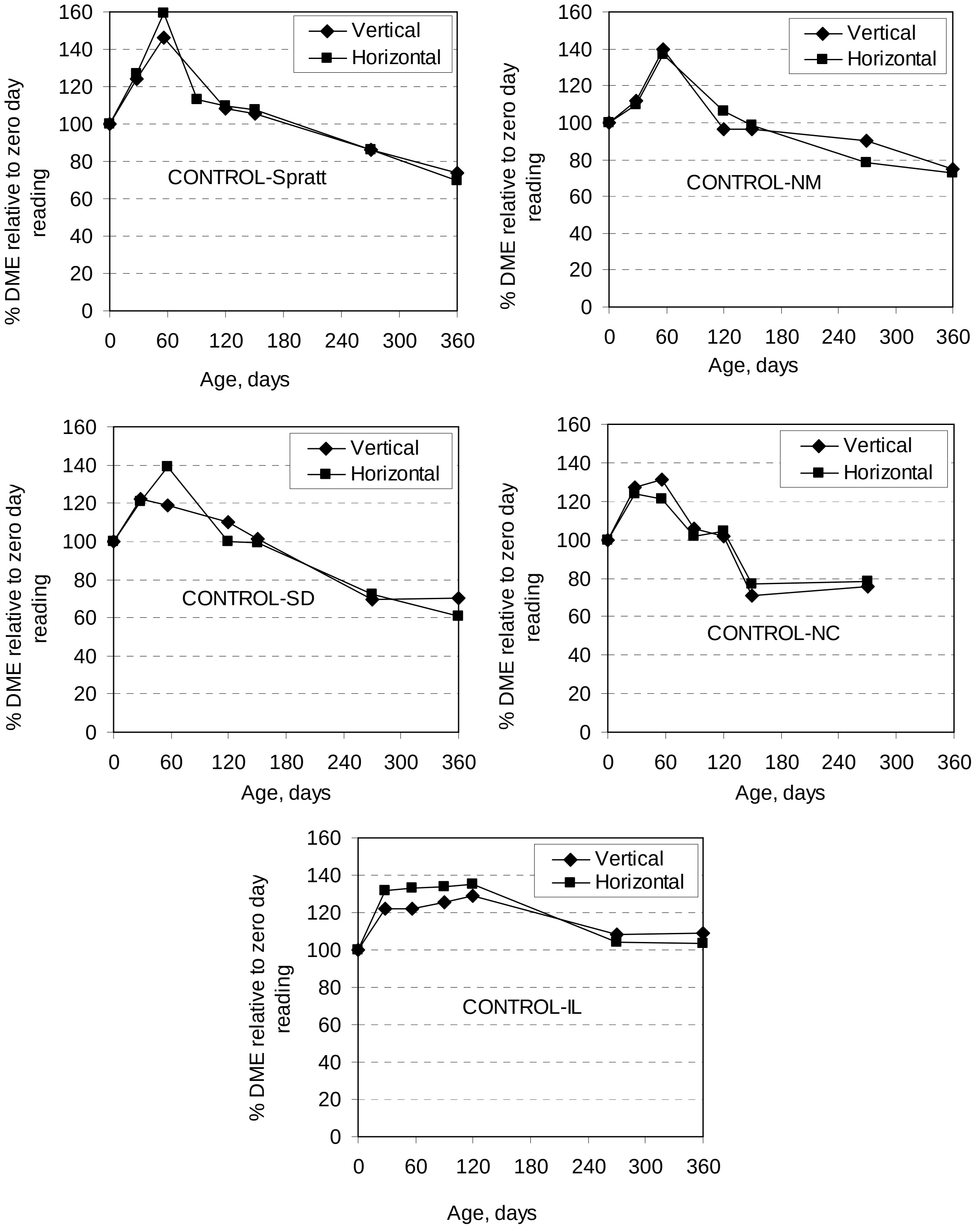

FIGURE 82. CHANGE IN DYNAMIC MODULUS OF CONCRETE PRISMS IN THE STANDARD ASTM C 1293 TEST

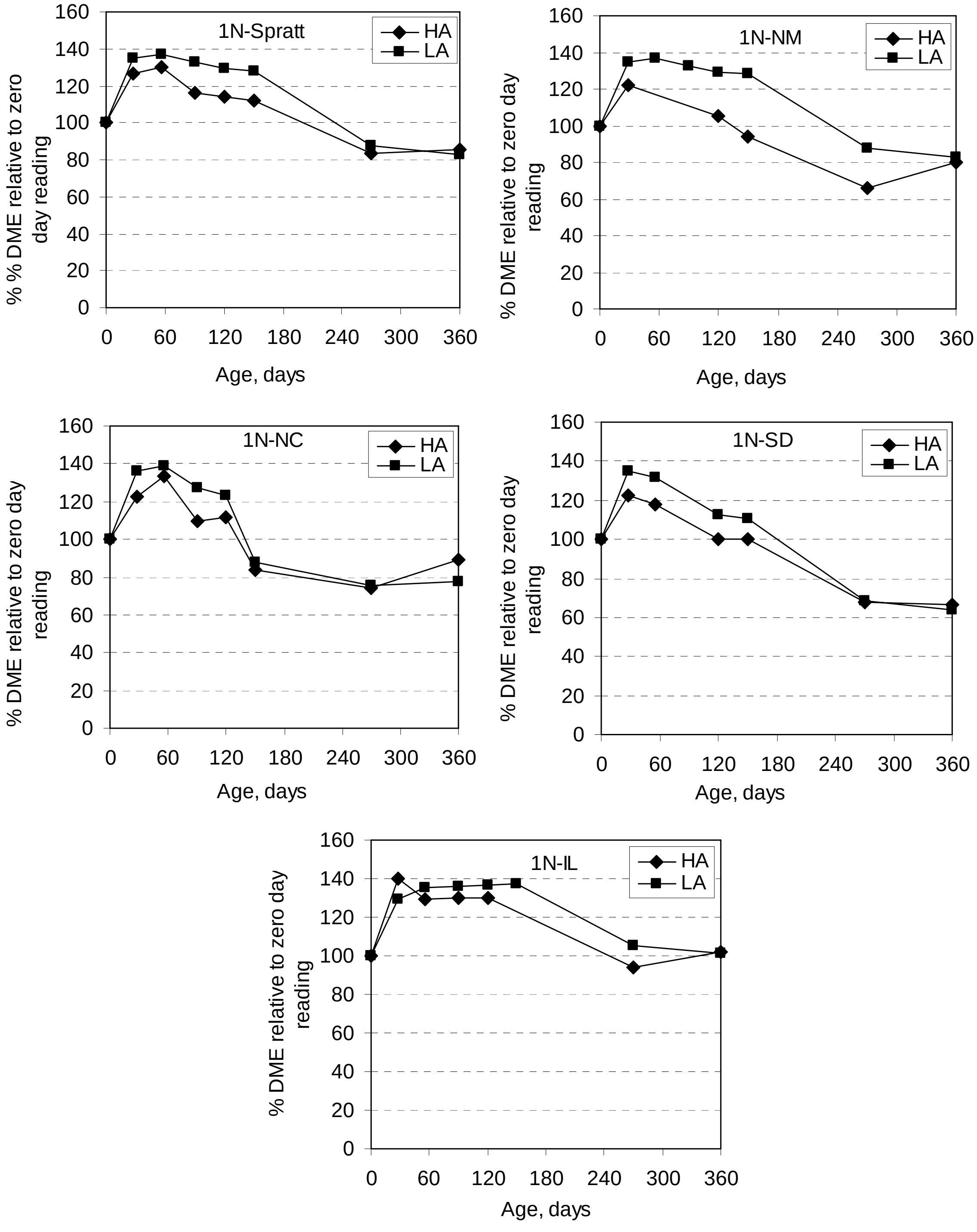

FIGURE 83. CHANGE IN DYNAMIC MODULUS OF CONCRETE PRISMS EXPOSED TO 1 N NaOH SOLUTION IN THE MODIFIED ASTM C 1293 TEST

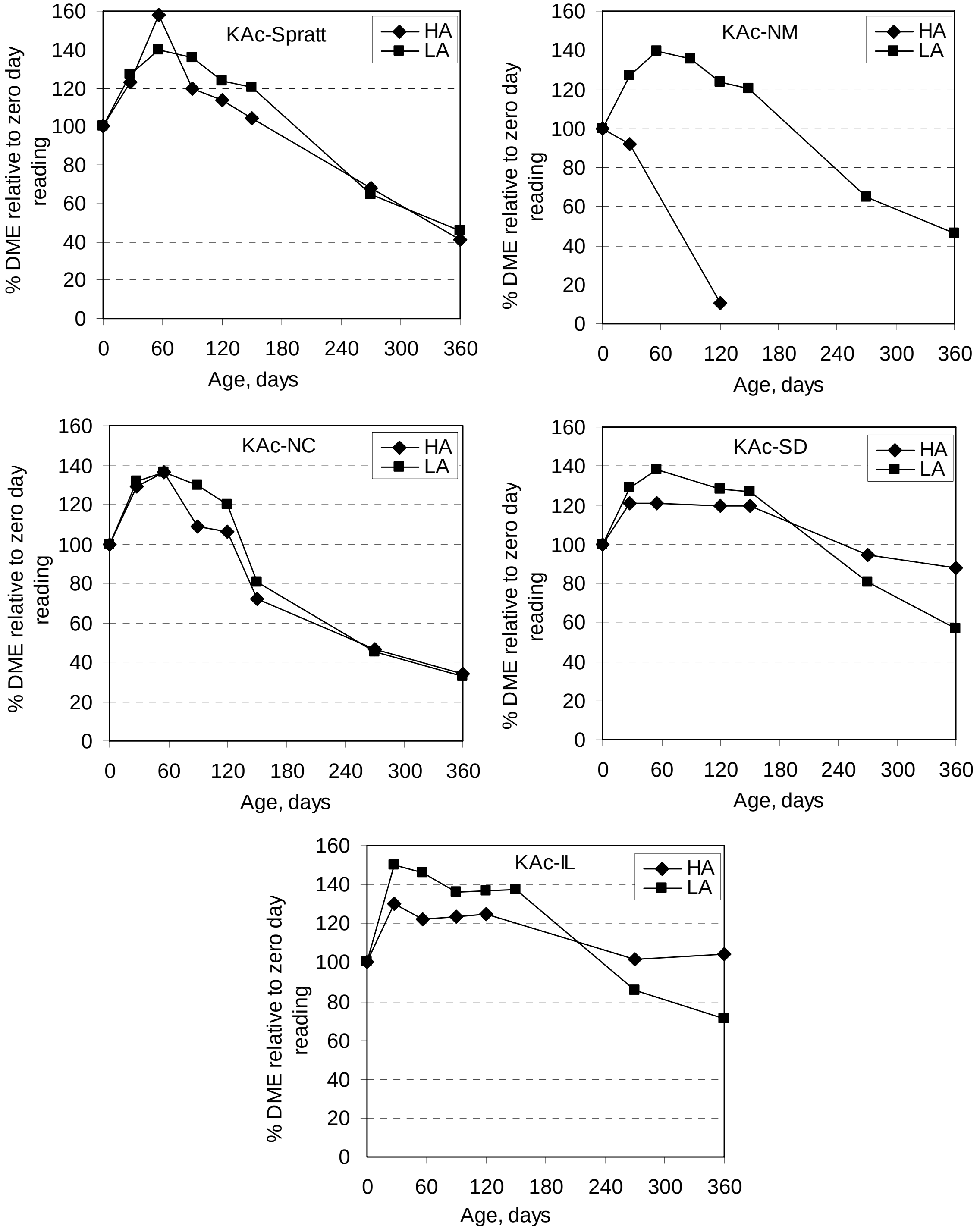

FIGURE 84. CHANGE IN DYNAMIC MODULUS OF CONCRETE PRISMS EXPOSED TO POTASSIUM ACETATE DEICER SOLUTION IN THE MODIFIED ASTM C 1293 TEST

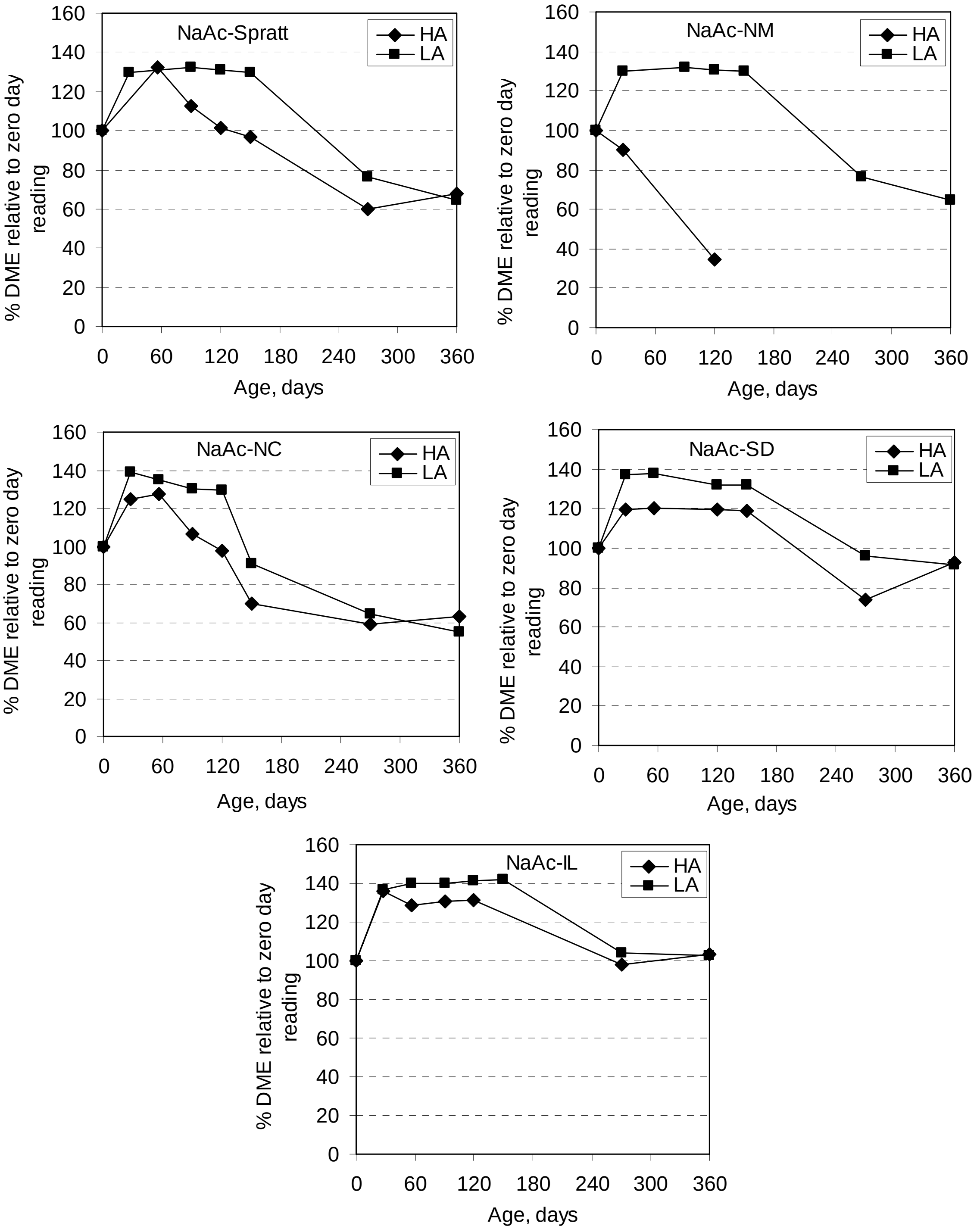

FIGURE 85. CHANGE IN DYNAMIC MODULUS OF CONCRETE PRISMS EXPOSED TO SODIUM ACETATE DEICER SOLUTION IN THE MODIFIED ASTM C 1293 TEST

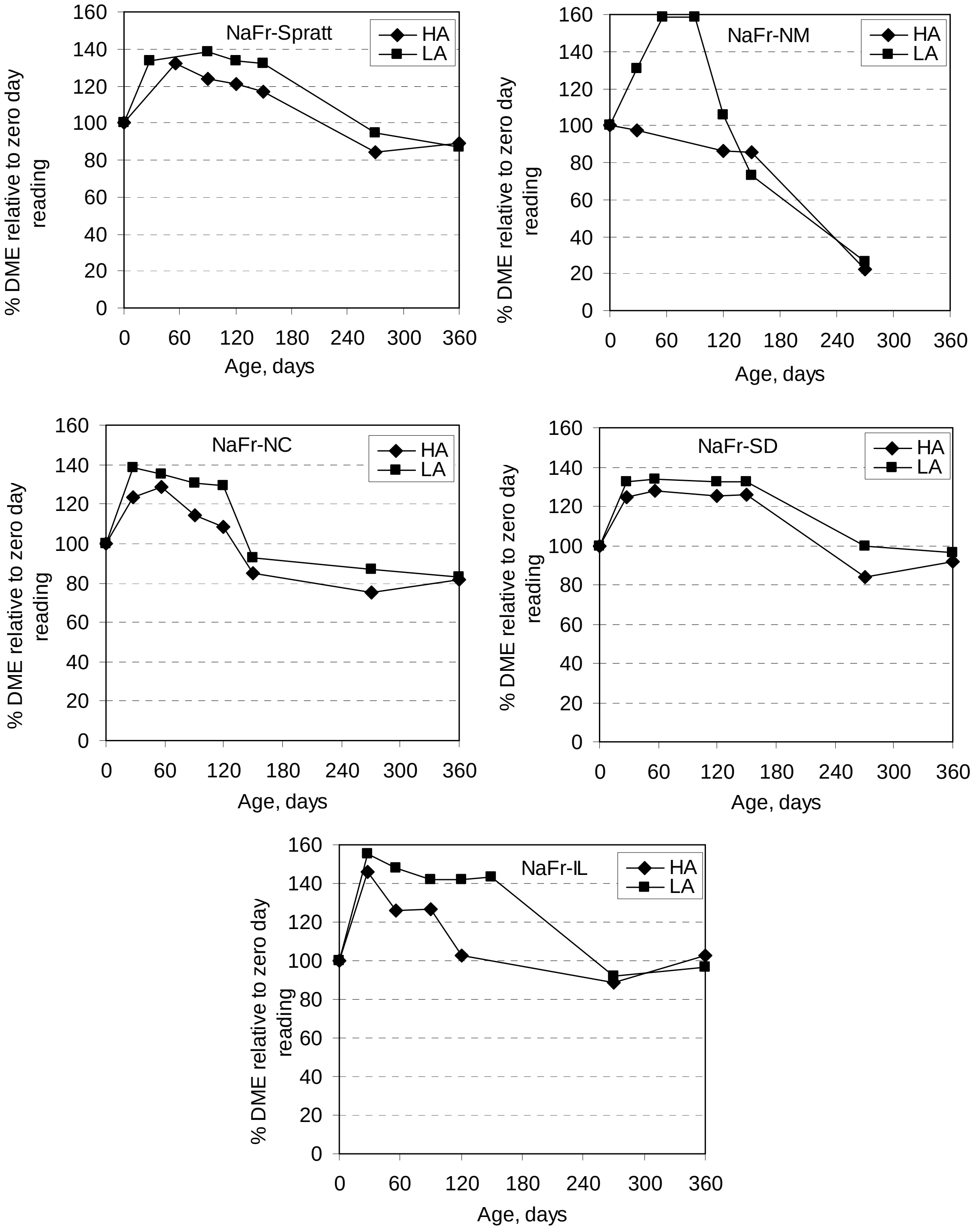

FIGURE 86. CHANGE IN DYNAMIC MODULUS OF CONCRETE PRISMS EXPOSED TO SODIUM FORMATE DEICER SOLUTION IN THE MODIFIED ASTM C 1293 TEST

6.3. pH CHANGES IN SOAK SOLUTIONS

The pH of the soak solutions, from which concrete prisms were removed after six months of exposure, was measured to study the interaction of the soak solutions with the concrete prisms. Figure 87 shows the pH values of soak solutions exposed to concrete prisms prepared with different aggregates and low-alkali cement after 6 months in the modified ASTM C 1293 tests. For each type of soak solution, the white bar in Figure 87 representing "plain solution" provides the pH of a solution in which no concrete prisms were immersed.

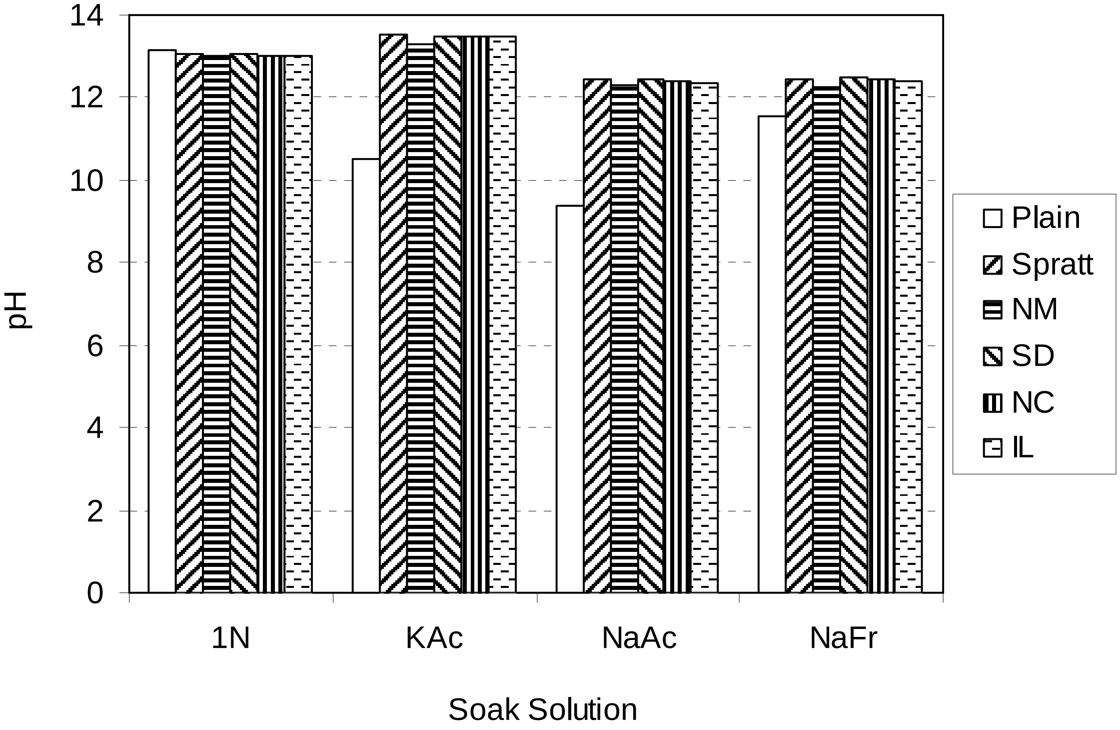

FIGURE 87. pH VALUES MEASURED IN SOAK SOLUTIONS RECOVERED FROM THE MODIFIED ASTM C 1293 TESTS WITH LA CEMENT, AND OF CORRESPONDING SOLUTIONS NOT EXPOSED TO CONCRETE.

Although pH readings of soak solutions were taken at the end of 6 and 11 months of the test program, there was virtually no change in the pH of the soak solutions between 6 and 11 months. It is observed from these results that for the 1N sodium hydroxide solution (first group of bars) virtually no difference in pH is observed between the "plain" solution and the solutions in which concrete prisms with different aggregates were stored. However, for the deicer solutions (potassium acetate, sodium acetate and sodium formate) a significantly higher pH was observed in the solution in which concrete prisms had been stored. Particularly for the acetate solutions, a pH difference corresponding to three orders of magnitude increase in OH^- ion concentration was observed. This clearly indicates that the deicer soak solutions interacted with the concrete prisms to induce the observed pH change. For the sodium formate deicer solution, the pH of the plain solution was substantially higher than other deicer solutions, and the change in pH observed upon exposure to concrete prisms was much smaller.

The trends in the pH changes of soak solution in modified ASTM C 1293 tests are very similar to those observed in the modified ASTM C 1260 tests (see Section 5.3). However, the magnitude of change in pH of the potassium acetate and sodium acetate deicer soak solutions in the ASTM C 1293 tests are less pronounced than the changes observed in the modified ASTM C 1260 tests. This might be due to the difference in temperatures at which the soak solutions were stored (38ºC for concrete prism soak solution and 80ºC for mortar bar soak solutions) and the temperatures at which the pH were measured (38ºC for concrete prism soak solutions and 25ºC for mortar bar soak solutions). The alkali content of the cement used did not have any influence on the changes in pH of the external soak solution. Instead, as previously discussed in Section 5.3, it appears that interaction between deicer solutions and calcium hydroxide present within the matrix of concrete appears to cause the observed jumps in pH.

6.4. MICROSTRUCTURE OF CONCRETE SPECIMENS

This section of the report summarizes the main features observed during the SEM examination of concrete specimens tested using either standard or modified ASTM C1293 protocol as described in Sections 3.2.3 and 3.2.4, respectively, of this report.

All SEM specimens were prepared following the procedure described in Section 3.2.7 of this report. In total, 20 different specimens were examined, as listed in Table 13. The symbols shown in Table 13 represent the designation of the Appendix which contains a selection of SEM micrographs taken of the individual specimens. For example, the series of micrographs collected for North Carolina argillite exposed to sodium acetate solution can be found in the Appendix **B-III-3**. Appendices B contain pictures of concrete samples which were stored in corrosive environment for 3 and 6 months. The SEM examinations were made only for 6-months samples. Although on average about 10 micrographs were taken for each specimen, only selected ones were included in the Appendix so as to limit the overall size of the report.

TABLE 13. TEST MATRIX FOR SEM/EDX ANALYSIS OF CONCRETE SPECIMENS

Specimen Type	Soak Solution	Non-Reactive Aggregate	Reactive Aggregate			
		Standard Ottawa Sand	Spratt Limestone	NC Argillite	NM Rhyolite/Andesite	SD Sioux Quartzite
Reference	1N Sodium Hydroxide	**B-I-1**	**B-I-2**	**B-I-3**	**B-I-4**	**B-I-5**
Test	Potassim Acetate	**B-II-1**	**B-II-2**	**B-II-3**	**B-II-4**	**B-II-5**
	Sodium Accetate	**B-III-1**	**B-III-2**	**B-III-3**	**B-III-4**	**B-III-5**
	Sodium Formate	**B-IV-1**	**B-IV-2**	**B-IV-3**	**B-IV-4**	**B-IV-5**

Due to the large number of pictures involved, it was impractical to analyze each of them individually. Instead, the authors of the report adopted an approach in which the effects of the deicers on the microstructure of concretes were evaluated in three broad categories: (i) the presence and location of cracks, (ii) the presence and location of gel, and (iii) the alteration of paste composition (see Tables for the individual deicers in the next section). For each of these categories, the severity of the effect was assigned a relative rating (ranging from light to severe) as shown in Table 14. The discussion presented in the remaining part of this chapter is an attempt to generalize the main changes in the characteristics of microstructure resulting from exposure to different deicers.

TABLE 14. RELATIVE RANKINGS OF SEVERITY OF MICROSTRUCTURAL CHANGES OBSERVED DURING THE SEM/EDX ANALYSIS OF CONCRETE SPECIMENS

Relative Ranking of Severity	Description
"no"	The feature of interest not observed
"+"	The feature of interest present but the intensity was *light*
"++"	*Moderate* intensity of the feature of interest
"+++"	*Severe* intensity of the feature of interest
"-"	Not possible to confirm if the feature of interest was present due to lack of supporting evidence (e.g. no EDX in the paste)

6.4.1. Concrete Specimens Exposed to 1N Sodium Hydroxide Soak Solution

Table 15 summarizes the main features observed during the SEM observations of concrete specimens exposed to 1N sodium hydroxide solution for 6 months during the modified ASTM C1293 test.

TABLE 15. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF CONCRETE SPECIMENS EXPOSED TO 1N SODIUM HYDROXIDE SOLUTION (MODIFIED ASTM C1293 TEST)

Main Features of Microstructure		**Sodium Hydroxide (NaOH)**				
		Illinois	Spratt	NC	NM	SD
Cracking - general appearance		+*	+	+	+	+
	within the aggregate	no	+	+	+	+
	within the paste	+	+	+	+	+
	at the interfaces	no	-	+	+	+
Gel presence		no	+	+	-	+
	within the aggregate	no	+	+	-	-
	within the paste	no	+	+*	-	-
	at the interfaces	no	+	+	-	+
Paste altered						
	increased level of K	-	no	-	no	-
	increased level of Na	-	+	-	no	-
	increased level of S	-	-	-	-	-
	increased level of Al	-	-	-	-	-
	presence of Na-Ca-S	-	-	-	-	-
	presence of K-Ca-S	-	-	-	-	-
	presence of monosulfate	-	-	-	-	-

*only in the paste

For concrete samples made with Illinois dolomite aggregate (which is considered an inert, reference aggregate), only some fine cracks were observed within the paste (see Figure 88). No gel or other visible signs of aggregate deterioration were observed.

For all of the reactive aggregates, cracks were seen both in the aggregate and in the paste, but the intensity of cracking was rather low. In addition to the cracks observed within the aggregates grains and within the paste in concretes made with three of the reactive aggregate (i.e. NM rhyolite, SD quartzite and N Argillite) cracks at the interface could also be observed (Figure 89). ASR gel was found in concretes made with three of the reactive aggregates, i.e. Spratt limestone, SD quartzite and NC argillite. The ASR gel was found within the aggregates (Spratt limestone, NC argillite), within the paste (Spratt limestone, NC argillite) and at the interfaces between aggregate and paste (Spratt limestone, NC argillite, and SD quartzite). In case of NM rhyolite, no discreet deposits of ASR gel were observed within the sample. However, this does not necessarily rule out the possible presence of small amounts of gel in areas of the concrete that were not examined. In concretes made with the Spratt limestone and the NC argillite aggregates, the gel appears to flow out of the aggregate grains into the surrounding paste (see Figure 90). In prisms made with NC argillite aggregate deposits within some of the air voids are also visible (Figure 91).

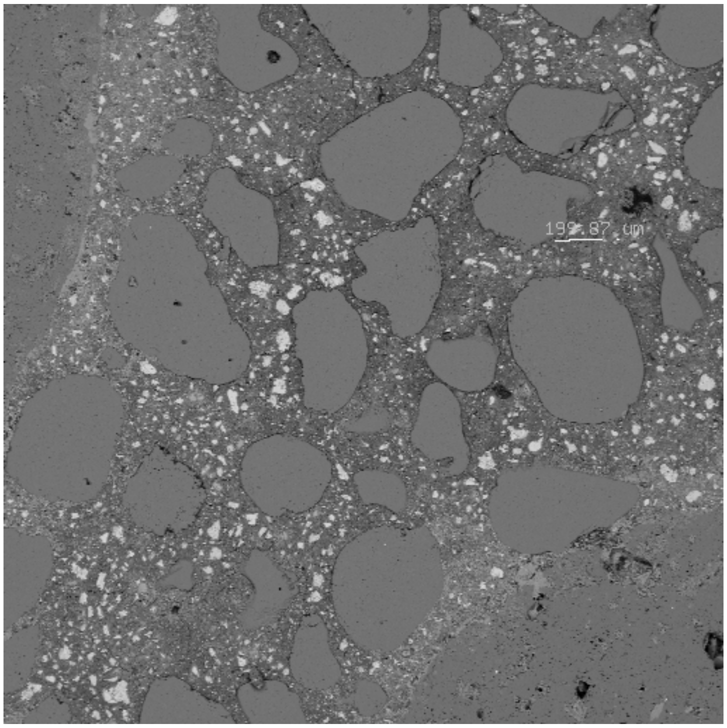

FIGURE 88. TYPICAL MICROSTRUCTURE OF ILLINOIS DOLOMITE CONCRETE AFTER 6 MONTHS OF EXPOSURE TO 1N NaOH SOLUTION

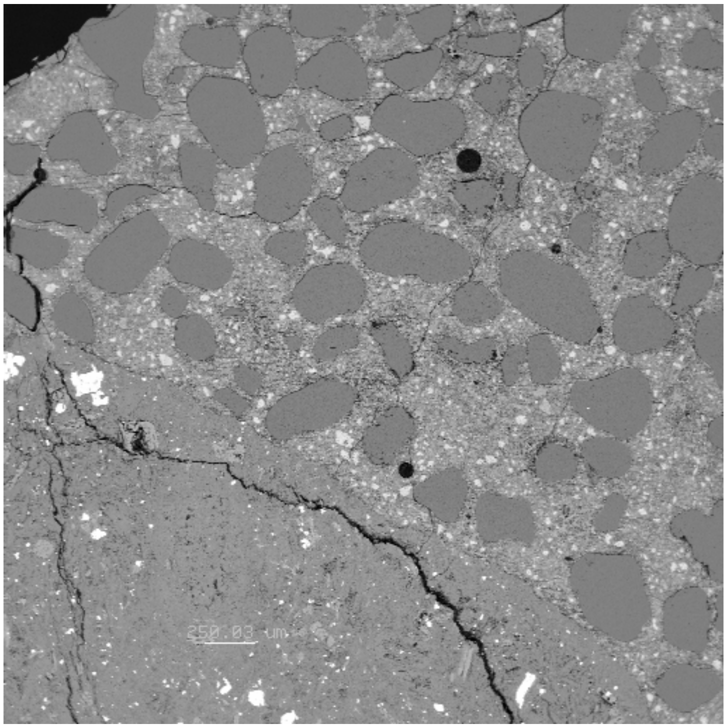

FIGURE 89. CRACKS WITHIN NM AGGREGATE GRAIN, WITHIN THE PASTE AND AT THE INTERFACES.

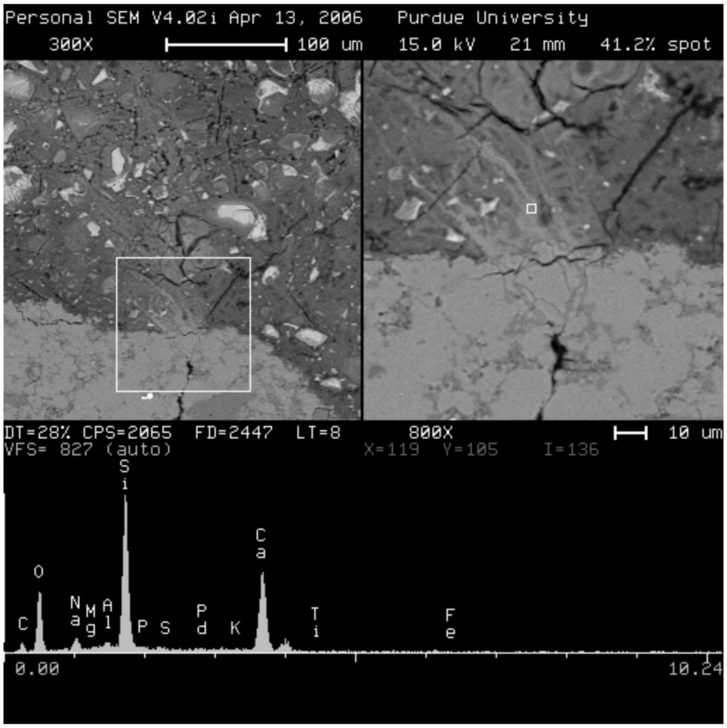

FIGURE 90. Si-Ca-Na GEL FLOWING OUT OF THE AGGREGATE (SPRATT SILICEOUS LIMESTONE)

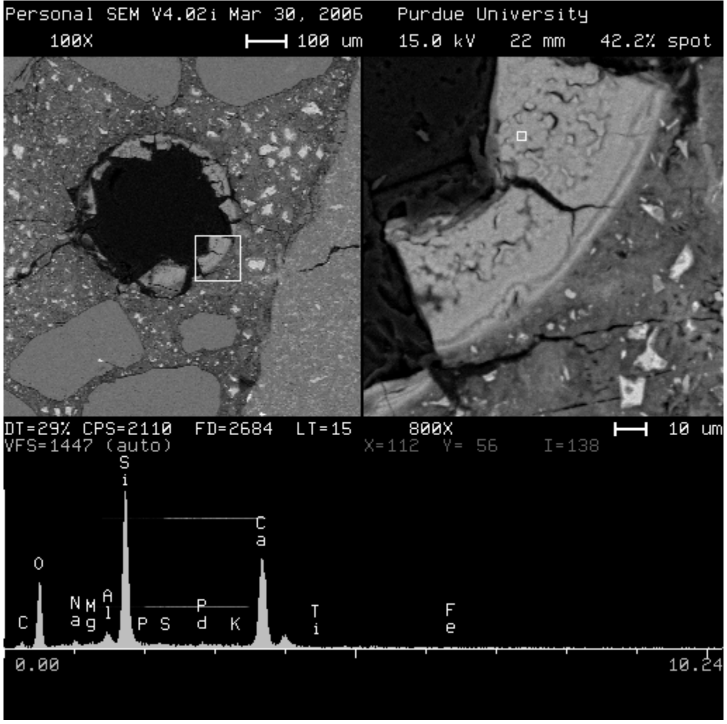

FIGURE 91. AIR VOID PARTIALLY FILLED WITH Si-Ca-Al-Na DEPOSIT (NORTH CAROLINA ARGILLITE AGGREGATE)

6.4.2. Concrete Specimens Exposed to Potassium Acetate Deicer Soak Solution

Table 16 summarizes the main features observed during the SEM observations of concrete specimens exposed for 6 months to potassium acetate solution during the modified ASTM C1293 test.

TABLE 16. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF CONCRETE SPECIMENS EXPOSED TO POTASSIUM ACETATE SOLUTION (MODIFIED ASTM C1293 TEST)

Main Features of Microstructure		**Potassium Acetate (KAc)**				
		Illinois	Spratt	NC	NM	SD
Cracking - general appearance		+*	++	+	+++	+ (-)
	within the aggregate	no	++	-	+	-
	within the paste	+*	++	+	+++	+
	at the interfaces	no	+	+	+++	-
Gel presence		-	++	+	+	+
	within the aggregate	-	+	-	+	+
	within the paste	-	+++**	-	no	no
	at the interfaces	-	++	+	no	+
Paste altered						
	increased level of K	+	+	-	-	-
	increased level of Na	no	no	-	-	-
	increased level of S	no	+	-	+	-
	increased level of Al	no	-	-	-	-
	presence of Na-Ca-S	no	no	-	no	-
	presence of K-Ca-S	no	+	-	++	-
	presence of monosulfate	-	-	-	-	-

*only very few in the paste
**rivers of gel within the paste

Reference aggregate concrete containing IL dolomite aggregate showed very few cracks within the paste; in contrast cracks in the paste were present in all other concretes studied. Concrete made with the NM rhyolite aggregate was the most severely cracked of these. The cracks in these concrete prisms were wide, and ran through the paste and also along the interface between paste and aggregates (see Figure 92). Concretes made with all of the reactive aggregates except the SD quartzite showed cracks along the aggregate–paste interface.

No gel was found in concrete prisms with IL dolomite aggregate. All other concrete samples contained visible gel. Concrete prisms containing Spratt siliceous limestone contained the most amount of gel. In these concrete prisms the gel was located mainly within the paste, forming “rivers of gel” (Figure 93) or to a lesser extent at the paste-aggregate interface. Gel was also present to some extent within the aggregate grains. For other reactive aggregates, no gel was observed within the paste, but gel was located either within the aggregates (NM rhyolite, SD quartzite, Figure 94) or at the interface (NC argillite and SD quartzite). Gel composition was found to be mainly Si-Ca-K (see Figure 94).

In several cases the alteration of paste itself was also observed. In concretes with Illinois dolomite and Spratt limestone the paste contained areas rich in potassium. Spratt limestone concrete paste also contained areas rich in sulfur, especially near the edges of the aggregate particles. Similar sulfur-rich areas were also observed in the paste of New Mexico rhyolite concrete. In addition, both in Spratt limestone and new Mexico rhyolite concretes some areas of the paste contained S-K-Ca deposits, most likely indicating the presence of syngenite or other sulfate-bearing phases (Figure 95).

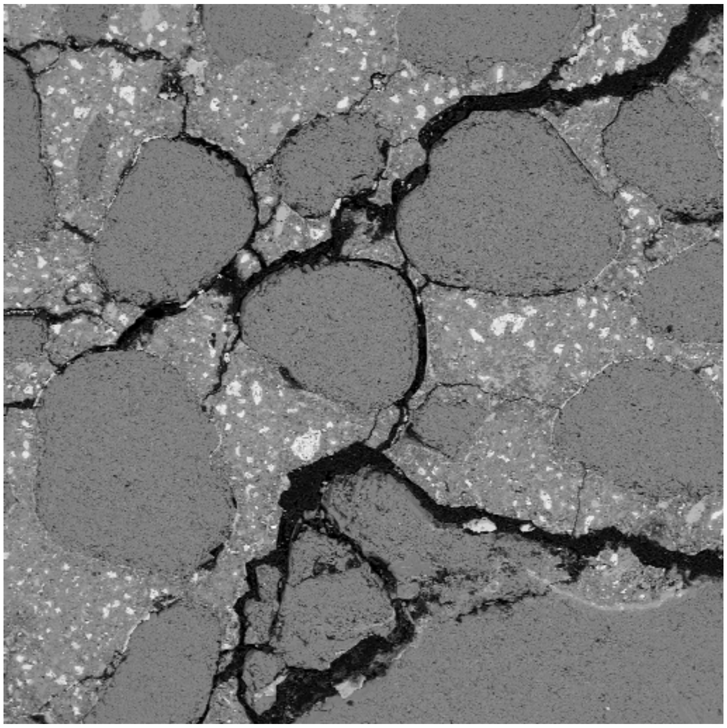

FIGURE 92. SEVERE CRACKING WITHIN THE PASTE AND SOME CRACKING WITHIN AGGREGATES IN NEW MEXICO RHYOLITE CONCRETE

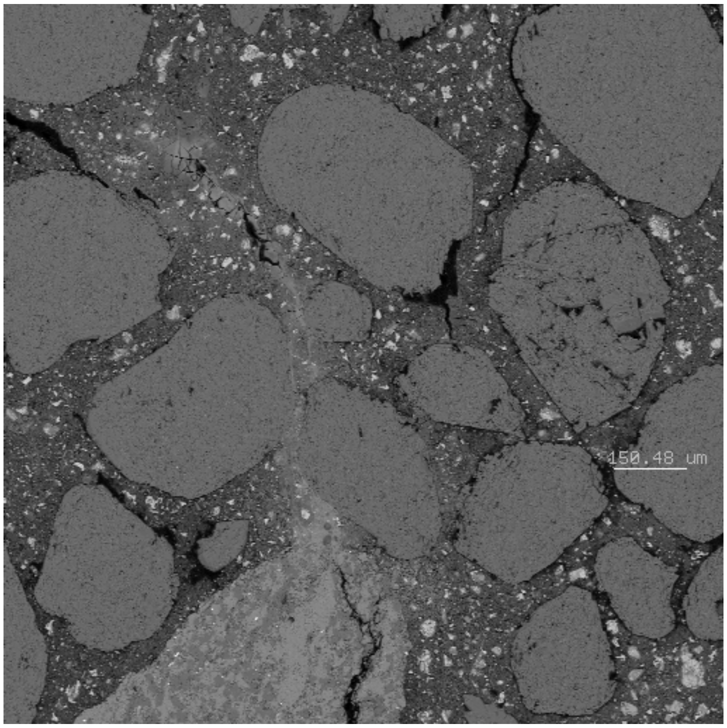

FIGURE 93. RIVER OF GEL IN SPRATT SILICEOUS CONCRETE SAMPLE

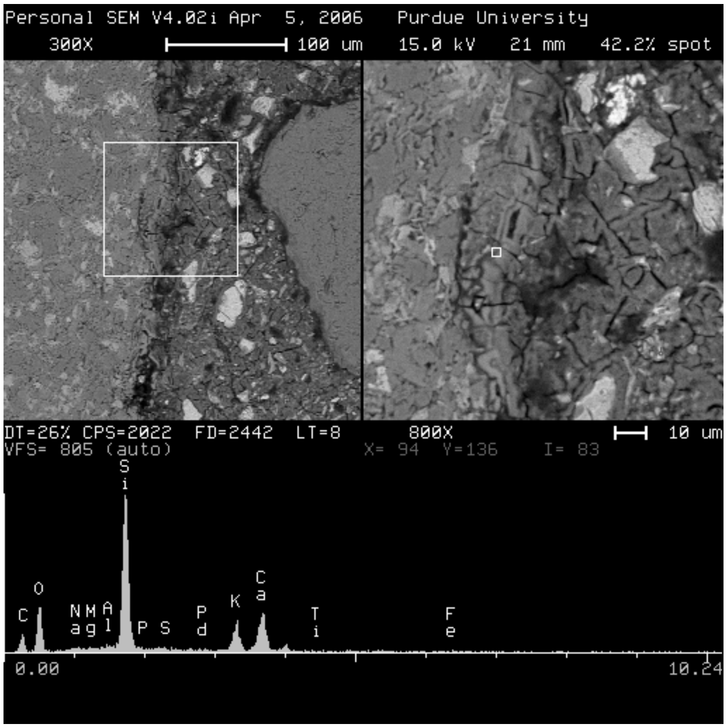

FIGURE 94. GEL PRESENT AT THE PASTE-AGGREGATE INTERFACE (NC ARGILLITE)

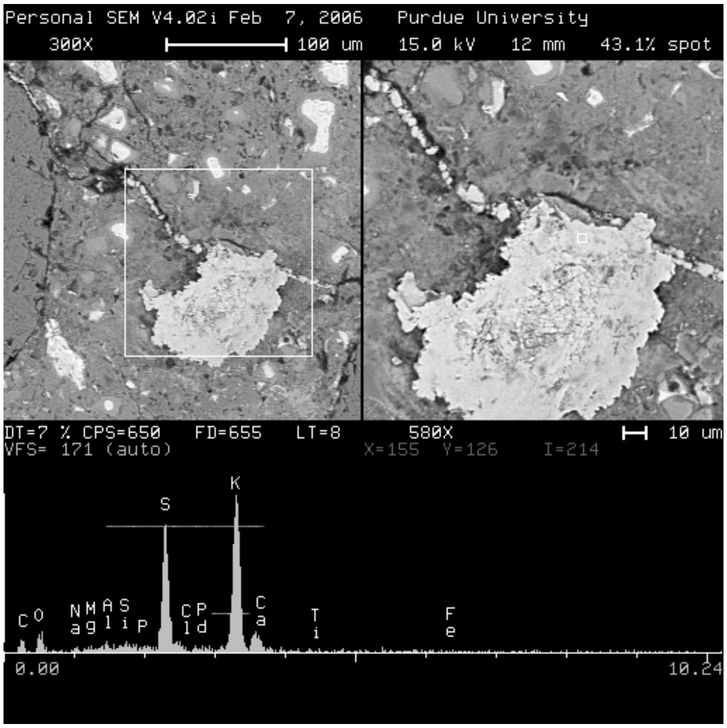

FIGURE 95. S - K - Ca DEPOSIT (NM RHYOLITE)

6.4.3. Concrete Specimens Exposed to Sodium Acetate Deicer Soak Solution

Table 17 summarizes the main features observed during the SEM observations of concrete specimens exposed to sodium acetate solution for 6 months during the modified ASTM C1293 test.

TABLE 17. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF CONCRETE SPECIMENS EXPOSED TO SODIUM ACETATE SOLUTION (MODIFIED ASTM C1293 TEST)

Main Features of Microstructure		**Sodium Acetate (NaAc)**				
		Illinois	Spratt	NC	NM	SD
Cracking - general appearance		no	+	+	+	+
	within the aggregate	no	-	+	+	-
	within the paste	no	+	+	no	+
	at the interfaces	no	+	++	+	+
Gel presence		+	+	++	+	+
	within the aggregate	no	-	+	+	
	within the paste	+	-	++*	no	
	at the interfaces	no	+	+	no	+
Paste altered						
	increased level of K	-	-	-	no	no
	increased level of Na	-	+	-	+**	+
	increased level of S	-	-	-	+	+
	increased level of Al	-	-	-	+	no
	presence of Na-Ca-S	-	-	-	no	no
	presence of K-Ca-S	-	-	-	no	no
	presence of monosulfate	-	-	-	+	-

*rivers of gel
** not very much

Concrete samples containing the non-reactive IL dolomite aggregate were not affected by the sodium acetate deicer solution. There were no cracks visible and no gel present in these samples. Concrete prisms prepared with all the reactive aggregates showed some, but not extensive, cracking. In all cases, cracks were present at the paste-aggregate interface (see Figure 96). In concrete made with NM rhyolite aggregate such cracks were visible in 3-month old samples. Concrete samples with NC argillite and NM rhyolite also showed cracking within aggregate grains (Figure 97).

Gel was present in all of the sodium acetate-exposed concretes made with reactive aggregates. Of the various concretes, the largest content of gel was found in that made with the NC argillite. It was present as “rivers of gel” in the paste or at the interfaces, even in the vicinity of the non-reactive fine aggregates (Figure 98). For NC argillite and NM rhyolite aggregates, gel was also present within the aggregate grains. The composition of gel was primarily Si-Ca-Na.

In general, the paste in concretes was rich in Na, presumably due to ingress of the sodium acetate deicer solution. With the NM rhyolite and SD quartzite aggregate concretes many monosulfate deposits were observed. The paste in the concrete prisms made with NM rhyolite aggregate also had elevated Al content.

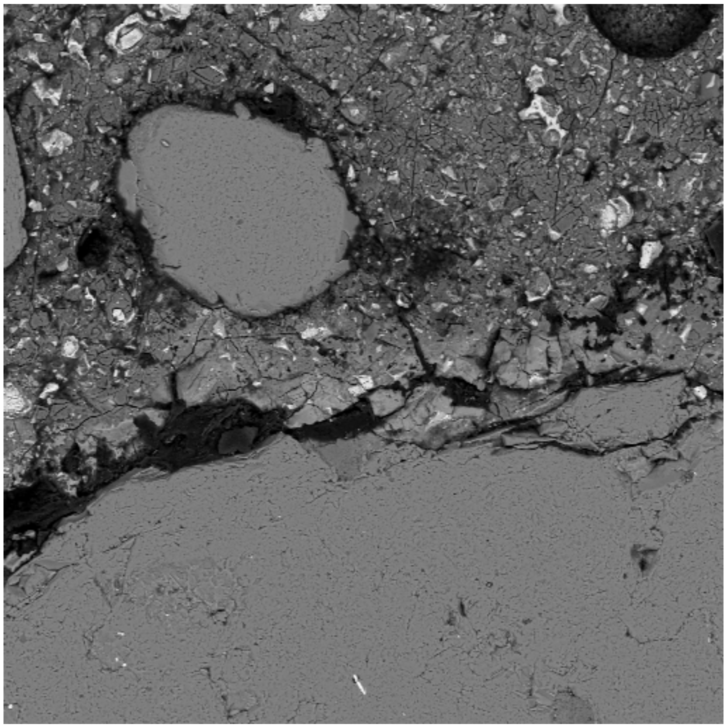

FIGURE 96. CRACKS ALONG THE INTERFACE AND ALSO WITHIN THE PASTE (NM RHYOLITE CONCRETE)

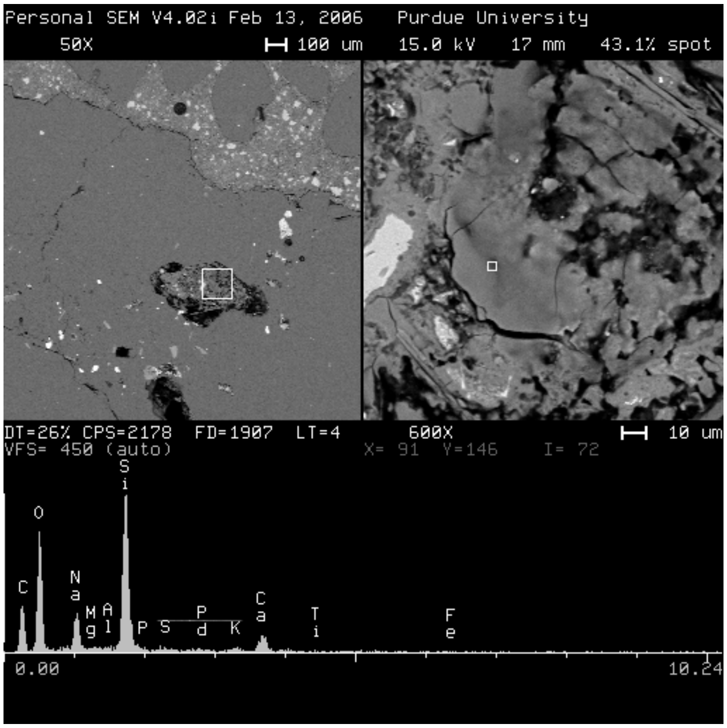

FIGURE 97. CRACKS WITHIN THE AGGREGATE. ALKALI - SILICA GEL VISIBLE INSIDE THE "POCKET" WITHIN THE AGGREGATE (NM RHYOLITE CONCRETE)

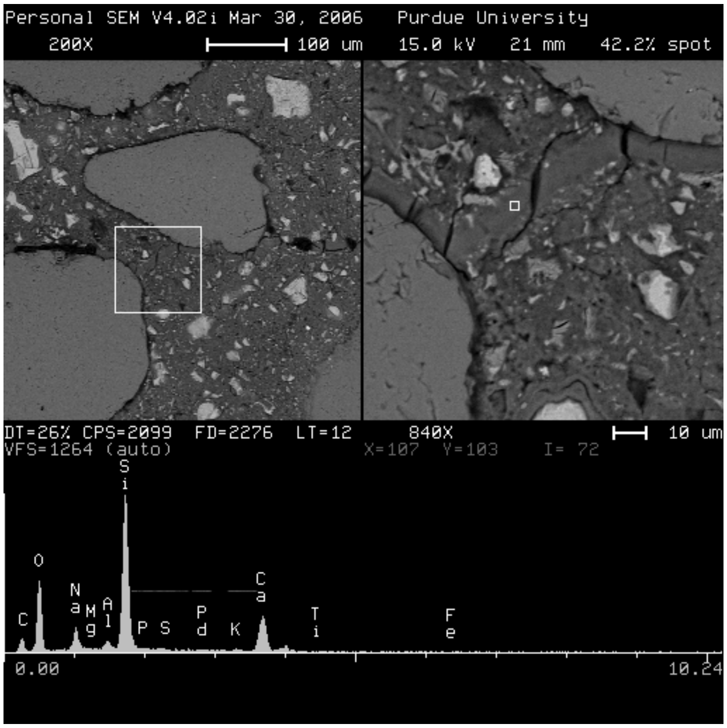

FIGURE 98. CRACK WITHIN THE PASTE AND AT THE INTERFACE FILLED WITH GEL (NC ARGILLITE CONCRETE)

6.4.4. Concrete Specimens Exposed to Sodium Formate Deicer Soak Solution

Table 18 summarizes the main features observed during the SEM observations of concrete specimens exposed to sodium formate solution during the modified ASTM C1293 test.

TABLE 18. RELATIVE INTENSITY OF THE MAIN MICROSTRUCTURAL FEATURES OF CONCRETE SPECIMENS EXPOSED TO SODIUM FORMATE SOLUTION (MODIFIED ASTM C1293 TEST)

Main Features of Microstructure		**Sodium Formate (SF)**				
		Illinois	Spratt	NC	NM	SD
Cracking - general appearance		no	+	++	+	+
	within the aggregate	no	+	-	-	-
	within the paste	no	+	++	+	+
	at the interfaces	no	+	++	+	+
gel presence		no	+*	+	-	+*
	within the aggregate	no	+	-	-	-
	within the paste	no	++	+*	-	+
	at the interfaces	no	+	+	-	+
paste altered						
	increased level of K	no	no	-	no	no
	increased level of Na	+	+	+	+	+
	increased level of S	-	-	-	-	+
	increased level of Al	-	+	+	-	+
	presence of Na-Ca-S	-	-	-	-	no
	presence of K-Ca-S	-	-	-	-	no
	presence of monosulfate	-	-	+	-	-

There was no sign of deleterious reaction in the control concrete with Illinois limestone aggregate. In contrast, all of the concretes with reactive aggregates showed cracks within the paste and at the interface. The cracking in the concrete made with NC argillite aggregate was more extensive than in the other concretes (see Figure 99). For prisms made with Spratt limestone and NC argillite aggregates, cracks within the aggregate grains were also observed (see Figure 100).

All of the concrete made with reactive aggregates, except that made with NM rhyolite aggregate contained gel. The gel was found mainly in paste (see Figure 101) and at the interfaces (Figure 102). Concrete with Spratt limestone and NC argillite aggregates contained gel within the grains (Figure 103). An interesting feature - a rim of gel around inert fine aggregate - was observed in the Spratt limestone concrete prism (Figure 104). Na content in paste was markedly increased for both control and reactive aggregate concretes. In addition, the Al level was elevated.

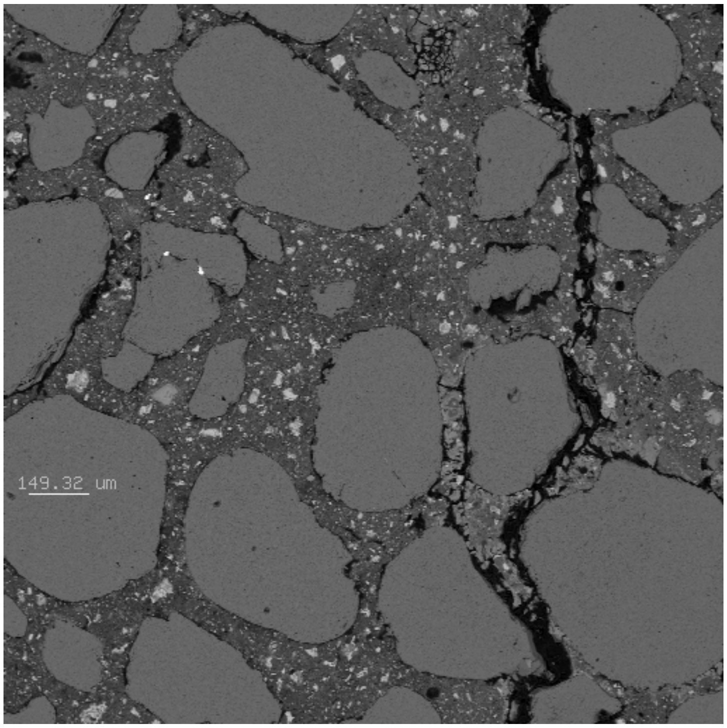

FIGURE 99. CRACKING WITHIN THE PASTE AND AT THE INTERFACE (NORTH CAROLINA ARGILLITE CONCRETE)

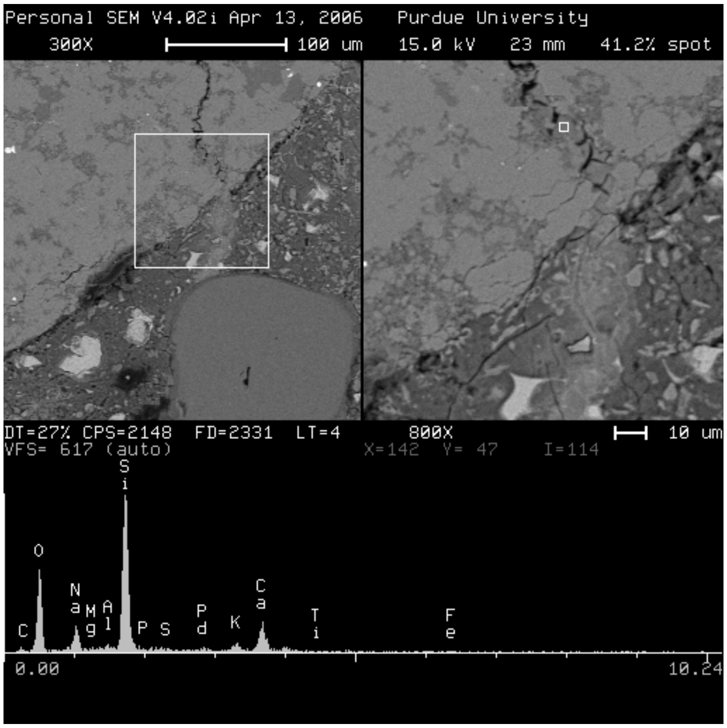

FIGURE 100. CRACK WITHIN THE AGGREGATE. GEL INSIDE THE CRACK (SPRATT SILICEOUS LIMESTONE CONCRETE)

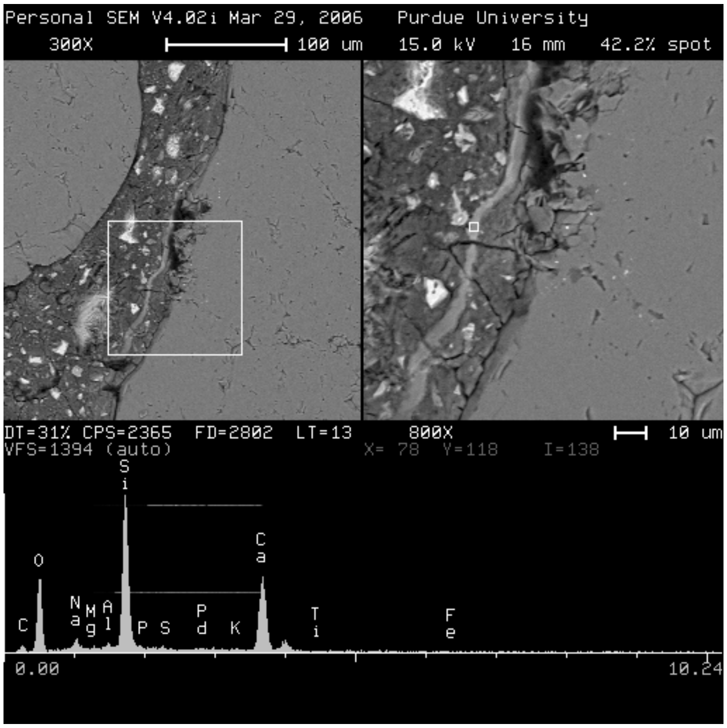

FIGURE 101. RIVER OF GEL ALONG FINE AGGREGATE GRAIN (SOUTH DAKOTA QUARTZITE)

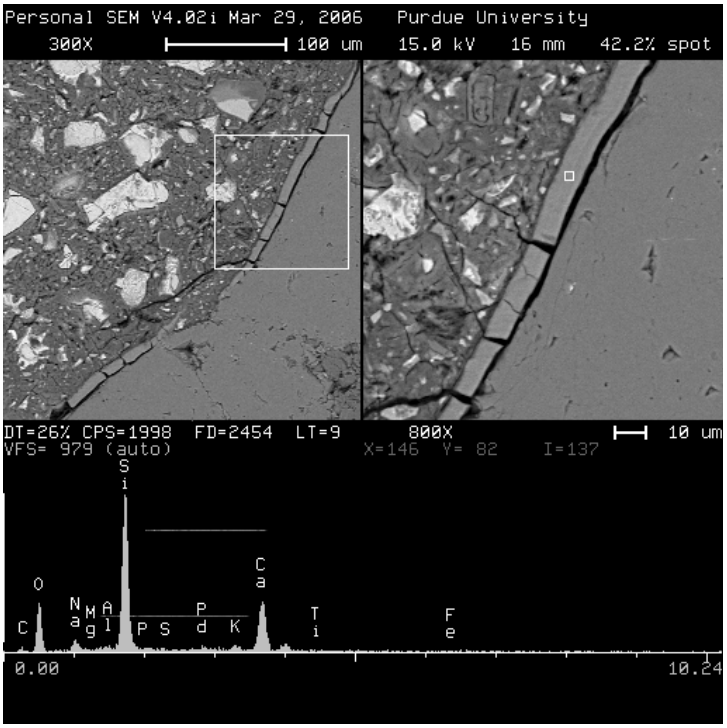

FIGURE 102. LAYER OF GEL AROUND AGGREGATE GRAIN (SOUTH DAKOTA QUARTZITE)

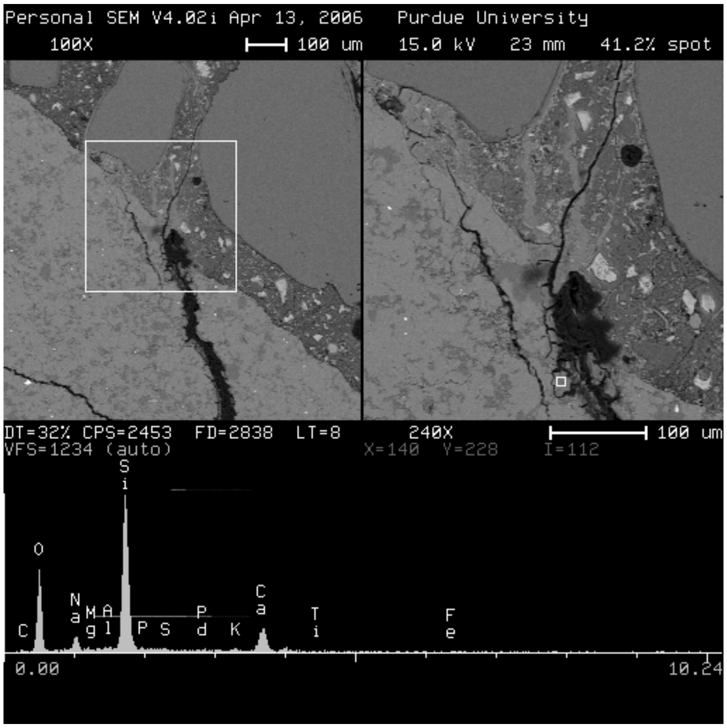

FIGURE 103. GEL WITHIN THE AGGREGATE (SPRATT LIMESTONE)

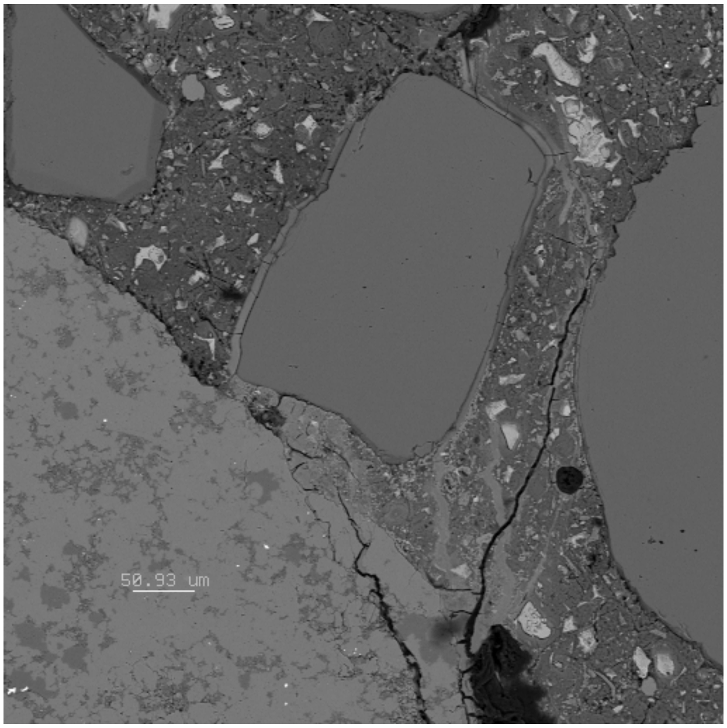

FIGURE 104. GEL RIM AROUND NON-REACTIVE FINE AGGREGATE (IN SPRATT LIMESTONE CONCRETE PRISM)

6.4.5. Summary of the Effects of Deicers on the Microstructure of Concretes

The discussion presented in sections 6.4.1 to 6.4.4 of this report clearly indicates that although the individual effects varied, all deicers used during this research program had strong influences on the microstructure of concretes. The degree of changes observed in the microstructure (i.e. the severity of the attack) varied as a function of both the type of the deicer and the type of the aggregate. These effects are briefly summarized below.

6.4.5.1. Presence and Location of Cracks

The presence of cracks was observed in the individual grains of the aggregates, within the paste and at the interfaces between the paste and the aggregate. The aggregate cracks were encountered most frequently in the grains of Spratt limestone and NM rhyolite and were more severe where sodium hydroxide and potassium acetate were used as deicers. In all cases, the pastes in concretes containing reactive aggregate were cracked, with severe cracking being associated with potassium acetate, sodium hydroxide and sodium formate deicers. The interface cracks were most intense in concretes with NC argillite and NM rhyolite aggregates and in the presence of potassium acetate and sodium formate deicers. The highest overall level of cracking was associated with potassium acetate deicer and with NC argillite, NM rhyolite aggregates.

6.4.5.2. Presence and Location of Gel

In most cases, the presence of gel was strongly linked to the presence of cracks. As a result, the presence of gel was analyzed with respect to the location in the grains of aggregate, in the paste or at the interface. Gel present within the aggregate grains was most commonly encountered with Spratt limestone concrete prisms exposed to potassium acetate deicer. ASR gel within the paste was most frequently encountered with Spratt limestone and NC argillite bearing concrete prisms exposed to sodium acetate deicer. Gel at paste-aggregate interface was most frequently associated with Spratt limestone bearing concrete exposed to potassium and sodium acetate deicers. The overall content of gel seemed to be greatest for Spratt limestone and NC argillite bearing concretes exposed to either potassium acetate or sodium acetate deicers.

6.4.5.3. Alteration of Paste Composition

The most extensive signs of alteration of paste composition were associated with Spratt limestone and NM rhyolite aggregates and with potassium acetate, sodium acetate and sodium formate deicers.

6.5. PORE SOLUTION ANALYSIS

The pore solution analyses were conducted for concretes soaked in sodium hydroxide and in deicer solutions for 90 days at 38°C. The K^+, Na^+ and Ca^{2+} estimated concentrations were determined by spectrophotometer. The OH^- ion concentration was estimated by titration with dilute hydrochloric acid with phenolphthalein indicator. The SO_4^{2-} and CH_3COO^- ion concentrations were determined with ion chromatography.

The results of cation concentrations in pore solutions obtained from high alkali cement concretes soaked in different deicer solutions are given in Table 19. In general, very high concentrations of K^+ were detected in the pore solutions of concretes soaked in salt solutions containing K^+ ions (potassium acetate deicer). Similarly, high concentrations of Na^+ were also observed in pore solution of concretes soaked in solutions containing Na^+ ions (sodium acetate and sodium formate deicers). The origin of this phenomenon is, obviously, the transport of cations from the external solution to the inside of the prisms driven by the differences in concentrations between sample and external solution. The concentrations of K^+ and Na^+ ions in pore solutions of concretes soaked in solutions bearing K and Na, respectively, increased with time (3 months versus 6 months old samples). The concentration of ions which were not present in the soak solution was virtually stable with time. In the case of concrete soaked in 1N NaOH, the Na^+ concentration was far lower than that in concretes soaked in sodium acetate and sodium formate solutions, and did not change between 3 and 6 months, reflecting the lower concentration of Na^+ in 1 N NaOH solution as compared to Na^+ concentration in sodium acetate and sodium formate.

Analyzing the Ca^{2+} concentration for 3 months old concrete, it was seen that for concretes exposed to potassium acetate deicer solution the concentration of Ca^{2+} is unexpectedly high, between 13 and 85 mM. For the other solutions this concentration is generally low – ranging from 7 mM to down below the detection limit (b.d.l.) of the equipment. In concrete soaked in potassium acetate deicer solution for 6 months, Ca^{2+} concentration was also very high (68 mM), while the others were low (below 2 mM).

The concentrations of OH^- ions in pore solutions were estimated by titration with phenolphthalein as an indicator and are shown in Table 20 and in Figures 105 and 106.

TABLE 19. CATION CONCENTRATIONS IN PORE SOLUTIONS OF HIGH ALKALI CEMENT CONCRETES EXPOSED TO DIFFERENT SOAK SOLUTIONS AT THE END OF 3 MONTHS AND 6 MONTHS

Aggregate	K^+ Conc. [moles/dm^3]				Na^+ Conc. [moles/dm^3]				Ca^{2+} Conc. [moles/dm^3]				SO_4^{2+} Conc. [moles/dm^3]				CH_3COO^- Conc. [moles/dm^3]			
	KAc	NaAc	NaFr	1N NaOH	KAc	NaAc	NaFr	1N NaOH	KAc	NaAc	NaFr	1N NaOH	KAc	NaAc	NaFr	1N NaOH	PA	SA	SF	1N NaOH
NM - 3 mos.	4.57	0.14	0.13	0.06	0.25	3.76	3.10	0.55	0.085	0.005	0.002	b.d.l.	-	-	-	-	-	-	-	-
NM - 6 mos.	5.99	0.12	0.10	0.22	0.27	4.00	4.24	0.54	0.068	0.101	0.002	0.002	0.0076	0.0149	0.0690	-	5.26	4.00	-	-
S Dakota	3.77	0.38	0.30	0.17	0.49	2.86	2.24	0.73	0.015	0.005	0.002	0.002	-	-	-	-	-	-	-	-
Spratt	3.47	0.20	0.17	0.08	0.39	3.50	3.93	0.73	0.013	0.007	0.002	b.d.l.	-	-	-	-	-	-	-	-
NC - 3 mos.	4.33	0.23	0.22	0.13	0.38	4.05	2.77	0.65	0.027	0.007	0.002	b.d.l.	-	-	-	-	-	-	-	-
NC - 6 mos.	-	-	-	-	-	-	-	-	-	-	-	-	0.0221	0.0176			3.56	4.47	-	-
Illinois	4.18	0.31	-	0.15	0.34	3.32	-	0.76	0.042	0.005	-	b.d.l.	-	-	-	-	-	-	-	-

b.d.l. = below detection level

PA = KAc; SA = NaAc; SF = NaFr

TABLE 20. OH^- IONS CONCENTRATIONS IN PORE SOLUTIONS OF HIGH ALKALI CEMENT CONCRETES MADE OF DIFFERENT AGGREGATES AND SOAKED IN DIFFERENT SOAK SOLUTIONS AT THE END OF 3 MONTHS AND 6 MONTHS

Aggregate	OH^- Concentration [moles/dm^3] – 3 months				OH^- Concentration [moles/dm^3] -- 6 months			
	Soak Solution				Soak Solution			
	KAc	NaAc	NaFr	1N NaOH	KAc	NaAc	NaFr	1N NaOH
New Mexico	0.035	0.140	-	0.607	0.060	0.089	0.520	0.580
South Dakota	0.060	0.188	-	0.720	-	-	-	-
Spratt	0.051	0.095	0.212	0.439	-	-	-	-
North Carolina	0.044	0.095	0.224	0.662	-	-	-	-
Illinois	0.030	-	-	0.620	-	-	-	-
Average	0.044	0.130	0.218	0.610				
Std. Dev.	0.012	0.044	0.009	0.105				
Coeff. of Var.	0.27	0.34	0.04	0.17				

The results of the OH^- analysis were rather surprising. To start with, the pH values determined by conventional glass-electrode standardized to calcium hydroxide showed much higher values than indicated by the titration results. In point of fact, the titration indicated that the concentrations of OH^- ions (in case of concretes soaked in potassium acetate deicer solution) were very low – between 0.030 and 0.060 M. This is not the concentration range which would be able to cause ASR in terms of the conventional mechanism of this reaction. For sodium acetate and sodium formate deicer solutions, the indicated concentrations of hydroxyl ions by titration were somewhat higher, but they were also far below the concentration considered necessary for triggering the ASR. The only exception was the pore solution of the concretes soaked in sodium formate for 6 months, where the OH^- ions concentration was estimated by the titration to be about 500 mM. What is even more unusual, these values were substantially lower than those expected for normal concrete. It is also worth noting that the indicated differences between the hydroxyl ions concentrations for different aggregates were far less than the concentration differences between average concentrations for different soak solutions. The indicated hydroxyl ion concentration in sodium hydroxide soak solution were far higher than those of the deicer solutions and were, as expected, in the range considered as a potentially dangerous for reactive aggregates.

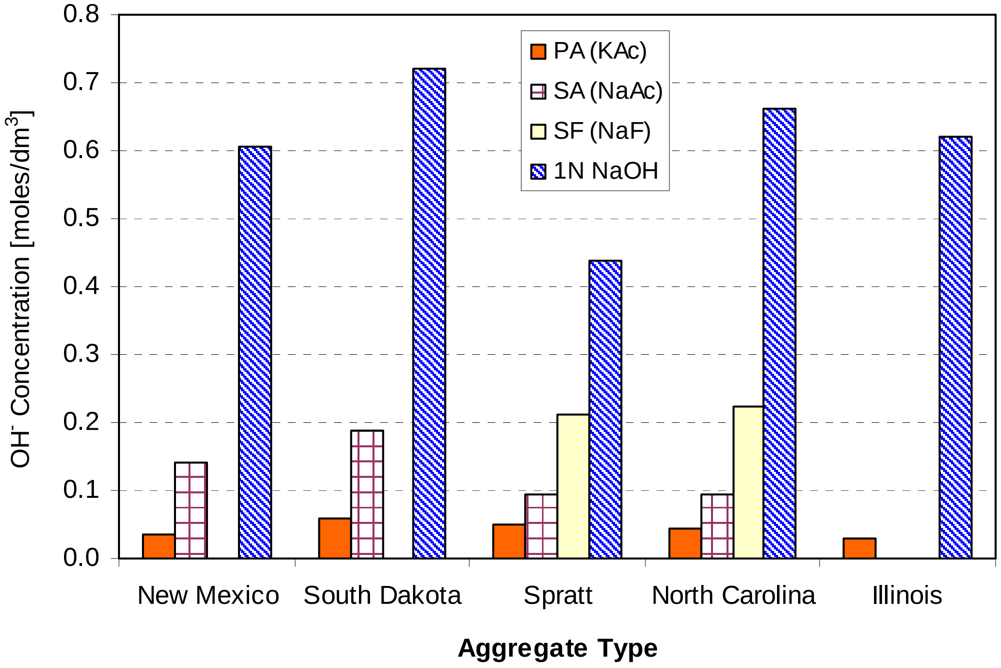

FIGURE 105. OH^- ION CONCENTRATIONS IN PORE SOLUTIONS OF CONCRETES EXPOSED TO DIFFERENT DEICERS SOLUTIONS AT THE END OF THREE MONTHS

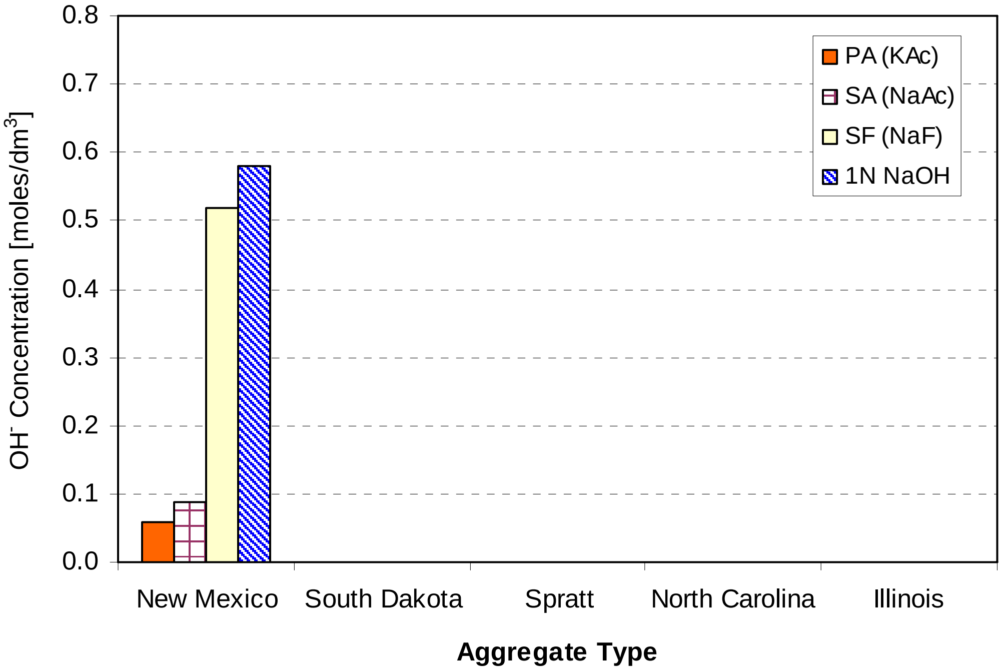

FIGURE 106. OH^- ION CONCENTRATIONS IN PORE SOLUTIONS OF CONCRETES EXPOSED TO DIFFERENT DEICERS SOLUTIONS AT THE END OF SIX MONTHS

It is also worth noting that the concentration of Ca^{2+} for potassium acetate deicer solution concretes was above the solubility level for saturated $Ca(OH)_2$ in water which is about 0.02 mol/dm^3. This may indicate that the calcium ion solubility product was significantly influenced by the high concentration of acetate ions and that the OH^- ions in the presence of acetate ions may not be controlling the Ca^{2+} ions concentration, as it does in normal concrete pore solutions. Nevertheless, as expected, when we compare the concentrations of Ca^{2+} and OH^- ions for different soak solutions, we can see that the higher the hydroxyl ions concentration, the lower the calcium concentration.

The analyses of acetate ions concentrations indicated some interesting trends. These analyses were only performed for 6 month old concretes. The concentration of acetate ions in the various pore solutions were between 3.6 M (NC-HA-KAc) and 5.3 M (NM-HA-KAc). This means that the pore solutions are essentially potassium or sodium acetate solutions (for acetate-based deicers). It can be expected, that for formate deicers, the situation is probably similar, and the pore solution is probably mainly potassium or sodium formate.

The sulfate ion concentration in the pore solutions expressed from 6-month old concretes exposed to potassium acetate deicer solutions was low, in the range between 8 and 22 mM. For sodium acetate deicer soaked concretes, the concentration was moderate – between 15 and 18 mM. The highest concentration of sulfates was found in pore solution from sodium formate soaked concretes (69 mM).

Some fundamental differences are seen when comparing pore solutions of concrete soaked in sodium hydroxide and those soaked in deicers solutions. One of these differences is that for concretes soaked in deicers the total concentrations of ions in pore solutions are much higher than for sodium hydroxide soaked concretes (up to and even in some cases slightly over 6 M). In addition, the difference is not only in concentrations, but also in the species of anions. In sodium hydroxide soaked concrete, the anionic constituent of the liquid phase is almost entirely OH^-, balanced by Na^+ and some K^+. SO_4^{2-} anions probably also is present (although sulfate analysis was not conducted for concretes soaked in 1N NaOH). In contrast, for deicers soaked concretes, the main ion constituents are acetate (or formate) anions from soak solutions, with apparently only small amount of hydroxyl ions (at least as estimated by conventional titration procedures).

In addition, there are significant differences in ionic strengths of pore solutions (for NaOH soaked concretes the values of ionic strength are below 1 M whereas for deicer soaked concretes they are usually over 3.5 M, even up to about 5.3 M). These increases will cause differences in the activity of water, and may influence ion product of water. The influence of this factor on ASR is not known, but it may play role in reactions within the paste, thus leading to paste expansion.

Although the hydroxyl ion concentrations estimated by titration for the pore solutions of concretes soaked in deicer solutions are very low, the evidences of concrete deterioration are very significant. These factors suggest that the mechanism of this kind of deterioration might be different in some respects from that commonly encountered for typical ASR.

7. DISCUSSION OF RESULTS

Based on the results presented in Section 5 (mortar bars tests) and Section 6 (concrete prism tests) it is evident that mortar and concrete test specimens containing reactive aggregate exposed to deicer solutions experienced significant expansion (i.e. greater than 0.1% at 16 days in mortar bar tests, and greater than 0.04% at one year in concrete prism tests). The degree and magnitude of the expansion of test specimens in any given deicer solution appeared to be a function of specific combination of the aggregate mineralogy and the cement composition.

Among all the deicers solutions evaluated potassium acetate deicer was found to be the most aggressive in its attack, both in terms of expansion and of cracking of test specimens, in particular with aggregates such as NM rhyolite, NC argillite and Spratt limestone. Compared to potassium acetate deicer solution, sodium acetate and sodium formate deicer solutions were slightly moderate in their attack with these aggregates. With the limited testing conducted on mortar bar test specimens, potassium formate deicer was also found to be very severe in its attack with all the reactive aggregates. It should also be noted that test specimens prepared with all the reactive aggregates showed much more expansion in the presence of potassium acetate than with 1N sodium hydroxide solution. Also, the rate of expansion with potassium acetate deicer was found to be significantly higher than that observed in 1N sodium hydroxide solution. This finding raises an important question of whether or not the existing standard ASTM test methods to evaluate the potential reactivity of aggregate (such as ASTM C 289, ASTM C 227, ASTM C 1260 and ASTM C 1293) would be meaningful when the concrete elements will potentially be exposed to deicing chemicals such as potassium acetate.

Among all the aggregates evaluated, mortar bars and concrete prisms prepared with NM rhyolite were found to be the most severely attacked by all the different deicer solutions and by 1N sodium hydroxide solution evaluated in this study. Test specimens containing NC argillite and Spratt limestone aggregate were moderately attacked by all deicer solutions followed by those containing the SD quartzite aggregate.

Mortar bars prepared with SD quartzite aggregate at 80ºC exhibited significant deterioration in the presence of all the deicer solutions and with 1N sodium hydroxide solution. However, concrete prisms prepared with SD quartzite and exposed at 38ºC exhibited high levels of distress only in presence of potassium acetate and 1N sodium hydroxide solutions. Also, in the concrete prism tests, the degree of distress and the rate of deterioration were particularly dependant on the alkali content of the cement used. No significant expansion was observed in SD quartzite bearing concrete prisms exposed to sodium acetate and sodium formate deicer solutions.

Mortar bars prepared with the reference non-reactive sand – Ottawa sand – did not exhibit deleterious levels of expansion in the presence of any of the deicer solutions or of 1N sodium hydroxide solution. However, it was observed that mortar bars exposed to potassium acetate deicer solution exhibited slightly higher levels of expansion than those exposed to other solutions. It should be noted that Ottawa sand is a fine aggregate made of pure quartz, and in highly aggressive conditions such as those posed by solutions such as potassium acetate deicer, even Ottawa sand can be expected to undergo some reaction.

Concrete prisms prepared with non-reactive IL dolomite aggregate exhibited no distress with any of the soak solution regardless of the alkali content of the cement, with the exception of one combination of deicer and cement. In case of IL dolomite prisms prepared with low-alkali cement and exposed to potassium acetate deicer solution, deposits of a potassium sulfate phase were observed in cracks and voids around the coarse and fine aggregate particles. ASR gel was not observed in these test specimens. It should be noted that isolated deposits of potassium sulfate phases were also observed in other test specimens containing reactive aggregate exposed to potassium acetate deicer solution. However, in those cases ASR gel was invariably present as a dominant reaction product through out the matrix.

It is likely that the hydrated sulfate phases present in the cement paste such as ettringite and monosulfate may have reacted with the potassium acetate deicer solution to result in this distress. Future investigation is necessary to study this phenomenon.

In a vast majority of the tests, changes in dynamic modulus of elasticity corresponded well with expansions observed in test specimens exposed to different deicer solutions and 1N sodium hydroxide solution. This strongly suggests that the length-changes observed in test specimens were associated with weakening of the matrix caused by deleterious reactions induced by deicer solutions or 1N sodium hydroxide solution.

Microstructural studies of affected mortar bars and concrete prisms showed extensive evidence of distress in the form of cracks and reaction products in aggregate, in paste and at the paste-aggregate interface. The composition of the principal reaction product observed in all of the distressed test specimens (with reactive aggregates) exposed to each of the deicer solutions was consistent with what is normally considered to be an ASR gel. Similar ASR gel was found in test specimens exposed to 1N sodium hydroxide solution. In some cases, particularly with potassium acetate deicer, a potassium sulfate rich phase was observed in-filling cracks in the paste and around the coarse and fine aggregate particles, either along with ASR gel for test specimens with reactive aggregates, or by itself with the non-reactive IL dolomite aggregate.

Another principal finding of this study was the changes observed in the pH of the deicer solutions upon exposure to mortar and concrete test specimens. The rapid increase in the pH of the soak solution was most significant in case of potassium acetate and potassium formate deicer solutions followed by sodium acetate and sodium formate solutions. Experiments conducted using reagent grade chemicals indicated that addition of calcium hydroxide – a primary hydration product of portland cement – to alkali-acetate and alkali-formate solutions resulted in dramatic increase in their pH. Particularly, in case of potassium acetate, potassium formate and sodium acetate solutions a pH jump equivalent to 3 orders of magnitude of indicated OH^- ion activity was realized upon addition of calcium hydroxide. The similarity of the results between the response of the reagent grade chemicals and commercial deicers conclusively proved that the pH jump phenomenon was not unique to a particular deicer brand, rather it was a fundamental chemical phenomenon associated with alkali-acetate and alkali-formate salts.

While the elevated pH levels in the deicer solutions suggests high levels of hydroxyl ions that are potentially available to penetrate into concrete and induce ASR in test specimens, results from titration of pore solutions expressed from concretes prisms subjected to deicer solutions for hydroxyl ions with phenolphthalein end point, did not support this hypothesis. In light of these facts it appears that the ASR distress induced by deicer solutions may be significantly different in its mechanism from that induced by alkali hydroxides.

8. CONCLUSIONS

Based on the results from mortar bar and concrete prism tests along with the microstructure, pore solution and soak solution analysis the following principal conclusions are drawn:

1. All the deicers evaluated in this study – potassium acetate, sodium acetate, sodium formate and potassium formate – were found to induce ASR distress in test specimens containing reactive aggregates.
2. Test specimens containing non-reactive aggregates did not exhibit deleterious affects associated with ASR when exposed to any of the deicer solutions.
3. The rate of expansion and the degree of distress were dependant on the specific combination of aggregate mineralogy, deicer solution type and alkali content of the cement used in preparing the test specimens, particularly in concrete prism tests. Specimens containing high-alkali cement showed more rapid expansions in presence of all the deicer solutions compared to those containing low-alkali cement in concrete prism tests. However, alkali content of the cement did not have a distinct influence in mortar bar tests.
4. Potassium acetate deicer solution caused significantly more expansion in test specimens than did 1N sodium hydroxide solution in both mortar bar and concrete prism tests. The level of expansion of test specimens in sodium acetate and sodium formate deicer solutions relative to that observed in 1N sodium hydroxide solution depended on specific combination of aggregate and cement employed.
5. In mortar bars and concrete prisms exposed to potassium acetate deicer solutions, minor amounts of a secondary reaction product – a potassium sulfate phase – was found in-filling cracks and voids in test specimens. In most cases however, ASR gel was the predominant reaction product.
6. All the deicer solutions showed a phenomenal increase in their pH upon exposure to mortar bars and concrete prisms and reagent grade calcium hydroxide. Experiments with reagent grade deicer chemicals yielded similar trends.
7. The pH of 1N sodium hydroxide solution did not change upon soaking mortar bars or concrete prisms.
8. Microstructural investigation of deicer-affected mortar bars and concrete prisms revealed that distress occurred primarily in the form of extensive cracks in aggregate, paste and at the aggregate-paste interface.
9. Deposits of ASR gel were frequently observed in cracks. In tests with low-alkali cements, the predominant alkali in the ASR gel was the alkali ion derived from the deicer solution.
10. In case of tests involving potassium acetate deicer solution presence of a secondary reaction product that is rich in potassium sulfate phase was observed in-filling cracks and voids and as rimmed deposits around aggregate particles.
11. While ASR appears to be the primary mechanism leading to the distress, the mechanism of ASR associated with deicing chemicals appears to be somewhat different than that caused by alkali hydroxide solutions.

9. RECOMMENDATIONS

Further investigations are necessary to develop better understanding of the interaction between deicer solutions and calcium hydroxide in hydrated portland cement paste in order to explain the sudden and the rapid jump in pH. In addition, reactions leading to formation of potassium sulfate rich phases in cement paste and their effect on the integrity of the test specimens (as observed in IL dolomite prisms prepared with LA cement and soaked in potassium acetate deicer solution) needs to be investigated.

It was observed in this study that both mortar and concrete prisms showed significantly higher expansion in presence of certain deicer solutions compared to 1N sodium hydroxide solution. In light of this finding, the validity of the existing standard test methods to characterize the reactivity of the aggregate, particularly when the aggregate is to be used in pavements that are likely to be exposed to deicing solutions, needs to be evaluated. The procedures developed as part of this study – modified ASTM C 1260 test and modified ASTM C 1293 tests – should be considered as interim test methods for evaluating aggregates for concretes that will potentially be exposed to deicing chemicals.

Results from the preliminary and comprehensive investigations clearly showed the ability of the modified ASTM C 1260 test to satisfactorily identify deleterious interactions between reactive aggregates and deicer solutions. No such effects were observed when non-reactive aggregates were evaluated in this test method. Based on the results from this research study, it is recommended that an expansion limit of 0.1% at 16 days for mortar bars in the modified ASTM C 1260 test be considered as a safe limit for accepting aggregates for use in concrete pavements that are likely to be exposed to alkali-acetate or alkali-formate deicer solutions. Appendix C contains a detailed description of the modified ASTM C 1260 test method to evaluate aggregate reactivity in presence of deicer solutions.

It should be noted that the recommendations from this study are based on a few tests with a limited number of moderate to highly reactive aggregates, two cements and one representative deicer from each of the main formulations used on airfields. The suggested expansion limits should be reevaluated when results from tests on larger data sets of aggregates and cements become available. Another limitation of the present study is that, all the aggregates considered in this study were either moderate to highly reactive or non-reactive aggregates. Therefore, both the standard ASTM C 1260 test and modified ASTM C 1260 test characterized the aggregate to be reactive based on the 0.1% expansion limit. It is recommended that additional investigations be conducted with marginal aggregates having expansions around 0.1% at 16 days in the standard ASTM C 1260 test method.

Findings from this study also suggest that modified ASTM C 1293 test (with a concrete prism expansion limit of 0.04% at one year) would be able to identify aggregates that may potentially be reactive in presence of deicer solutions. However, additional research is needed to validate the expansion limits and to decipher some secondary interactions between the hydrated compounds and deicer solutions. In addition, a separate study should be conducted to evaluate if the nature of the hydration products as well as the type and location of distress in the field concrete correlates with the findings obtained from laboratory tests.

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11. APPENDICIES

APPENDIX – A: SEM Images of Mortar Test Specimens Subjected to Standard and Modified ASTM C 1260 tests.

APPENDIX – B: SEM Images of Concrete Test Specimens Subjected to Standard and Modified ASTM C 1293 tests.

APPENDIX – C: Modified ASTM C 1260 Test Method to Evaluate Aggregate Reactivity in Presence of Deicer Solutions.