Effects of Aggregate Microfines and Potassium Acetate Interactions on Concrete Performance

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A dissertation submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

(Materials Science)

at the

UNIVERSITY OF WISCONSIN-MADISON

2012

Date of final oral examination: 5/3/2012

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To my father, mother, sister, twin, and husband, without their unending support through my education and life, I would not be the person I am today.

EFFECTS OF AGGREGATE MICROFINE AND POTASSIUM ACETATE DEICER INTERACTIONS ON CONCRETE PERFORMANCE

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The principal objective of this research is to elucidate the role that microfines from coarse and fine aggregates play in the development of the Alkali Silica Reaction (ASR) related distress observed in airport pavements subject to anti-icing agents. As a secondary objective, it was proposed to identify other potential impacts of microfines and deicers on concrete durability.

It was determined that combinations of microfines at less than 5% of the total aggregate weight and potassium acetate deicer (KAC Deicer) exposure caused significant deterioration of concrete that may be mistaken for ASR cracking and expansion. However, our analyses suggest it was not ASR, at least as traditionally diagnosed through the presence of ASR gel and reaction rims around aggregates. Expansions in modified ASTM C1293 produced expansions from 0.05% to 0.70% at one year depending on the type of microfine. Expansions of specimens containing microfines but not exposed to KAc Deicer produced negligible expansion. Expansions were larger with base aggregate known to be prone to ASR, but significant expansions (up to 0.50% at one year) also occurred in specimens with unreactive aggregates. Degradation combined with the reduction in entrained air content

led to dramatic loss of freeze-thaw durability. These degradations were associated with specific mineralogical profiles of microfines in the presence of KAc Deicer and these profiles consistently were associated with corresponding levels of degradation. The KAc Deicer transformed in the concrete pore solutions to form potassium sulfate and calcium-bearing potassium sulfate compounds. During the transformation of the potassium acetate the level of hydroxide increases dramatically in the pore solution and can lead to reformation of silica species released by the microfines and the aggregates. While these reactions do not appear to be the classical alkali silica reaction, they may exhibit some similarity and create an environment where expansion internally within concrete leads to deterioration.

Acknowledgements

First, I would like to truly thank my academic advisors, Professor Steven M. Cramer and Professor Marc A. Anderson, for their direction and support through all of the research which they have afforded me the fortunate opportunity to participate in. I also want to express my sincerely gratitude to Dr. Isabel Tejedor for working with me. I aspire to one day be such an exceptional scientist. I am infinitely appreciative for all of their contributions and patients in helping me through this research.

Thank you to Prof. Michael Oliva, Prof. Husain Bahia, Prof Donald Stone, and Prof. Ray Vanderby for their participation as committee members. Along with them, I would like to acknowledge the time, expertise, and assistance of Jose Muñoz, Jacob B. Effinger, Ruipeng Li, William Lang, and Carole Kraak which have helped me to complete this research.

Lastly, I would like to show my appreciation for the collaboration of the Wisconsin Concrete Pavement Association (Kevin W. McMullen, P.E.), the gracious instruction of the Schmitt Technical Services Laboratory (James Schmitt, Greg Schmitt, and Elizabeth Otteson), the guidance of the Innovative Pavement Research Foundation – IPRF (James L. Lafrenz, P.E.), the partnership of the Wisconsin Department of Transportation – WisDOT (James Parry, P.E.), and the innovative inspiration of the Center for Freight and Infrastructure Research and Education – CFIRE. Financial support for the research program by the IPRF under project IPRF-01-G-002-06-5, the CFIRE under projects 03-13 and 05-12, and the WisDOT under project ID 0092-10-11 is greatly appreciated.

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Chapter 1

Project Description

1. PROLOGUE

Concrete is considered a strong durable paving material utilized in areas where great forces are applied and surface characteristics must be robust. One such application includes airport runways. These pavements require long term stable materials, as reconstruction causes a great impact on the air travel industry. Despite this need, such materials are not always the actuality. There have been cases reported in the western states indicating early failure in normally durable concrete. *(1)* At times, this degradation appears as map cracking mimicking degradation associated with alkali silica reactions (ASR) and many of the airfields confirm related damage. *(1-3)* One study investigating the potential of the interactions to be ASR, concluded that indeed, some pavements had ASR, but it was not the case in all of the studied materials. *(3)* Therefore, ASR may not always be the culprit causing degradation and other reactions are likely to blame.

In June 2007, the Innovative Pavement Research Foundation (IPRF) contracted with the University of Wisconsin-Madison to undertake the study entitled "Role of Dirty Aggregates in the Performance of Concrete Exposed to Airfield Pavement Deicer". The principal objective of this research was to elucidate the role that microfines from coarse and fine aggregates play in the development of the Alkali Silica Reaction (ASR) related distress observed in airport pavements subject to anti-icing agents. A secondary objective was to identify other potential impacts of microfines and deicers on concrete durability.

The research reported here investigates the deterioration found prematurely in concrete airport pavements. In order to determine the cause of the deterioration, environmental factors are considered including subjecting concrete to potassium acetate based deicer solution (KAc Deicer). Potassium acetate deicers have not been proven to cause degradation in all problem pavements so particular interaction with specific materials may be to blame in these instances. Given that the degradation is seen in various areas of the country, aggregate sources have been studied with an emphasis on the type and quantity of microfines associated with these locations. Microfines are investigated as they are small in size thereby creating a large total surface area, increasing the potential for reactions to occur. It has been speculated that the combinations of certain microfines and deicers produce degrading characteristics. The particular materials are emphasized because individually they seem to pass inspection under current specifications, and are not being screened-out for this interaction. This research investigates given physical chemical reactions in order to help understand their mechanism affecting the durability of concrete and to identify potential problem materials. Several aggregate microfine sources were tested in conjunction with a readily available airport deicing solution. First, the microfine material was studied in great detail. Once the materials were thoroughly characterized, concrete specimens were cast incorporating varying microfine materials in controlled mix designs. The specimens created were then subjected to various testing protocols.

Two main conclusions are sought from the research. First, do all microfines react with the potassium acetate based deicer? The answer to this question should reveal if the interactions depend on the type of microfine present. Second, is deterioration linked with ASR or does it incorporate a different reaction and/or mechanism? In these studies we used a Scanning Electron Microscopy (SEM) to examine the microstructure of our concrete specimens to determine changes that had occurred in comparison to unaffected concrete. These differences hopefully unveil the mechanism responsible for the degradation of concrete. While investigating these questions, various data was collected through expansion measurements, durability tests, microscopy, and petrographic analysis. The combination of these results should lead us to the answers sought.

2. OBJECTIVE

The overall objective of this research has been to determine the role that microfines play in the development of the described ASR-related distress in the presence of KAc Deicer and to identify the other potential impacts of microfines and KAc Deicer on concrete durability. Sub-objectives for this project are:

To determine how dispersed materials introduced into the concrete as aggregate coatings influence the Alkali Silica Reaction (ASR).

In the absence and presence of mineral fines, quantify the durability and potential for deterioration of concrete in the presence of potassium acetate based deicers.

To develop an understanding of the mechanism by which microfines affect the microstructure and hydration products in concrete with fines introduced as coatings on aggregates (“dirty aggregates”).

3. HYPOTHESIS

The hypothesis driving this research is that microfines react with potassium acetate deicer in concrete to form deleterious compounds which affect the overall durability of the material. Previous research has shown that in some cases deicers accelerate ASR and in some cases do not. *(3)* In these studies, data has shown that there are different species in existence than typical ASR products although ASR may also exist. *(4, 5)* These studies have utilized different materials than in the preparation of our concrete specimens and as a result we have seen different outcomes. Although ASR may exist, especially in cases where reactive aggregates are employed, our hypothesis is that other reactions are also occurring which may be as important as or even more important than ASR. These reactions likely cause a form of chemical degradation that could mimic ASR degradation. By using different microfines, and therefore introducing different particles for reaction with the deicer, we have attempted to isolate problematic materials. From this research we have been able to uncover some of the physical implications of using the deicer when microfines exist and have been able to identify microstructural differences that manifest themselves from reactions between microfines and deicers.

We also hypothesize that the potassium acetate causes some expansive degradation to the concrete when certain types of microfines are incorporated. Concrete in the field has produced reactions that exhibit characteristics of ASR of which expansion has been linked. To date, these deicer fluids have not been explicitly proven to be detrimental to concrete in general. However, if certain microfines exist that possess problematic qualities, such as high surface area and increased reactivity or siliceous compositions, deterioration could be provoked with the use of deicers.

4. BACKGROUND

The purpose of this research has been to determine the role of natural microfines in ASR-related distress when KAc Deicer is present. Several studies were performed to investigate the effect of microfines when they are added mostly as a replacement of aggregate. From those studies, it has been shown that various properties of the microfines have differing degrees of impact on the concrete material. Microfines may affect concrete durability to greater or lesser extents depending on their mineralogy, quantity, ability to disperse, and reactivity.

There has also been some research conducted on the impacts of potassium acetate on concrete pavements. Three such investigators: Rangaraju, Giebson, and Wang, found varying results. *(3-6)* Rangaraju performed two studies on this topic, the earlier of which was a laboratory study that found KAc Deicer to be problematic. The later study reviewing cores from airfields found ASR in some cases. *(3, 6)* The study by Giebson found that KAc Deicer accelerated ASR damage when utilizing reactive aggregates. *(4)* The study by Wang revealed that the KAc Deicer did not induce significant deterioration. Wang's study used limestone aggregates in the concrete materials. *(5)* Both Giebson and Wang found that when KAc Deicer was used, the formation of an ettringite like needle structure was found during SEM analysis. However, this species differs in composition from normal ettringite.

(4, 5) It seems that investigations look to KAc Deicer as a problem, but given the varying results the deterioration associated with the deicer is not completely understood.

4.1. Explanation of ASR

Since the discovery of the alkali silica reaction (ASR) some 80 years ago, considerable literature has been published regarding this phenomenon. Most of these publications have focused on unraveling the mechanism of the ASR. At the same time, efforts from the scientific community have attempted to identify the deleterious effects of this reaction. As a consequence of these efforts, the four most common methods proposed to avoid the ASR in concrete are considered to be: 1) avoiding the use of reactive aggregates, 2) reducing the alkaline content of the cement paste, 3) using supplementary cementitious materials such as Class F fly ash, and 4) adding lithium compounds in order to mitigate the ASR. Finally, during the last decade, it has been proposed that the use of certain types of deicers provoke a surface deterioration by accelerating the ASR in pavements that are less than 10 years in age. This observation leads to a third line of investigation concerning the inter-relationship between deicers and ASR.

ASR requires the combination of alkali hydroxides, silica, and humidity. *(7-11)* Alkali hydroxides can come from various sources including cement or supplementary cementitious materials (SCM), admixtures, the aggregates, or post treatment sources like deicing agents. The siliceous particles can emanate from aggregates or microfines and are mostly amorphous or low in crystallinity. *(9)* The combination of these components can produce a hydrated silica gel which is capable of absorbing water and expanding. *(7, 8)* The hydration of this gel can cause cracking resembling map cracking in pavements. *(9)* For the reaction to take place the alkali ions must exist in high quantities to react with siliceous particles and there must be a high relative humidity. *(9)*

If alkali hydroxides are present, hydroxide (OH^-) ions will be plentiful. These hydroxyl ions trigger the ASR by modifying amorphous silica to form negatively charged silica based ions. The alkali portion of the alkali hydroxides whether it be Na^+ or K^+, will balance these new negative charges. These new combinations can hydrate in the presence of water and form the alkali silica gel. *(10)* This gel is responsible for the deterioration as it expands with further hydration. More recently, it has been recognized that the expansive capabilities are linked to Ca^{2+} ions. *(8, 12, 13)* This latest reaction sequence was developed by Ichikawa and Miura. *(12)* The reaction mechanism has three parts. First, the alkalis react with silica and the gel is formed. Next, $Ca(OH)_2$ from the concrete matrix dissolves to produce more OH^- ions as they are consumed in the production of the silica gel. Lastly, the remaining Ca^{2+} ions react with the gel forming a calcium, rich reaction rim around the gel which encapsulates the aggregates. The theory explains that this rim mimics a membrane which allows OH^- ions to enter, but slows the gels diffusion into the paste. This unequal flux causes pressure which in turn causes cracking of the surrounded aggregate and/or the paste. *(12)*

Therefore, one looks for various concentrations of calcium, potassium, and silica along with the gel structure in order to identify if the concrete contains ASR products. A study by Thaulow analyzed the composition for the gel associated with ASR. It was found that depending on the location of the gel and the stage of its evolution, the ratio of Si, Ca, and

Na and/or K can vary. The study found the ratios can range in atomic percentage of Ca at 50-70, Si at 15-30, and Na and K at 15. The study also reported that the calcium content seems to increase and silica decreases with distance away from the aggregate. *(14)*

4.2. Mineralogy of Microfines

As stated, one of the primary objectives of this study is to determine the role of various microfines in the deterioration found in pavements utilizing deicers. The mineralogy is known to be a key factor in the degree of impact to the pavement and thus investigating the role of mineralogy impacting concrete has been a major portion of this study. In this study, microfines were limited to particles passing the No 200 (75µm) sieve. They exist as particles mixed with or attached to aggregates. *(15)* Microfines are generally composed of stone dust, calcium carbonates, and clays. *(15-17)* It is important to identify which type of microfine exists with the aggregates as various microfines can affect the concrete differently. For instance, southern Wisconsin typically has microfines incorporating carbonates. *(18)* These are usually not seen to be detrimental to the system while clays can have a higher potential for deleterious impacts. *(18, 19)* In this study, the microfines were identified and classified to ascertain their potential for provoking ASR within the concrete matrix.

Stone dust offers relatively little change with respect to the microstructure of the concrete. Typically this type of microfine exists as an inconsistency in the bulk matrix. It provides relatively little chemical alterations, but is important because by having too many stone dust microfines they interfere with the water demand and porosity of the paste. *(15)*

Carbonates are known to contribute minimal negative effects to the concrete as well. *(15, 19)* Clays on the other hand, have been known to have greater impacts on concrete. Clays exist in different families and are characterized by their either 1:1 or 2:1 structure. The structure refers to the layering of the silica sheets. The layering dictates different swelling properties of the clay materials. Swelling can cause delamination of the layers and expansion of the clay. *(20)* Another important consideration in regard to clay microfines is the exchangeable cation within the clay structure. For example, calcium or sodium can exist and will have different ionic strengths which will affect the amount of swelling that occurs when the clay is subjected to water. *(20, 21)* These properties of the microfines are important to consider with respect to knowing what chemicals enter the matrix and are essentially available for reactions with the KAc Deicer.

5. SCOPE OF THE RESEARCH

The objective of this research has been to identify the role of aggregate-based microfines in determining the durability of airport concrete that is exposed to KAc Deicer. Particular emphasis has been placed on the potential for alkali silica reaction (ASR) and similar deleterious chemical reactions. In pursuit of this objective, a laboratory study has been conducted that examines the nature and chemical reactivity of microfines associated with alluvial deposits of aggregates from select locations across the western half of the United States.

Although eight specimens had been initially studied, a set of five microfines were selected to cover a variety of mineralogies found in problematic regions within the United States.

Microfines were selected by the IPRF board of advisors and were subsequently acquired from California, Colorado, Utah, Wisconsin, and Wyoming. Two sets of fine and coarse aggregates were also obtained in quantities sufficient to prepare concrete specimens. One set of aggregates was obtained from Wisconsin as it was established to be largely unreactive dolomitic gravel. At the other end of the activity spectrum, granitic gravel was obtained from Utah that was known to be alkali-silica reactive. These materials were used to prepare concrete specimens for evaluating physical durability measurements when subjected to KAc Deicer. Control samples were included for every combination of materials in order to determine which microfines participate in the changes found and if KAc Deicer is to blame for deterioration.

The study was divided into two main components to answer if and how microfines react with KAc Deicer. The first component evaluated the macro-scale physical distress caused by the interactions of microfines and KAc Deicer. This component included evaluating the durability of the concrete and the expansion changes that occurred in these samples. The second component evaluated the microstructural changes that occur in concrete incorporating microfines when exposed to KAc Deicer. This component of the study focused on the behavior of the microfines with respect to alterations formed in the concrete matrix due to both the nature of the microfine and the interactions with KAc Deicer.

6. GENERAL RESEARCH PLAN

This study consisted of the 3 major tasks as shown in Table 1. Further details of the Tasks are described below and correlate to the chapters of this thesis.

Table 1. Research Plan Tasks

Task
Task 1: Aggregate Screening and Microfine Characterization
Task 2: Measurement of Concrete Durability through Mechanical Testing
Modified C1293 Testing
Modified C666 Testing
Modified ASTM C1260 Testing
Other related tests
Task 3: Microstructural Testing of the Reactivity of Microfines in Concrete
Microstructural Analysis using SEM/EDS
Petrographic Analysis

6.1. Microfine Characterization and Reactivity

Microfines were characterized through a battery of tests that included the methylene blue test, California cleanness values, percent of microfines passing the No. 200 sieve, particle size distribution, alkali silica reactivity, X-ray diffraction, thermogravimetric analysis, and others. All sources were categorized by their potential to cause deleterious reactions in concrete. The microfines were also evaluated for potential reactivity by subjecting the microfines to alkaline solutions similar to what would occur in concrete.

6.2. Microfines and Potassium Acetate Effects on Mechanical Properties of Concrete

Concrete specimens were prepared to assess the impact of the microfines in concrete exposed and unexposed to the potassium acetate commercial pavement deicer. Matched concrete specimens were prepared with each base aggregate, one from Wisconsin and one from Utah. Each condition consisted of the base aggregate washed clean of any microfines (control condition) and those with the individual addition of the microfines from the five different locations.

The primary mechanical evaluations of the concrete specimens consisted of two modified ASTM C1293 length-change protocols and a modified ASTM C666 freeze-thaw durability protocol. One modified C1293 protocol involved specimens prepared with no sodium hydroxide addition and subject to elevated temperature 100% humidity curing. The other modified C1293 protocol involved soaking similar specimens in potassium acetate deicer at elevated temperatures. Periodic length measurements were the primary measure of change in both protocols. The modified ASTM C666 protocol included a 48 hour soak in KAc Deicer and 60 freeze-thaw cycles in water. To examine the influence of sodium hydroxide additions, a series of ASTM C1260 tests were conducted on mortar bar specimens using each fine aggregate source and the microfines. Also, Infrared Spectrometry (IR) analysis was used to establish the penetration levels of the potassium acetate.

6.3. Microfines and Potassium Acetate Effects on Microstructural Properties of Concrete and Mortar

A series of microstructural investigations were undertaken on the concrete specimens to determine if any chemical and/or microstructural changes could be associated with the deterioration observed. Scanning Electron Microscope/Energy Dispersive Spectroscopy (SEM/EDS) analyses were conducted on concrete specimens that were exposed to the modified ASTM C1293 environments. By using SEM, the fate of the microfines introduced as coarse aggregate coatings in cured concrete were examined to determine their distribution between the interfacial transition zone (ITZ) surrounding aggregate particles and bulk cement matrix. In addition, this technique allowed us to examine how the microfines reacted with the cement paste. By using SEM back scattering we could image the cement aggregate interface and by employing energy-dispersive X-ray spectroscopy (EDS) we could determine the mineralogical makeup of the microstructure. Thermodynamic simulations were used to complement these results.

Petrographic analysis was also conducted on the concrete which was subjected to potassium acetate deicer from modified ASTM C1293. Using a cross polarizing light microscope, thin sections were analyzed after 1 year of subjecting the specimens to the KAc Deicer. Sulfate measurements were also conducted on the microfines using AASHTO T290-95 (2007) Method A and X-ray fluorescence (XRF).

7. ORGANIZATION OF THE THESIS

This thesis is organized into three content chapters. The first describes the microfine testing conducted to gain information about the mineralogy and characteristics of the microfines. The second chapter reflects the findings of the physical modification incurred by the concrete when microfine infused concrete is subjected to KAc Deicer. The third chapter reports on the microstructural modifications found in the concrete material based on interactions of microfines and KAc Deicer. The latter two chapters are written for publication and are of a format required for given journals.

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Chapter 2

Analysis of Natural Microfines

1. INTRODUCTION

This investigation of microfines was initiated to determine the role of natural microfines in concrete when the concrete is exposed to potassium acetate deicer. This specific research will report on the materials and testing used to characterize the various microfines used in the future portions of the investigation incorporating concrete infused with microfines. The conclusions of this initial study will be a characterization of each of the microfines studied and the evaluation of each for its potential to react with potassium acetate in concrete. The testing used for evaluation includes many methods to distinguish the morphology, mineralogy, and projected reactivity of the microfines.

1.1. Definition and Effects of Microfines

For this research, microfines are defined as natural material found with aggregates measuring 75µm or smaller. The microfines typically exist as one of three materials: stone dust, clay particles, or calcium carbonates. *(1, 2)* Microfines can either be attached to the aggregates or detached. In the situation where the microfines are attached or are acting as a coating around the aggregate, the aggregates are considered “dirty aggregates”.

Dirty aggregates have been investigated and current mitigation techniques include various washing procedures designed to remove the microfines from the aggregate. Despite washing efforts, microfines can remain adhered to the aggregate surfaces. The adhesion of the microfine coatings to the aggregate surface generally follows the mineralogical classification of microfines. Most clay particles are held tightly to the aggregate surface and cannot be easily removed by a normal washing process. In contrast, stone dust and calcium carbonate coatings weakly adhere to the aggregates and can be more readily removed by washing. In the case of unwashed aggregates, dust and calcium carbonate coatings will likely be released into the water during concrete mixing and become a component of the mortar region in the concrete.

It is generally recognized that, during the mixing of concrete, a layer of microfines that coat the aggregates can totally or partially detach from the aggregate and enter the bulk region of the concrete or remain attached to the surface of the aggregate and therefore be a part of the interfacial transition zone (ITZ). *(3)* Therefore, one can imagine two different scenarios by which microfine coatings may affect the quality of concrete, one by changing the chemistry and/or microstructural properties of the bulk paste, the other by disrupting the bond between the aggregate and the cement paste. *(2-4)* Recently, Muñoz et al. discovered that when aggregates coated with a layer of clay are used to prepare concrete, a fraction of the clay enters the water phase before adding the dry cement. *(5)* The fraction of detached clay depends on the nature of the clay: Na-montmorillonite mostly remains on the aggregate upon mixing; however, Ca-montmorillonite and kaolin readily detach and enter the water phase.

Once microfines enter the mixing process, various characteristics of the microfines can affect the concrete uniquely. Extensive studies have been conducted to determine which properties are responsible for various changes that occur in concrete mixing and can be found in the ICAR 107-1 report on microfines. *(6)* Size and shape of the microfines can influence the water/cement (w/c) ratio required for proper workability and therefore play a role in determining the quality of the concrete. *(7, 8)* Along with morphology, mineralogy of the microfines is also important to concrete systems because various mineralogies can affect general bulk properties of the concrete differently. *(3, 7-10)* It has been recognized that stone dust and calcium carbonate particles decrease the slump and increase compressive strength *(3, 9)*, shrinkage, and porosity. In comparison, clay microfines have been seen to cause the greatest problems in concrete *(5, 11)* including deterioration, low compressive strength, and increased shrinkage *(12)*. Clay microfines are particularly important because they are also often times the most difficult type of microfines to remove by simple washing techniques.

Beyond mixing, microfines have also been linked to problems in hardened concrete. Hanna et al. claim that the presence of microfines on aggregates can affect certain properties of concrete and therefore alter the quality of resulting concrete pavements. *(13)* Grattan-Bellew also suggest that when certain types of alkali-bearing clays (such as illites) are present within the matrix of certain rock types, these clays can potentially dissolve upon exposure to alkaline solutions to further augment the alkali levels in the concrete, and thus the potential for developing alkali silica reactions (ASR). *(14)* Since Krøyer et al. demonstrated that the presence of blends of kaolin and bentonite induced changes in the calcium silicate hydrate (CSH) structure in cement pastes, it is possible that clay coatings might also lead to changes in the morphology of other hydration products such as calcium hydroxide, which will alter the reactivity of these materials with deicers and potentially the development of the ASR. *(15)*

Recently, it has reported that microfines may be the cause of early deterioration in airfield pavements which were known to contain a high content of microfines. These pavements were also known to have been subjected to potassium acetate deicer (KAc Deicer) and it is therefore the overall objective of this research to determine how the microfines and deicers interact to cause these reported problems.

2. OBJECTIVE

The overall objective of this research is to determine the potential impacts of microfines and deicers on concrete durability and to identify the role that microfines play in the development of the ASR in the presence of KAc Deicer. The purpose of this chapter is to ascertain which microfines likely pose the greatest problems to concrete which is subjected to potassium acetate deicer. Several sources of aggregates have been acquired to gain knowledge of various types of microfines. Many tests will be conducted on the microfines to understand the general morphology, mineralogy, and reactivity of the microfines in order to determine which mineralogies will likely cause the greatest impact to concrete exposed to KAc Deicer.

3. SOURCES OF MICROFINES

Seven aggregate sources were selected for initial characterization from aggregate producers across the western half of the United States. These aggregates provide a broad spectrum of different mineralogies. All sources are referred to using standard state abbreviations; Arizona (AZ), California (CA), Colorado (CO), Utah (UT), and Wyoming (WY). Some of these materials were chosen because of their known or suspected reactivity with respect to the ASR. A comparison sample of an alluvial deposit from Wisconsin (WI) was also chosen adding an eighth source. This sample was chosen because geology found in Wisconsin does not generally provoke the ASR. The general locations of all the microfines are shown in Table 2. Coarse and fine aggregates were obtained for the UT and WI sources with UT representing ASR granitic gravel and Wisconsin representing unreactive dolomitic gravel. Coarse, fine, and pit-run materials from UT and WI were shipped to the University of Wisconsin-Madison. Pit-run materials were obtained from the remaining sources to allow extraction of the microfines associated with each source.

Table 2. Aggregate source initial sampling

Sample	General Location
AZ	Southern Arizona
CA	South-Central California
CO-I	North-Central Colorado
CO-II	Northwest Colorado
CO-III	North-Central Colorado
UT	Northern Utah
WI	Northern Wisconsin
WY	Wyoming

Based on the analyses conducted and described below, five aggregates were selected for more extensive analysis and concrete sample preparation in later efforts. These five microfine sources were characterized using additional tests and therefore, some analysis of the microfines described in this chapter will not always include all eight sources. Larger volumes of aggregate were obtained from the sources associated with: CA, CO-I, UT, WI, and WY.

3.1. Collection of Microfines from Source Aggregates

Prior to analysis, all the samples were oven dried over night at 70°C. After the drying process, the samples were placed in a Gibson sieve shaker and separated using 4.75mm (No. 4) and 75 µm (No. 200) sieves. Three fractions were collected for each sample: coarse aggregate, fine aggregate, and dry sieve microfines. The microfine coatings that remained attached to both fine and coarse aggregate fractions after dry sieving were extracted by washing with water after which they were dried and ground for testing.

4. TESTING OF MICROFINES

Previous studies have been performed that have investigated the effects of microfines typically added as a replacement of aggregate. Based on these references, the variables were classified in Table 3 according to their estimated degree of impact on the performance of concrete.

Table 3. Matrix of Variables that Control Effect of Microfines on Concrete

Variable	Definition	Degree of Impact	References
Mineralogy	Type of microfines	High	Abou Zeid 2003 *(9)* Moukwa 1993 *(16)* Bonavetti 1994 *(10)* Tasong *et al*. 1998 *(17)* Caliskan *et al*. 2002 *(18)* Krøyer *et al.* 2003 *(15)*
Amount	Quantity of microfines	High	Gullerud 2002 *(11)* Muñoz et al. 2007 *(19)*
Curing Conditions	Sudden loss of water in concrete during the first hours of hydration could induce significant microstructural damage and could be exacerbated by the presence of microfines	High	Nassif et al. TRR 1834 *(20)* Muñoz et al. 2007 *(19)*
Dispersibility	Agglomerations of ASR active microfines could provoke ASR damage	High	Rangaraju 2000 *(21)*
Dispersion	Distribution of microfines in the concrete	High-Moderate	Muñoz et al. 2007 *(19)*
Pozzolanic Activity	Microfine with significant pozzolanic activity can affect autogenous shrinkage	Moderate	Nassif et al. TRR 1834 *(20)*
ASR Activity	ASR active microfines may provoke damage in concrete and be nucleation sites for wider scale ASR	Undetermined	--

Based on previous studies, a set of tests was selected to determine the properties of the aggregates with the anticipation that most samples received would be ungraded pit-run materials. To determine the physical properties, the microfines were characterized following the testing protocols described in ASTM C136, ASTM C117, the California Test 227, and particle morphology using scanning electron microscopy (SEM). The mineral composition of the microfines was characterized using the AASHTO TP 57 procedure, thermogravimetric (TG), X-ray diffraction (XRD), and in some cases scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) techniques. Chemical properties of the microfines were tested using leaching and cation exchange capacity studies, conductivity testing, and a chemical method to determine alkali-silica reactivity. A summary of the methodology to characterize microfines is shown in Table 4. Many of these tests were conducted and findings determined with Jose Muñoz. The findings are reported in this thesis because they are pertinent to the concrete research done in the remainder of the thesis.

Table 4. Methodology used to characterize each aggregate sample

Test	Standard	Information
Sieve Analysis	ASTM C136	Size Distribution
Material finer than No. 200 sieve	ASTM C117	P200 Percentage
Evaluation of Alkali-Silica Reactivity	Chatterji, 2005 *(22)*	Potential for ASR Development
Thermogravimetric Analysis	UW-Madison	Microfine Mineralogy
X-ray Diffraction	UW-Madison	Microfine Mineralogy
Leaching and Cation Exchange Capacity Analysis	UW-Madison	Identification of Soluble Compound and Exchangeable Cation
Methylene Blue Test	AASHTO TP 57	Methylene Blue Value (MBV)
California Cleanness Test	California Test 227	Cleanness Value (CV)
Scanning Electron Microscope Analysis and Energy Dispersive Spectroscopy	UW-Madison	Size and Morphology
Conductivity Test	Luxán et al, 1989 *(23)*	Pozzolanic Activity

4.1. Physical Properties of Source Material and Associated Microfines

4.1.1. Sieve Analysis

A sieve analysis was performed on the materials following the requirements of ASTM C136. The size distributions of coarse and fine aggregates are shown in Figure 1 and Figure 2, respectively, where the mass percentage passing is represented versus the corresponding standard sieve number. The graphs show the dispersion of material, and included as points of reference, the dotted lines in Figure 2 outline the ASTM C33 limits for concrete aggregates. Since these sieve analyses are based pit-run material there is no implication about the general acceptability of aggregates processed from these pits.

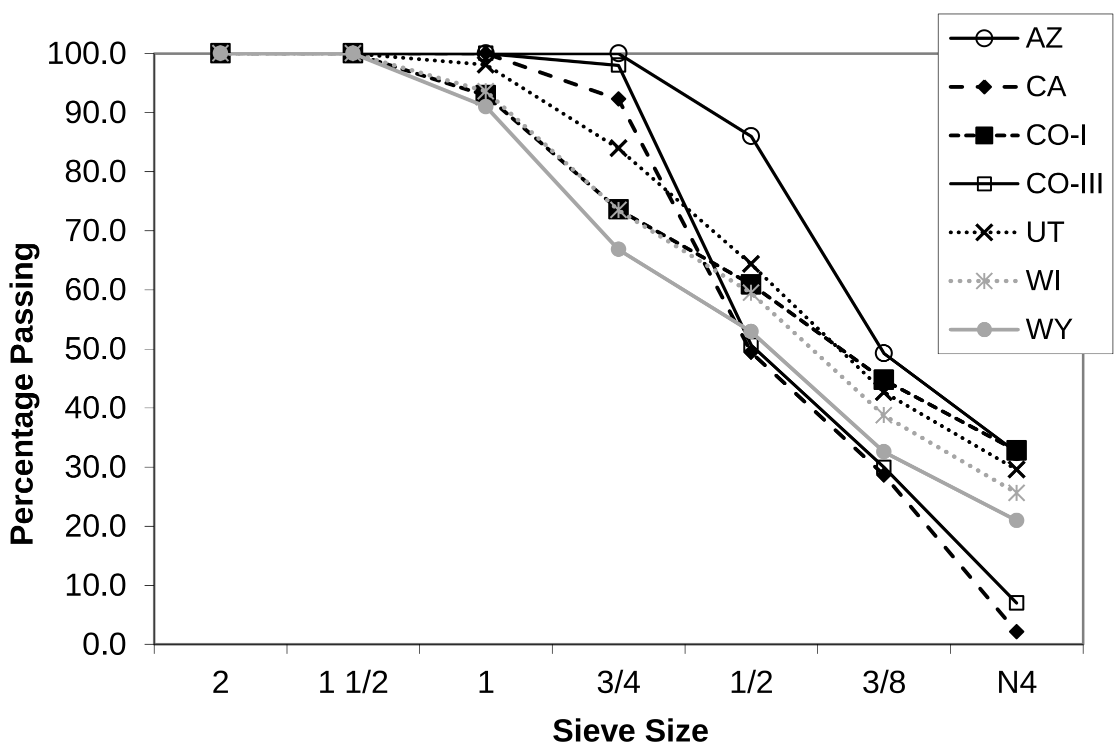


Figure 1. Size Distribution of Coarse Aggregates

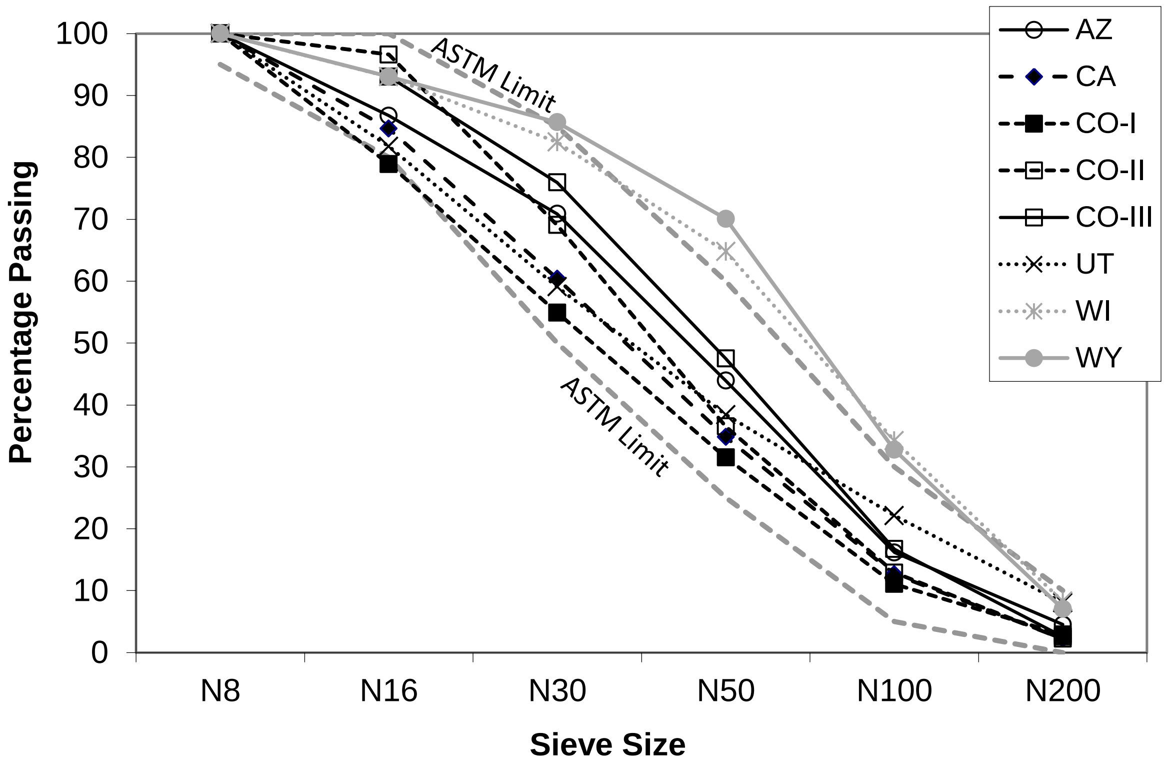


Figure 2. Size Distribution of Fine Aggregates

4.1.2. Particle Size following ASTM C117 (P200)

The material quantities finer than No. 200 sieve from coarse and fine aggregates were established by repeated washing of the sample until the resulting wash water was visibly clear. The P200 percentage was calculated based on the material passing the No. 200 sieve during the washing process and the results are shown in Table 5. These values are an indication of how well microfines adhere to the base aggregates since these are quantities established after washing. These results reveal the upper limit of microfines that could occur again because they are based on pit-run material samples. Unlike the other samples, the CO – III sample was received prewashed. Location A and B reported for CA and WY represents material sent from two locations within one source pit/quarry. These are reported individually in Table 5 and in future tables when applicable. The P200 test is important because large quantities of microfines can affect workability and adhesion between the aggregate and the cement paste.

Table 5. Microfine Content (P200) of Coarse and Fine Aggregates

Sample	Location	Coarse Aggregate (%)	Fine Aggregate (%)
AZ	--	1.5	8
CA	A	3.5	9.2
	B	1.4	4.5
CO-I	--	3.8	4.0
CO-II	--	--	3.0
CO-III	--	0.6	1.8
UT	--	1.4	21.0
WI	--	0.7	5.3
WY	A	2.3	18.9
	B	2.4	8.1

4.1.3. Particle Size Distribution

Particle size distributions of the microfines are similar to a sieve analysis of the aggregate material. The combined distributions of the microfines are shown in Figure 3. The microfines ranged in size from 0.1 microns to 100 microns with the microfines from Utah presenting the finest distribution. The percentages passing 45 microns (as one indicator of the difference in fineness) for each set of microfines were as follows: CA 68%, CO 77%, UT 95%, WI 65%, WY 85%.

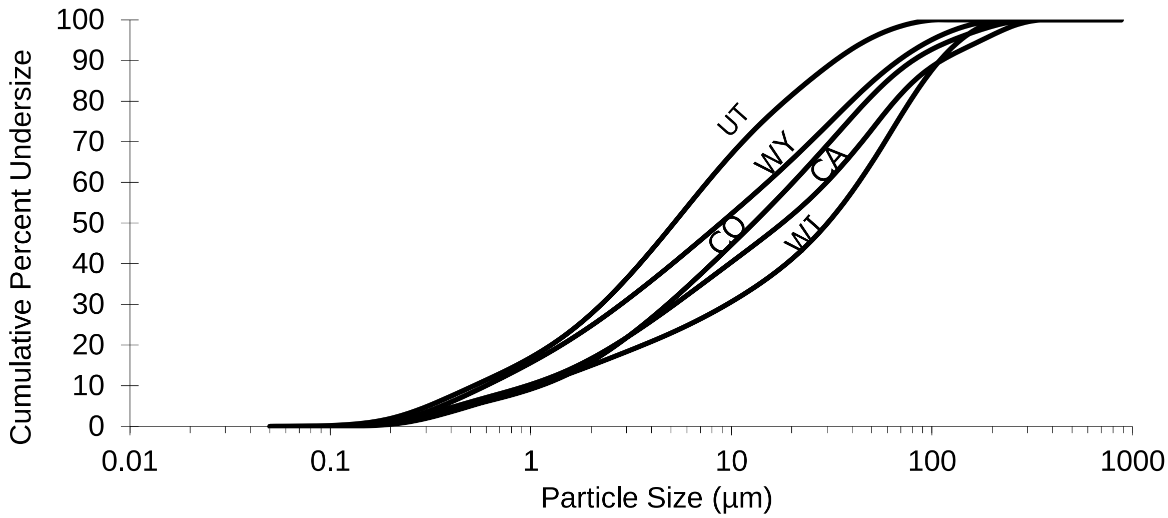


Figure 3. Particle size distributions for the microfines

4.1.4. California Cleanness Test 227 (CCT)

In the CCT, the aggregate is mechanically washed to remove adhering fines. The wash water is then passed through a No. 200 sieve, placed in a graduated cylinder, and mixed with a solution of glycerin and calcium chloride. After 20 minutes, the height of the sediment is measured and assigned a cleanliness grade from 0 (dirty) to 100 (clean). The California Department of Transportation requires a value of at least 75 for coarse aggregate used in concrete highway construction. This cleanliness value is indicative of the particle size, and, to some extent, the mineralogy of a specific type of clay mineral. Lower cleanliness values indicate longer times to settle and are associated with aggregates that possess smaller microfines and/or clay minerals with macroscopic swelling. The results of the CCT are represented in Figure 4.

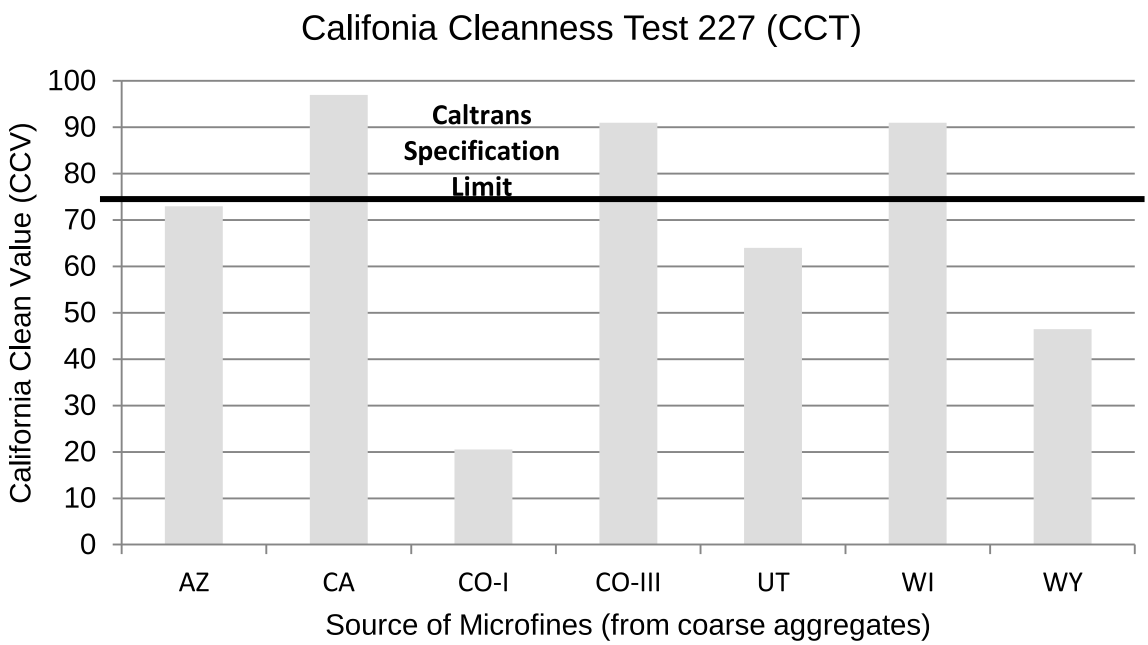
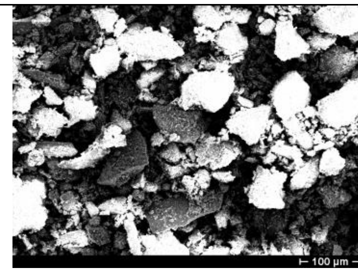
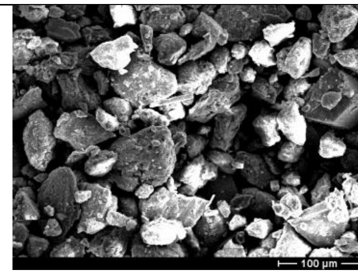
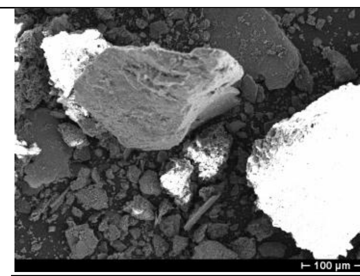
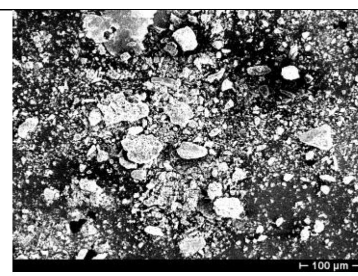
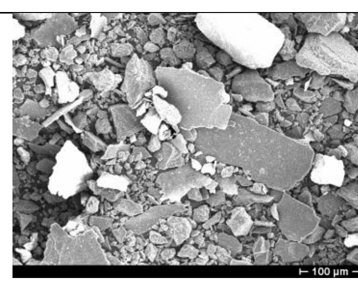


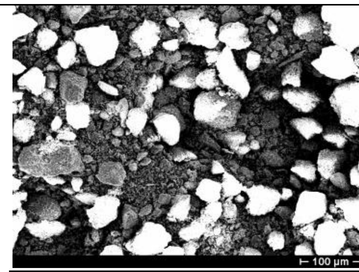
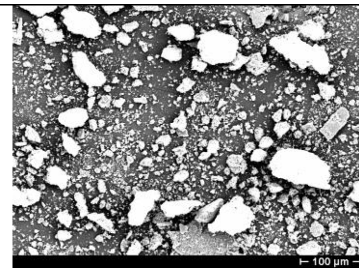
Figure 4. CCT Values for Microfines from Coarse Aggregate Fraction

4.1.5. Particle Morphology

Scanning electron microscopy (SEM) analyses were performed using a JEOL 6100 Scanning Electron Microscope with gold-coated samples of microfines. The samples were observed and analyzed under the following conditions: 15 kv accelerating voltage and 15 mm working distance. Each original image was 800 x 640 pixels with a resolution of 1,860 pixels/mm (47,058 pixels/inch), and the acquisition magnification was 200x. The results are summarized in Table 6.

Table 6. Morphology of Microfines from SEM

AZ Microfines show a high homogeneity among particles. All of them have a round shape. The sizes are between 80 and 5 µm.	
CA Similar particles with an average size of 25 to 150 µm. Microfines appear to be mostly derivatives from the larger aggregate particles.	
CO-I Particles of different morphologies such as round, flat, and elongate particles. Size varies from 10 to 200 µm.	
CO-II Mix of round and planar particles with a range of sizes that vary from 2 to 50 µm.	
CO-III Two different types of particles: flat and elongated big particles 50 to 300 µm, and smaller round particles 10 to 50 µm.	

UT Particles with a broad range of seizes from less than 5 up to 100 µm. Large particles are coated with smaller particles.	
WY Different sizes of particles from 100 µm down to less than 10 µm. A closer view reveals that some of these smaller particles are conglomerations of particles of 2 µm.	

4.2. Mineral Composition of Microfines

4.2.1. Methylene Blue Test

The Methylene Blue Test (AASHTO TP 57-01) is based on the unique properties of certain clay minerals to absorb this particular dye. The test is conducted by titrating a water suspension of P200 material with methylene blue. The endpoint of the titration is visually detected by placing a drop of the suspension on white filter paper and observing the development of a light blue halo. The final amount of absorbed dye is used to calculate a methylene blue value (MBV) indicative of the cation exchange capacity (CEC) of the microfines. The MBV obtained for microfines from dry sieving and washing of the fine aggregate fraction are shown in Table 7. The results show which microfines have an increased ability to absorb the dye and consequently indicate in general the amount of total clays present in the microfines.

Table 7. MBV of Dry Sieve and Fine Aggregate Microfines

Sample	Location	Dry Sieve	Fine Ag.
AZ	--	24.8	31.9
CA	A	0.35	0.25
	B	1.56	0.125
CO-I	--	28	91.50
CO-II	--	5.5	--
CO-III	--	--	4
UT	--	11.9	14.8
WI	--	3.3	5.4
WY	A	43.0	55.3
	B	40.3	94.4

4.2.2. Thermogravimetric Analysis (DTG/TG)

The thermal analyses of the microfines for this characterization were performed with a simultaneous TG/DTA Metller Toledo 851. The thermogravimetric methodology involved heating the microfines up to 1000°C at 5°C/min and under flowing air at a rate of 60 ml/min in two atmospheres. Both air and carbon dioxide were used to differentiate dehydroxilation reactions from decomposition of carbonates, and to collect additional information about the nature of the carbonates. Weight losses on the TG curves recorded in air and carbon dioxide provides information on the carbonate and clay content present. The clay content describes the amount of either 2:1 clay or 1:1 clay based on the hydroxide content found in the analysis. A 1:1 clay is structured with a tetrahedral sheet layered with one octahedral sheet (e.g., kaolinite) where a 2:1 clay consists of an octahedral sheet between two tetrahedral layers (e.g., illite). The 1:1 clay type has nearly twice the hydroxide (OH^-) content of the 2:1 type. The magnitude and temperature of the weight loss in the TG curves provide information on the type and quantity of clay. However, it is important to know OH^- groups associated with metal hydroxyls are also released in the same range of temperatures as those coming from OH^- groups associated with the clays. In addition, the crystallinity of the clay and impurities can also influence its temperature of dehydroxylation. Thus, data from the TG analysis should be used in conjunction with XRD to obtain a more exact interpretation with respect to the composition of these microfines. The results of the TG testing alone are found in Table 8. Information regarding clay content is important because particularly 2:1 type clays can cause swelling when in contact with water and potentially redirect water from the cement hydration process.

Table 8. Thermogravimetric Analysis (DTG/TG)

Microfine Samples	Carbonates Content (% w)	Carbonate Species	Clay Content (% w) † 2:1	1:1
AZ- C	5	Proto-Dolomite	74	25
AZ- F	-	Proto-Dolomite		
AZ-D	5	Proto-Dolomite		
CA	<<	-	67	21
CO I-C	2	-		
CO I-F	-	-		
CO I-D	2	-	52	16
CO II	8	Proto-Dolomite		
CO III	20	Dolomite + Calcite + Proto-Dolomite	56	19
CO III-C	23	Dolomite + Calcite + Proto-Dolomite	50	16
UT-C	21	Dolomite + Proto-Dolomite	79	26
UT-F	23	Dolomite + Calcite + Proto-Dolomite		
UT-D	25	Dolomite + Calcite + Proto-Dolomite		
WI-C	41	Dolomite + Proto-Dolomite		
WI-F	27	Dolomite + Proto-Dolomite		
WI-D	37	Dolomite + Proto-Dolomite		
WY a-C	21	Proto-Dolomite		
WY a-F	-	-		
WY a-D	27	Calcite + Proto-Dolomite		
WY b-C	18	Proto-Dolomite	68	23
WY b-F	-	-		
WY b-D	30	Calcite + Proto-Dolomite	36	12

Note: † In the ‘Clay Content (% w)’ column, if the clay is structured in a 2:1 layer system, it is reported first, if it is in a 1:1 system it is reported second. “a” and “b” after the sample name indicates the location within the source. “C”, “F”, and “D” after the sample name indicate how the microfines were collected. “C” indicates washed from coarse aggregate, “F” indicates washed from fine aggregate, and “D” indicates the microfines are from dry sieving the aggregates.

4.2.3. X-Ray Diffraction

X-Ray Diffraction studies were performed using a High Star 2-D X-ray diffractometer. The diffractograms were registered in a single run and in step mode. Unknown crystalline phases present in the sample were identified by matching the diffraction pattern to the patterns stored in the Powder Diffraction Files (PDF). The XRD can help identify certain crystallography of the minerals. However, amorphous materials will not be detected using this method. The results of the test have been compiled and are reported in Table 9.

Table 9. X-Ray Diffraction Results

Sample	Observations on the nature of microfines from x-ray diffraction
AZ	Presence of quartz and rich calcium, sodium silicate. Sample similar to CO-I.
CA	Quartz, and 1:1 phyllosilicates (iron enrich kaolin or serpentine type)
CO-I	Quartz, and a rich calcium, sodium silicate. Diffractogram similar to AZ sample.
CO-II	Quartz and calcite in small quantities, low angle peaks of 2:1 phyllosilicates. Possible presence of sodium rich silicate hydroxide
CO-III	High quartz peak and a combination of calcite and in less amount dolomite. Also low angle peaks of 2:1 phyllosilicates. Similar to UT sample.
UT	Quartz, mix of calcite and dolomite in a lower content with respect to quartz, and low angle peaks of 2:1 phyllosilicates.
WI	Quartz, and low angle peaks of 2:1 phyllosilicates.
WY	Mix of calcite and quartz with low angle peaks of 2:1 phyllosilicates.

As indicated, by combining the TG and XRD analysis, one obtains a more complete understanding of the microfine mineralogy. The five microfines selected for use in preparing concrete in future studies are described in Table 10 from the combination of the two techniques.

Table 10. Microfine analysis from XRD and TG

Microfine Samples	Carbonates Content (% w)	Carbonate Species	Clay Type
CA	<<	-	1:1 and 2:1
CO	2	-	1:1 and 2:1
UT	21-23	Dolomite + Calcite + Proto-Dolomite	1:1 and 2:1
WI	27-41	Dolomite + Proto-Dolomite	-
WY	18-30	Calcite + Proto-Dolomite	2:1

4.2.4. Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)

SEM and EDS analyses similar to the morphology analysis were conducted on gold-coated samples of microfines using again a JEOL 6100 Scanning Electron Microscope. This study was only conducted on the five microfines used in later concrete testing. The samples were observed and analyzed under 15 kV accelerating voltage. Each original image was 800 x 640 pixels with a resolution of 1,860 pixels/mm (47,058 pixels/inch) for a magnification of 2,500x. EDS allowed us to evaluate the atomic percentage of the elements associated with the microfines. From this information, the mineralogy of different particles was determined. Table 11 summarizes the information collected from the SEM/EDS analysis.

Table 11. Description of microfine mineralogy

	Chemical Composition of the major constituents from EDS	
Source	General description	Some phases seen
CA	Contains primarily Si, Al, and Fe with small areas of Ca, K, and Mg.	Si4.5Al2.1Fe Mg0.5 (major phase) $Si_{5.6}$ Al $_{2.5}$ Fe Mg $_{0.3}Ca_{0.3}$ (from chemical analysis both are within the range of montmorillonite)
CO	Contains primarily Si, Al, and Fe with small areas including Na and K.	$Si_{18}Al_9Fe_3K_1Mg_1$ (montmorillonite) $Si_3Al_1Na_1$ (albite) $Si_3Al_1K_1$ (microcline) Quartz
UT	Contains a combination of Mg, Al, Si, K, Ca, and Fe.	quartz, calcite, dolomite $Si_3Al_1K_1$ (microcline) $Si_2Al_{1.5}Mg_1Ca_1$ (vermiculite) Si_2Al_1 (possibly illite)
WI	Contains primarily SI, Mg, and Ca.	dolomite, calcite, and areas of silica likely as quartz Si_1Mg_1 (talc) $Si_{16}Al_6Na_3Ca_1$ (feldspar) $Si_3Mg_1Ca_1Fe_1$ (pyroxenesilicates) $Si_3Al_1K_1$ (microcline)
WY	Composed of Silica Aluminum microfines mixed with varying levels of Ca or large aggregations of K.	calcite $Si_5Al_4K_1$ (possibly muscovite) $Si_5Al_3Ca_1Na_1$ (aggregate of albite and anorthite)

By combining the SEM/EDS results, in Table 11, with the ones from TG and XRD analysis found in Table 10, we can describe more precisely the mineralogical composition of the microfines. This is possible because SEM/EDS provides information on the different mineralogical phases of the microfines through the chemical composition of different particles. However, as a cautionary note, one may lose some minor phases because this is a microscopy technique and we are analyzing a small size of the sample. XRD, on another hand, provides an average analysis of a large size of sample and identifies the different crystal structures present in the microfines; however, it may underestimate or not show at all poorly crystalline materials. Thus, by coordinating results from both techniques the different mineral phases composing the microfines are more accurately established. By considering all of the data collected together from thermogravimetric analyses, X-ray diffraction, scanning electron microscopy/energy dispersive spectroscopy, and reviewing basic mineralogy of minerals, we were able to generally determine the constituents of the microfines. The following descriptions of the microfine mineralogy were made from the results.

CA – XRD and TG show the presence of 1:1 and 2:1 phyllosilicates, quartz, and low contents of carbonate species. In addition, from SEM/EDS analysis we found that quartz is present as very small particles and aggregate with other mineral phases. The major constituents are 2:1 phyllosilicates more closely resembling montmorillonite than vermiculite based on chemical composition. From the dehydroxylation loss in the TG curve and given that the major constituents are 2:1 type clays we can predict a high content of these minerals (≅ 67 %). To account for the total constituents of the microfines, carbonates made up about 2%, some humidity water accounts in general for less that 3% of the microfines weight; thus the remaining portion of the sample should be due to the contribution of microclinic and quartz (seen only by XRD).

CO I – From the XRD and TG we see 1:1 and 2:1 phyllosilicates, a low content of carbonates similar to the CA, and also some kaolinite, microcline, albite, and quartz. The three later minerals were also identified by SEM/EDS as individual particles. In addition, we found particles of montmorillonite (rather than vermiculite) as one of the major constituents. Since most of the hydroxylated silicates belong to the 2:1 type clays, the content of these minerals could be close to 52%.

UT – From XRD and TG analysis it was established that these microfines have between 21% to 23% dolomite and calcite. These techniques also allowed us to identify the presence of quartz, non-hydroxylated silicates as microcline, and clays (1:1 and 2:1). Information extracted from SEM/EDS analysis reaffirmed these findings and identified most of the clays as illite and vermiculite. We were unable to locate particles of kaolinite (phase shown by XRD) because these particles were likely small and forming aggregates with other mineral phases.

WI – TG analysis showed that 35% of the microfines are composed of dolomite. XRD showed quartz as the other major constituent. However, SEM/EDS data showed the presence of feldspar, pyroxenes, microcline, and talc as minor but independent phases.

WY – TG analysis and XRD showed the microfines were rich in calcite and dolomite, with some indication of the presence of 2:1 phyllosilicates (montmorillonite or vermiculite). SEM/EDS analysis showed mainly particles of calcite and aggregates of albite and anorthite as major constituents. Particles with the chemical composition of muscovite (clay) were also identified.

4.3. Reactivity of Microfines

4.3.1. Cation Exchange Capacity (CEC)

The CEC of the microfine was assessed using a leaching analysis evaluated by inductively coupled plasma (ICP). The leaching analysis also provided additional information as to the nature of exchangeable cations. In the leaching analysis, microfines were separated from the aggregate by sieving (fraction < 75 µm) and then were treated with solutions of KNO_3 or $Mg(NO_3)_2$ and MilliQ (MQ) water to determine principal exchangeable and soluble cations, respectively.

Testing was conducted following the procedure described. A mass of 0.25 g of microfines was added to 25 ml of 25 mN solution of either KNO_3 or $Mg(NO_3)_2$ and 25 ml of MQ water or only MQ water. The suspensions were shaken over night at 25°C. The solid phase was then separated from the solution by centrifugation at 7000 rpm. The solutions were then acidified with 100 µL of HNO_3 (12 N) and the concentration of Mg^{2+}, Ca^{2+}, and K^{+} were measured by ICP. The exchanged Mg^{2+} and Ca^{2+} were measured in the KNO_3 solution filtrates, while the concentration of exchanged K^{+} was measured in the $Mg(NO_3)_2$ solution filtrates. The concentration of cations associated with minerals soluble in water was measured in the MQ water filtrates. The measurements were taken using three samples of microfines for each of the solutions. The final results of both techniques are presented together in Table 11.

In Table 11 'Water Extractable (CEC)' refers to the ions leached out when the microfines where exchanged in water alone and reveals what exchangeable cations were present.

Each ion (Ca, Mg, Na, and K) was measured and the levels where recorded in milliequivalence/100 grams of microfines (mEq/100g). A mix of carbonates and 2:1 clays were found across most samples. During this test, calcium is leached and exchanges from within the carbonates out to the sodium in the clay and the sodium, in turn, moves from the clay into the water. As the calcium exchanges into the clay structure, the carbonates continue to dissolve. Similarly, the 'Exchangeable Cations (CEC)' data details the findings from the exchangeable solutions of KNO_3 and $Mg(NO_3)_2$. The results showed both calcium as well as some magnesium to be present. Therefore, potentially most of the clays are rich in calcium, but some also have magnesium and sodium. (Specifically the WY samples are typical.)

In the last column of Table 11 the % of alkalis and are derived from the Na and the K released when the microfines were subjected to the $Mg(NO_3)_2$ solution. This was calculated because alkali content is limited in cement production and is associated with the ASR. It is important to consider alternative sources of alkalis such as aggregate microfines. Arizona and Wyoming had the largest internal alkalis.

Table 12. CEC values, Principal Water Extracted and Exchangeable Cation, and Alkali Content of the Microfines

Sample	Microfine	Leaching Method (ICP) Water Extractable (CEC)†		Leaching Method (ICP) Exchangeable Cations (CEC)†		CEC† H2O	CEC† $Mg(NO_3)_2$	% Na_2Oeq
AZ	Fines	Ca(1.6) **Na(5.7)**	Mg(0.6) K(1.5)	**Ca(14.7)** --	Mg(2.8) K(1.76)	9.4	28.2	0.26
AZ	Dry Sieving	**Ca(5.3)** Na(1.5)	Mg(1.3) K(1.1)	**Ca(6.8)** Na(0.1)	Mg(1.7) K(0.9)	9.6	19.2	0.12
CA	Dry Sieving	**Ca (5.0)** --	-- K(0.1)	**Ca(10.0)** --	Mg(1.0) K(0.1)	5.2	16.2	0.006
CO-I	Fines	Ca(1.4) **Na(2.7)**	Mg(0.3) K(0.4)	**Ca(21.6)** Na(0.2)	Mg(2.7) K(0.6)	4.9	30.1	0.12
CO-I	Dry Sieving	**Ca(4.5)** Na (0.5)	Mg(0.30) K(0.3)	**Ca(10.7)** Na (0.2)	Mg(0.8) K(0.1)	5.6	17.4	0.036
CO-II	Fines	**Ca (4.4)** Na (0.3)	Mg(0.7) K(0.4)	**Ca(11.3)** Na (0.1)	Mg(0.7) K(1.3)	5.8	19.1	0.064
CO-III	Fines	**Ca(2.9)** Na(0.2)	Mg(0.31) K(0.3)	**Ca(7.9)** Na(0.1)	Mg(0.7) K(1.4)	3.7	13.7	0.057
UT	Fines	**Ca(2.9)** Na (0.1)	Mg (0.6) K(0.2)	**Ca(11.4)** Na(0.11)	Mg(0.7) K(0.3)	3.8	16.4	0.022
UT	Dry Sieving	**Ca(3.7)** Na (0.4)	Mg(0.6) K(0.3)	**Ca(10.7)** --	Mg(1.1) K(0.32)	4.4	17.0	0.03
WI	Fines	**Ca(2.9)** --	Mg(0.5) K(0.1)	**Ca(9.7)** --	Mg(0.8) K(0.1)	3.5	10.6	0.5E-3
WI	Dry Sieving	**Ca(2.7)** --	Mg(0.6) K(0.1)	**Ca(9.1)** --	Mg(0.8) K(0.1)	3.3	9.9	0.5E-3
WYa	Fines	Ca(2.2) **Na(5.0)**	Mg(0.7) K(0.2)	**Ca(12.3)** Na(0.6)	Mg(3.2) K(0.2)	8.1	24.4	0.18
WYa	Dry Sieving	Ca(4.1) **Na(5.1)**	Mg(1.2) K(0.2)	**Ca(12.5)** Na(1.7)	Mg(3.4) K(0.7)	10.5	29.0	0.24
WYb	Fines	Ca(1.7) **Na(9.2)**	Mg(0.7) K(0.2)	**Ca(9.3)** Na(1.3)	Mg(5.7) K(0.4)	11.9	28.7	0.34
WYb	Dry Sieving	Ca(2.2) **Na(4.2)**	Mg(0.9) K (0.2)	**Ca(12.5)** Na (1.86)	Mg(3.4) K(0.72)	7.5	24.8	0.17

Note: † CEC measure in mEq/100g

4.3.2. Pozzolanic Activity

Conductivity measurements were used to indicate pozzolanic activity of the microfines collected from washing fine aggregates and from dry sieving. The method described in Luxán et al. was followed. *(23)* A total mass of 5.0 g of microfines previously oven dried overnight, were diluted in 200 ml of saturated $Ca(OH)_2$ solution at 40 ± 1ºC. The conductivity was measured over a 2 minute period, and the variation between the initial and final reading is reported. The pozzolanic activity of a silica fume, Class C fly ash, slag, and quartz type sand were measured for comparison purposes. The final results are represented in Figure 5. An increase in conductivity correlates to an increase in pozzolanic activity potentially leading to a decreased need for adding additional cementitious material.

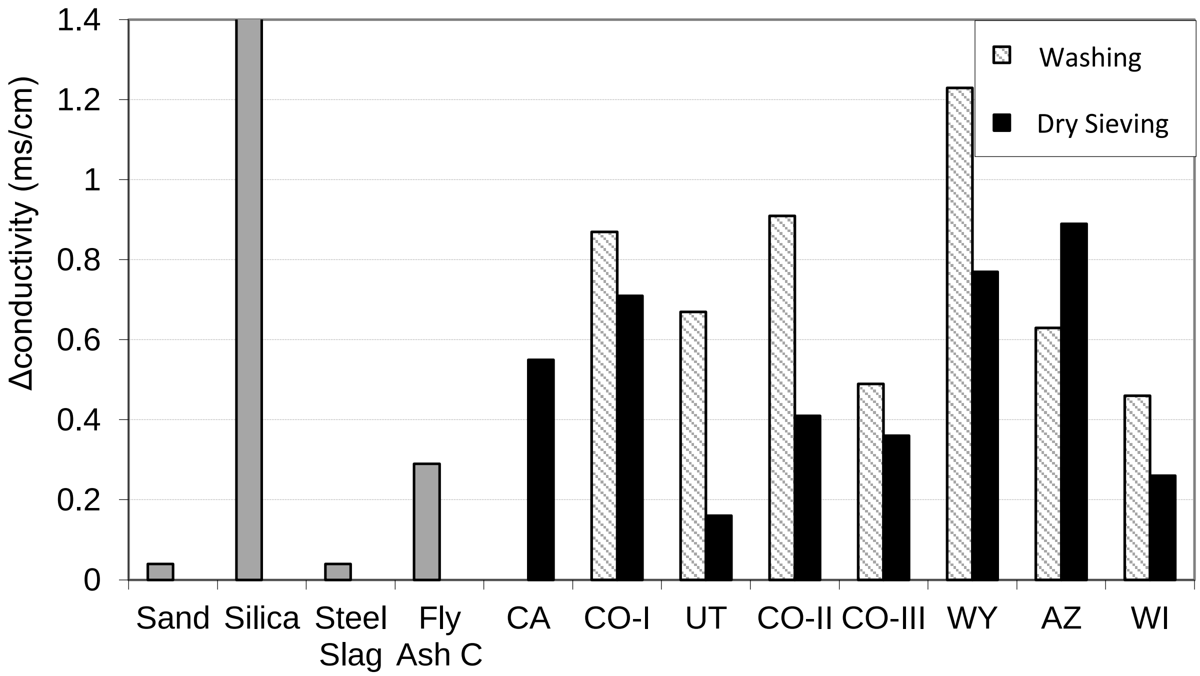


Figure 5. Δ Conductivity of Microfines from Washing Fine Aggregates and Dry Sieving

4.3.3. Evaluation of Alkali-Silica Reactivity (ASR)

Evaluation of alkali-silica reactivity of aggregates and microfines was achieved by the chemical method proposed by Chatterji. *(22)* This method is based in the following reaction:

$$\textit{Reactive silica} + Ca^{2+} + 2OH^{-} + K^{+} + Cl^{-} + H_2O \rightarrow$$

$$\textit{Hydrated lime-alkali-silica complex} + Ca^{2+} + 2Cl^{-}$$

This reaction is reproduced by suspending a mixture of CaO and the sample to be tested in a saturated solution of KCl maintained at 70ºC (158 ºF) for 24 hours. The final OH^- concentration is determined by titration against an HCl solution. The decrease in OH^- concentration compared with a control is indicative of the ASR reactivity. The results obtained for coarse and fine aggregates were compared against a blank (CaO in KCl solution) with an unreactive river sand, mostly composed of quartz. The ΔOH^- concentrations are shown in Table 13. Changes in OH^- concentration above 45 indicate an increasing tendency to support the ASR although we are uncertain as to how large of a value is indicative of prompting visible distress. As a comparison, ASTM C1260 values at 14 days are shown for the UT and WI fine aggregates. It is generally accepted that C1260 expansion values that exceed 0.20% at 14 days are typical of aggregates displaying the ASR-related distress in the field. The Utah source exceeds this threshold suggesting that changes in OH^- concentrations above roughly 200 may cause a deleterious reaction.

Table 13. Δ[OH-] in the aqueous suspension of aggregates compared to ASTM C1260

Sample	Δ OH^-			ASTM C1260 expansion (%) at 14 days (fine aggregate only)
	Microfines	Coarse	Fine	
Control Sand		--	45	
AZ	215	286	206	
CA	290	114	128	
CO-I	190	34	249	
CO-II	276	--	208	
CO-III	192	40	47	
UT	276	270	295	0.26%
WI	167	192	160	0.08%
WY	292	151	210	

5. CATEGORIZATION OF MICROFINES

After collecting all of the data, comparisons were made to gauge the severity of the microfines. Table 14 displays a comparison of the mineralogy for the various microfines, and links the composition to the cation exchange capacity rating the microfines as a low, moderate, or high potential for clays. Exchangeable cation levels are also important as they relate to the alkalinity of the microfines.

Table 14. Summary of Findings from Mineralogy Studies

Sample	X-Ray/TG/SEM-EDS	Extractable Cation in Water	Exchange -able Cation	CEC water	CEC Mg	NaOeq	Rating
AZ	Quartz + CaNa Silicate (Similar to CO-I)	Na(F) Ca(D)	Ca	9.4-9.6	19-28	0.12-0.26	High
CA	Quartz + 1:1 PhyloSi	Ca	Ca	5.2	16	0.006	Low
CO-I	Quartz + CaNa Silicate (Similar to AZ)	Na(F) Ca(D)	Ca	4.9-5.6	30-17	0.036-0.12	Mod
CO-II	Quartz + Calcite (small) + 2:1 PhyloSi + Na rich Silicate	Ca	Ca	5.8	19	0.06	Mod
CO-III	Quartz + Calcite + Dolomite (small) + 2:1 PhyloSi (Similar to UT)	Ca	Ca	3.7	13	0.057	Mod
UT	Quartz + Calcite + Dolomite + 2:1 PhyloSi (Similar to CO-III)	Ca	Ca	3.8-4.4	16-17	0.02-0.03	Low
WI	Quartz + 2:1 PhyloSi	Ca	Ca	3.5-3.3	9.9-10.6	5.00E-04	Low
WY	Quartz + Calcite + 2:1 PhyloSi	Na	Ca	7.5-11.9	24-29	0.17-0.34	High

Table 15 provides a summary of the findings from the remaining tests. Each sample is given a rating as compared to others. The methylene blue test describes the total quantity of clays where “low” indicates less clay content. The California Cleanness Test results point to the quantity and nature of the microfines where “high” is better for concrete. Particle size distribution information simply describes the natural material size dispersion with smaller particles typically being more reactive than larger particles. Pozzolanic activity can aid the concrete mix and levels are indicated - distinguishing higher activity as better. Alkali-silica activity can be harmful to the mix and a low potential for a reaction is desired.

Table 15. Summary of results for microfines

Sample	Methylene Blue	CA Clean Test	Pozzolanic Activity	ASR
AZ	High	Limit	Mod	Mod
CA	Low	High	Low	High
CO-I	Very High	Very Low	Mod	Low
CO-II	Low		Mod	High
CO-III	Low	High	Low-Mod	Low
UT	Mod High	Low	Mod	High
WI	Low	High	Low-Mod	Low
WY	Very High	Low	High	High

Table 16 relates the samples to one another and categorizes them into 3 general groups. This classification considers the characteristics of the base aggregate as well as the microfines. These general classifications are somewhat confounded because in some cases the performance of the base aggregate is significantly different than the microfines. For example, the Wyoming base aggregates show only moderate ASR potential but the microfines are highly reactive. These categorizations are therefore approximate and qualitative.

Table 16. Grouping of microfines by potential to contribute to ASR

Sample	Classification	Group	Anticipated Impact
AZ	G2 Mod Alkali	G1	Inducers of physical changes for ASR development and promoters of ASR by increased alkali content and ASR active material
CA	G2 Low Alkali		
CO-I	G2 Low Alkali		
CO-II	G2 Mod Alkali	G2	Potential inducers of favorable physical changes for ASR development (at high P200) and promoters of ASR by increased alkali content and ASR active material
CO-III	G3 Mod Alkali		
UT	G1 Mod Alkali		
WI	G3	G3	Little or no effects on physical properties nor potential source of ASR
WY	G2 High Alkali		

It was these classifications that lead to the selection of the five microfines used in the future concrete tests as they represent a diverse set of characteristics. Again the following microfines were chosen for future concrete tests as described earlier: CA, CO-I (in later chapters referred to as CO), UT, WI, and WY.

6. REACTIVITY OF MICROFINES IN SOLUTION

Once the microfines were well characterized, a reactivity test was conducted on the five selected microfines for future concrete studies. This test was conducted to determine how the microfine mineralogy might change or what reaction products would be produced under highly alkaline conditions in the presence and absence of potassium acetate deicer.

Table 17 shows the testing matrix for this reactivity test. The microfines were immersed in solutions at 50 g/L and 76°C. Solids were extracted at 1 and 3 weeks and subject to TGA and XRD evaluation. The three solutions used were:

- Solution 1: Saturated in $Ca(OH)_2$, 0.8M NaOH; pH = 13.4
- Solution 2: Saturated in $Ca(OH)_2$, 0.8M NaOH and 5M KAc; pH = 13.6
- Solution 3: Saturated in $Ca(OH)_2$, 5M KAc; pH = 12.6

Table 17. Matrix of microfines to be tested in solution

	Untreated		**Solution 1** (saturated $Ca(OH)_2$ in 0.8 M NaOH)		**Solution2** (saturated $Ca(OH)_2$ in 0.8 M NaOH and 5 M potassium acetate)	
Microfine	Washed	Dry Sieve	Washed	Dry Sieve	Washed	Dry Sieve
California	X	X	X	X	X	X
Colorado	X	X	X	X	X	X
Utah	X	X	X	X	X	X
Wisconsin	X	X	X	X	X	X
Wyoming	X	X	X	X	X	X

Thermogravimetric analysis revealed that the outcomes associated with solution 1 were approximately the same as those associated with solution 2. The major differences between the TG curves of treated and untreated microfines were associated with the evolution of Ca and Mg carbonates. Carbonate content was smaller in microfines treated with solutions 1 and 2. Carbonates consisting of Mg-poor dolomite (UT and WY) transformed in the solutions much faster than highly crystallized dolomite (WI).

Results from XRD analysis confirmed findings from the thermogravimetric analysis. In addition, these results suggest the presence of diopside ($CaMgSi_2O_6$) and the partial dissolution of quartz (smaller particles upon treatment). Above pH 13, Mg and Ca carbonates in microfines rich in SiO_2 evolved towards $Ca_2Mg_5Si_8O_{22}$ $(OH)_2$, $CaMgSi_2O_6$, $CaCO_3$, or a mixture of these minerals, depending on the Ca/Mg ratio. When the Ca/Mg ratio was greater than 2, the predominant phase at equilibrium was $CaCO_3$. When Ca/Mg ratio was less than 2, the predominant phase at equilibrium was $CaMgSi_2O_6$. In microfines having very small Ca/Mg ratios, the carbonates transformed into $Ca_2Mg_5Si_8O_{22}(OH)_2$.

TG results from the California microfines showed solution 2 carbonates and hydroxylated silicates were destroyed. XRD results showed silicates dissolving in the California microfines when subjected to solution 2. TG results for Colorado microfines indicated a decrease of species with hydroxide contents when subjected to solution 2. TG results for Utah microfines depicted losses in carbonate species. It was observed that the carbonate output was less defined meaning they react early, possibly changing to something less stable. It was also observed that magnesium was leached because the output shows it was not as crystalline as the untreated specimen. XRD results showed a decrease in crystalline dolomite at 2 theta angle 32 and a reduction in crystalline silica at 2 theta angle 39.5. TG results indicated the Wisconsin microfines change the least when subjected to the various solutions and compared to the other microfines. The results indicate the microfines which consist of well crystalline dolomite are barely attacked. From the TG results one can see that the Wyoming microfines consist of poorly crystalized dolomite which is more reactive. The hydroxylated silica species was minimally altered. They were not well defined in the DTG results, but losses were seen in the TG data. XRD results for Wyoming microfines indicated a reduction in vermiculite, quarts, and albite. In general, most species are disappearing.

From this analysis, some theories can be formed about the potential reactions that may occur when the microfines are put in concrete and then subjected to potassium acetate deicer. It can be said that CO and WY microfines are most easily transformed when subjected to potassium acetate as indicated by the transformations from solution 3.

Thermodynamic predictions and equilibrium diagrams were used to calculate the solid phases formed in the pore water of concrete in the presence of Mg and KAc. Assuming that the pore water is very rich in Ca and silicates, has a Mg concentration of 130 mM, and a pH above 13, 60% of the Ca could potentially be in the form of$CaSiO_3$, 30% as $CaCO_3$, and the rest as $CaMgSi_2O_6$; 100% of Mg should be $CaMgSi_2O_6$.

From these tests and analysis, given enough time, the presence of Mg Ca double carbonate microfines in aggregates should change the mineralogy of the ITZ and therefore affect certain properties of concrete. The magnitudes and timing of these impacts cannot be determined from the findings of this reactivity test alone.

7. CONCLUSION

In the analyses performed, particular attention was given in order to predict how the microfines may change when put in concrete and then subjected to potassium acetate. Various microfines could affect the system differently because of the level of silicates that could be in the minerals of the microfines, the level of clays, or if they are pozzolanic in nature. Silica is important because it plays a role in the formation of alkali-silica gels. Clays are important because they can absorb and exchange with the pore solution causing expansion. In this case, the greatest expansions come from the microfines which include montmorillonite which is highly expansive clay as opposed to vermiculite which has a smaller limit. Also, the clays may play with exchangeable cations causing problems with normal formation of cement products. Pozzolans are important because they may slow the ASR from occurring.

From these tests, the characteristics of the microfines were defined. It was determined that CA, CO-I, UT, WI, and WY would likely preform uniquely from one another when used in concrete which would be subjected to potassium acetate. Concrete will be produced and tested and when the results are collected, the characteristics defined in this chapter will be used to determine which characteristics are responsible for the results.

The following predictions can be made when concrete is made incorporating the microfines. For expansion, we should see CO, CA, UT, WY, and lastly WI in order of most to least based on the type and quantity of clay content in the fines. We caution that this is just something to watch for as the exact order of expansion in the tests may depend upon the different mechanisms of expansion. For example, ASR would cause expansion, but relate more closely to the silica content than clay content. In this case, WY, CA, UT, CO, and WI respectively would be more reactive. Other reactions may also occur as this system is very complex and difficult to predict solely on the microfines.

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Chapter 3

Physical Responses to the Interaction of Potassium Acetate Deicers and Natural Microfines

PHYSICAL RESPONSES TO THE INTERACTION OF DEICER AND NATURAL MICROFINES

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ABSTRACT

The interactions of natural microfines and potassium acetate deicer were investigated in laboratory specimens. Microfines (material smaller than 75 µm [0.003 in]) from 5 aggregate sources from locations across the western US were characterized and subsequently studied when subjected to deicer solution while in concrete. Expansion and freeze-thaw durability test specimens were monitored and evaluated for damage. Based on the incurred failures and mineralogy type, the microfines were assessed. Among the microfines tested, those incorporating phyllosilicates showed the greatest degradation of concrete when subjected to potassium acetate deicer over the duration of the study.

Keywords: concrete durability; expansion; freeze-thaw durability; deicer; microfines, ASR

INTRODUCTION

The research involves work predominantly in the laboratory to quantify the durability and potential for deterioration of concrete with and without mineral fines in the presence of deicers. The nomenclature "dirty aggregates" is recognized as aggregates coated with a layer of microfines (particle size smaller than 75 µm [0.003 in]). As a general classification, microfines can be divided into dust, clay particles, and minerals and can be deleterious and/or alter the concrete as the small particles have a high surface area and reaction rate.[1,2] The mineralogy of microfines can have an effect on the overall concrete and is a significant factor when considering the level of influence on the consequential deterioration.[3-7] In general, stone dust and carbonates decrease the slump and increase compressive strength, shrinkage, and porosity.[3-5] However, typically these effects can be neutralized through the use of the proper chemical admixture. Clay coatings on aggregates have been regarded as one of the problematic microfine types producing the most deleterious effects on concrete [8,9] and at the same time are the most difficult to resolve by simply washing the aggregate. Thus, a fraction of clay coatings is expected to remain attached to the surface of the coarse aggregate after the mixing process. Commonly reported effects of clay coatings with respect to the quality of mortars are lower compressive strengths, an increase in shrinkage, and altered microstructure of the cement phase.[10] Determining the effect of the microfines on ordinary Portland cement concrete (OPCC) durability when subjected to potassium acetate deicer is the target of this study.

RESEARCH SIGNIFICANCE

It was recently reported that the use of certain deicing chemicals in airports resulted in premature deterioration of concrete pavements.[11] The FAA noted, effects thought to be associated with the alkali silica reaction (ASR) were aggressive in particular airfield pavements where there were reportedly use of aggregates contaminated with excessive amounts of microfines as surface coatings (Jim Lafrenz, IPRF – Personal Communication). It is believed microfines maybe a key reaction instigator when concrete is exposed to potassium acetate deicing chemicals. By determining the particular components responsible for deterioration of concrete, measures can be taken to avoid the combination of these materials.

EXPERIMENTAL INVESTIGATION

Specimens with and without natural microfines were prepared utilizing a known alkali-silica reactive and a nonreactive aggregate source rendering the investigation of 12 different combinations of materials. Microfines were extracted from pit-run material received from pits/quarries in California (CA), Colorado (CO), Utah (UT), Wisconsin (WI), and Wyoming (WY). The microfines were included in mixes where the fine and coarse aggregate material was either from Utah (representing a reactive aggregate source) or Wisconsin (representing a non-reactive source). Various specimens were created for monitoring the length change incurred from subjecting the specimens to different environments and freeze-thaw durability testing.

Materials

Five primary components were used for this research including commercial deicing solution, cement, air entraining agent, fine and coarse aggregate, and microfines. The commercially used deicing solution consisted of primarily a 50% by weight potassium acetate solution in water with a corrosion inhibitor. The cement was ordinary Type I Portland cement of which the composition is detailed in Table 18. Several air entraining agents were tested ultimately leading to the incorporation of one multi-component synthetic air entraining agent shown to perform most consistently. The fine and coarse aggregate was from one of either a reactive or nonreactive source. Reactive aggregate composition consisted of granitic gravel while the nonreactive was composed of dolomitic gravel. Microfines came from five sources and varied in composition in an effort to determine which type of mineralogy was most reactive when combine with potassium acetate deicer in concrete. As a general overview of the dominant mineralogies in the microfines, principally the type and quantity of the carbonates and the presence of clay minerals, is summarized in Table 19.[12]

Table 18 – Cement composition

Testing Information: XRF FB, Vicat, Blaine, Soundness (Autoclave)						
FUSED BEAD (Loss Free)						
SiO2	Al2O3	Fe2O3	CaO	MgO	SO3	
20.05%	4.64%	2.68%	63.31%	2.39%	2.52%	Total 99.48%
K2O	Na2O	TiO2	P2O5	Mn2O3	SrO	
0.43%	0.23%	0.22%	0.13%	0.12%	0.06%	
	C3S	C3A	C2S	C4AF		
	60	7.8	12.3	8.2		
		Alkalis Eq.	0.51	%		
		Loss On Ignition	2.71	%		
		Blaine	4340	sg.cm./gm.		
Vicat Setting Time:		Initial	125	minutes		
		Final	240	minutes		
		Autoclave Expansion	0.013	%		

Table 19 – General characterization of microfine materials

Microfine Sources	Carbonates Content (% wt)	Carbonate Species	Clay Type
CA	<<	-	1:1 and 2:1
CO	2	-	1:1 and 2:1
UT	21-23	Dolomite + Calcite + Proto-Dolomite	1:1 and 2:1
WI	27-41	Dolomite + Proto-Dolomite	-
WY	17-30	Calcite + Proto-Dolomite	2:1

The microfine-coated aggregates were prepared by dipping, washed, dry aggregate in aqueous slurries of microfines. The slurry was made of a mixture of microfines that were extracted from an initial dry sieving followed by a washing of the pit run material from each of the five sources. The microfines were recombined in a ratio that mimicked the original extracted ratio and Table 20 lists the ratio of dry to wet microfines for each source. The microfines were weighed dry and then added to water making the slurry. By weighing the dry coarse aggregate before and after dipping, the percent of microfines that adhered to the aggregate was determined. The microfines were coated onto both unreactive WI aggregate and reactive Utah aggregate separately with an effective adhesion of approximately 1.5% ±0.1% by coarse aggregate weight. An additional 3.5% (based on total aggregate weight) of dry mixed microfines was added to the fine aggregate portion. In addition, the Wisconsin fine aggregate contained 0.8% microfines by weight and 1.7% for the Utah fine aggregate. These microfines were not removed for practical reasons prior to preparing materials for mixing.

Table 20 – Microfine recovery from aggregate sources.

Microfine Source	Microfines recovered from dry sieving [%]	Microfines recovered from washing [%]
California	34	66
Colorado	28	72
Utah	9	91
Wisconsin	61	39
Wyoming	27	73

Specimens

Concrete specimens were prepared to assess the impact of the microfines in concrete exposed and unexposed to potassium acetate commercial pavement deicer. Each condition consisted of the base aggregate washed clean of any microfines (control condition) and those with the individual addition of microfines from five different locations as described. All concrete specimens for a single condition (microfine type and aggregate type) were prepared from the same batch of concrete ensuring that slump, air content, and other mixing parameters were the same for all specimens associated with one condition. The mix consisted of 0.45 w/c mix with a target air content of 6% and no additives other than an air entraining agent. The concrete mix design is summarized in Table 21 and each condition was prepared in one batch of 2.3 ft^3 [0.065 m^3].

Table 21 – Concrete specimen mix design for ASTM C1293 and C666.

Mix Design Item	Quantity
Type I Cement	658 lbs/yd^3 [390kg/m^3]
Water/Cement	0.45
Coarse Aggregate	1715 lbs/yd^3 [1018 kg/m^3] (60%)
Fine Aggregate	1044lbs/yd^3 [620 kg/m^3] (40%)
Target air content	6% ± 1%

There was considerable difficulty in achieving the target air content even with large additions of air entraining agent. Additions of some air entraining agents at levels an order of magnitude greater than recommended did not produce predictable or adequate levels of entrained air. The microfines appeared to neutralize the air entraining admixture (AEA #1 - Inorganic Salt of Processed Oil). As indicated in Figure 6, with Wyoming microfines, the research team was unable to achieve target air levels independent of the amount of air entraining agent used. The air entraining agent used was a common agent provided by a national distributor. An alternative and less commonly used synthetic air entraining agent (Resin Solution) was ultimately selected for use in mixing. As shown in Figure 7, this AEA proved more effective though dosage rates far exceeded normal field levels. Figure 7 shows the air contents achieved with the second AEA in trial batches. Ultimately, AEA #2 produced air contents as shown in Figure 8 and Figure 9 with the dosage rates shown. These figures show that microfine-containing mixes require significantly larger dosages of AEA. The target air content was not achieved in all cases because of the unpredictability of the process. The outcome of the concrete batch and specimen fabrication process is shown in Table 22. These data highlight the large variation in slump and the challenge in managing air content with microfine additions that contain 1:1 and 2:1 phyllosilicates.

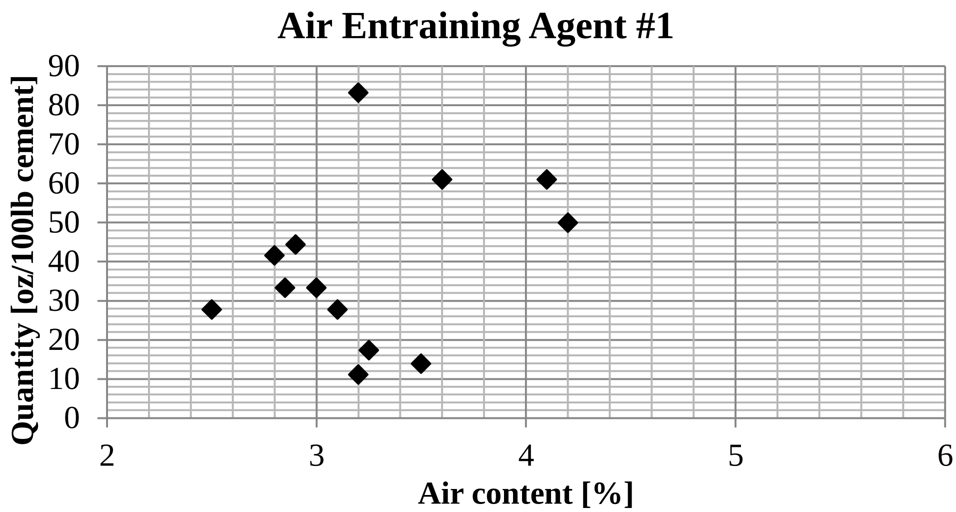

Figure 6 – Air content achieved in concrete batches containing WY microfines with different dosages of air entraining agent No. 1. The manufacturer's recommended typical field dosage falls between 1 and 3 fl. oz. [30 and 90 mL] per 100 lbs [45.5 kg] of cement.

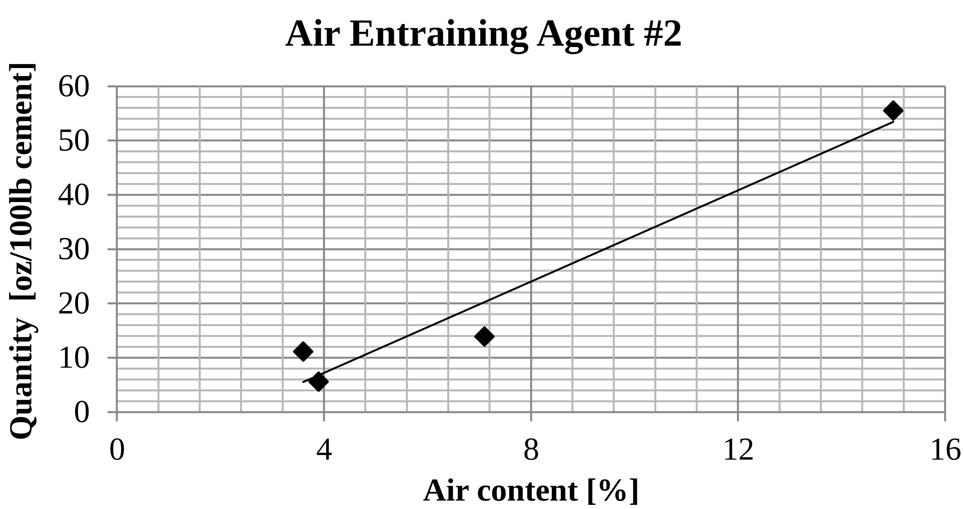

Figure 7 – Air content achieved in concrete batches containing WY microfines with different dosages of air entraining agent No. 2. The manufacturer's recommended typical field dosage falls between 0.15 and 3 fl. oz. [4.5 and 90 mL] per 100 lbs [45.5 kg] of cement.

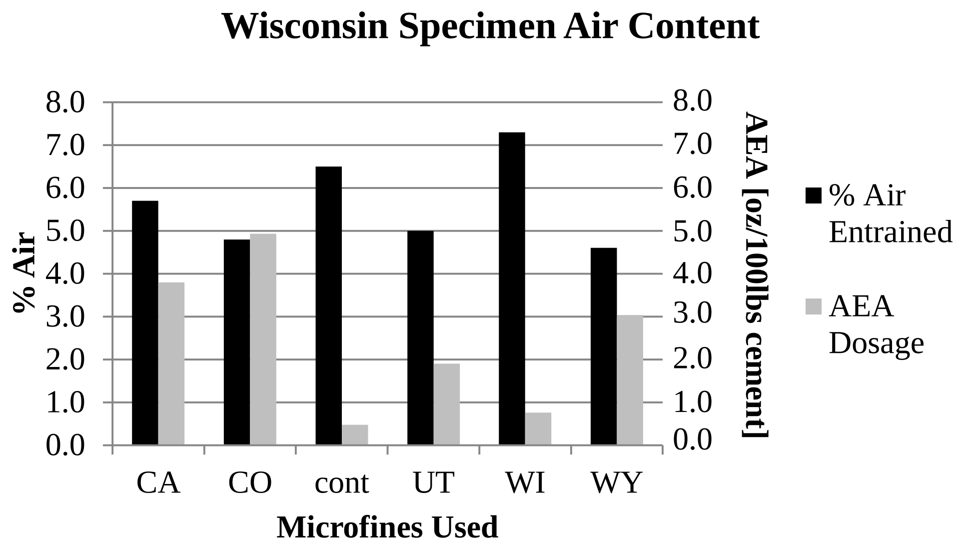

Figure 8 – Air content and air entraining agent dosages for concrete batches using Wisconsin aggregate. *1oz/100lbs is equivalent to 0.65mL/kg.

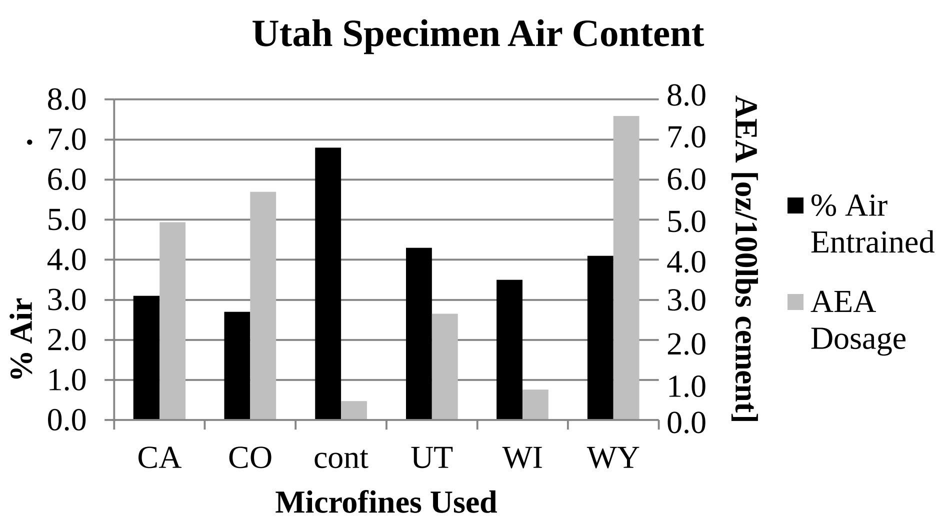

Figure 9 – Air content and air entraining agent dosages for concrete batches using Utah aggregate. *1oz/100lbs is equivalent to 0.65mL/kg.

Table 22 – Mix parameters associated with concrete specimen preparation.

Mix	Adhered Fines [% CA wt]	Total Added Microfines [% total aggregate wt]	Total Added Microfines [% FA wt]	Slump [in.; cm]	Fresh Air Content [%]	ounces AEA per 100 lbs [45.5 kg] cement
CA on WI	1.6	4.5	11.9	0.75; 1.9	5.7	3.80
CO on WI	1.5	4.4	11.7	0.375; 0.95	4.8	4.93
cont WI	0.0	0.0	0.0	9.5; 24.1	6.5	0.47
UT on WI	1.4	4.4	11.6	4.5; 11.4	5.0	1.90
WI on WI	1.3	4.3	11.4	2; 5.8	7.3	0.76
WY on WI	1.5	4.4	11.7	0.75; 1.9	4.6	3.04
CA on UT	1.4	4.4	11.6	0.25; 0.63	3.1	4.93
CO on UT	1.4	4.3	11.6	0	2.7	5.69
cont UT	0.0	0.0	0.0	6.25; 15.9	6.8	0.47
UT on UT	1.5	4.4	11.7	3; 7.6	4.3	2.66
WI on UT	1.3	4.3	11.4	1.25; 3.18	3.5	0.76
WY on UT	1.3	4.3	11.4	0.25; 0.64	4.1	7.59

Alkalinity

Since ASR was described as the possible method of deterioration, alkalinity was monitored in this study. Increased alkalinity translates to free hydroxide (OH^-) ions that can react and deteriorate siliceous aggregates. Often, increased alkalinity comes in the form of KOH or NaOH. The ions from these hydroxyls, K^+, Na^+, and OH^- are available to form secondary reaction products such as gels including alkali-silica gel. When the concentration of alkaline ions is large they can associate with other available anions such as sulfates by stripping them from products such as ettringite or monosulfate. In order to determine the total alkali content of the mix, the cement alkali content results were combined with the microfine

Na_2O equivalent level to determine a total percentage based on cement weight as shown in Table 23. The microfine alkali content as included in Table 23 accounts for only the exchangeable alkali cations of the clay minerals. The method used did not account for the total amount of alkali cations liberated due to dissolution under cement pore solution as might occur for mineralogical phases such as certain feldspars. This method used Inductively Coupled Plasma (ICP) to measure the sodium and magnesium released from the microfines after being treated with solutions to determine the principle exchangeable and soluble cations.

Table 23 – Alkali content of the cement and microfines.

Mix	Weight of fines added [lbs; kg]	Alkali content added from microfines	Total Na_2O [% cement wt]
CA on WI	10.58; 4.8	0.064	0.34
CO on WI	10.34; 4.69	0.807	1.67
WI cont	0	0	0.23
UT on WI	10.34; 4.69	0.259	0.69
WI on WI	10.11; 4.59	0.005	0.24
WY on WI	10.34; 4.69	2.637	4.93
CA on UT	10.34; 4.69	0.062	0.34
CO on UT	10.11; 4.59	0.788	1.63
UT cont	0	0	0.23
UT on UT	10.34; 4.69	0.259	0.69
WI on UT	10.11; 4.59	0.005	0.24
WY on UT	10.11; 4.59	2.577	4.82

Items of Investigation

The objective of this research was to determine if natural microfines combined with deicer instigate ASR or other durability related distress in concrete specimens. In order to fulfill this objective, concrete specimens were prepared containing microfines and macro-scale performance was evaluated using a variety of durability tests. The primary mechanical evaluations of the concrete specimens consisted of two modified ASTM C1293 (Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction) protocols and one modified ASTM C666 (Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing) durability protocol.

ASTM C1293 calls for the addition of sodium hydroxide to raise the NaO equivalent to 1.25% based on the mass of cement. This addition was not made for two reasons. First, there was concern that such an addition would mask the alkali contribution of the microfines. Secondly, such an addition would have necessitated separate batching of the modified C1293 specimens and create an inconsistency amongst specimens for different tests. After an initial 24 hours of curing, samples were subject to the modified ASTM C1293 protocols. One modified C1293 protocol involved specimens prepared with no sodium hydroxide addition and subject to 38°C 100% relative humidity curing. The other modified C1293 protocol involved soaking similar specimens in potassium acetate deicer at 38°C. (These specimens will be referred to as C1293-Humid to indicate the humid environment and C1293-Deicer to indicate the deicer soak.) Periodic length measurements taken at 7 days, 14 days, 28 days, monthly from 2 until 12 months were the primary measure of change in both protocols. Environmental chambers were constructed for these tests consisting of galvanized steel tanks wired to a heating system. The tanks were insulated around the sides with fiberglass insulation and the top and bottom with foam board insulation to prevent heat loss and to maintain the specimens under stable environment.

To examine the influence of sodium hydroxide addition, a series of modified ASTM C1260 tests (Standard Test Method for Potential Alkali Reactivity of Aggregates – Mortar-Bar Method) were conducted on mortar bar specimens using each fine aggregate source and the microfines. This test used gradations for fine aggregate as specified in the standard with additional microfines added at a dosage level of 11.6% of fine aggregate. This dosage rate is equal to the dosage rate (as a percentage of fine aggregate) as was used in the C1293 tests on average.

Modified ASTM C666 specimens were poured from the same batch as those for the modified ASTM C1293 procedures. The specimens were demolded after 24 hours of standard curing and then placed into a humidity room. After 28 days, the specimens were removed and the dimensions, weight, and transverse frequency measured after which the specimens were frozen until all specimens reached the same maturity. The specimens were dried and thawed for 24 hours in an environmental chamber held at 50% RH and 25°C [75°F] and then put into a standard freeze thaw cabinet and cycled 60 times between the temperatures of 10°F [-12°C] to 50°F [10°C]. At this point, the specimens were removed from the chamber and detached particles were rinsed from the surface, and subsequently placed into the environmental chamber for 24 hours. Specimens were then submersed in deicer at a temperature of 38°C [75°F] for 48 hours. The deicer bath was identical to that used in the C1293-Deicer test above. Specimens were then returned to the environmental chamber for 24 hours. Before returning the specimens to the freeze thaw cabinets, the specimens were measured. The tests and curing conditions for all tests are shown in Table 24.

Table 24 – Summary of concrete specimen curing conditions.

Test	Curing Conditions
Modified ASTM C1293-Humid	High relative humidity at 38 ºC [75°F] for 12 months (no addition of NaOH)
Modified ASTM C1293-Deicer	Immerse specimens in a KAc-based deicer solution at 38 ºC [75°F] for 12 months (no addition of NaOH)
Modified ASTM C666 Procedure A in presence of Deicer	Initial 28 days of wet curing conditions • Air dry at 25°C [75°F] 50% RH for 24 hours • KAc soak at 38 ºC for 48 hours • Air dry at 25°C [75°F] 50% RH for 24 hours • Freeze-thaw cycles for 60 cycles • Repeat
Modified ASTM C1260	Immersed in 1N NaOH solution at 80°C [176°F] for 28 days

A subset of specimens was analyzed according to ASTM C457 to determine hardened concrete air content. The linear transverse model was used to determine the spacing factor of the air void system. Table 25 allows comparison of the fresh air content to the hardened air content and corresponding spacing factors. The expectation was that the air content values would be within two percent of each other and as shown in Table 25 they were.[13] It is noted that the largest discrepancies occurred in the lowest air contents with spacing factors that were larger than what one might expect from the corresponding air contents.

Table 25 – Hardened air content and spacing factor of C1293 Humid specimens.

Specimen Name	Fresh Air Content [%]	Hardened Air Content [%]	Spacing Factor [in.; mm]
Recommended	5.0 - 7.0	5.0 - 7.0	0.004 to 0.008; 0.1 to 0.2
CA on WI	5.7	6.8	0.007; 0.18
WI on WI	7.3	7.2	0.006; 0.15
CA on UT	3.1	5.5	0.021; 0.53
CO on UT	2.7	4.5	0.023; 0.58

EXPERIMENTAL RESULTS AND DISCUSSION

Concrete Length Change in Various Environments

Expansion data for C1293-Humid testing are shown in Figure 10 and Figure 11. Expansions from specimens associated with each of the aggregate sources were negligible and all values of percent increase reported were below 0.02%. Since these specimens lacked the artificial alkali addition of NaOH, this result is perhaps not surprising. As such, it does not appear that any significance can be attached to the small differences in these values. It is interesting that the exchangeable alkalis in the clay microfines were not capable of triggering the ASR reactions, especially in the cases of CO and WY microfines with high values of "Na2O equivalent" above 1.25%. The pozzolanic character of some of these microfines (especially those with the higher content of Na2O equivalent) may have mitigated the ASR. Another possibility is that some of these alkali cations were exchanged with the calcium in the tap water during the extraction process of the microfines.

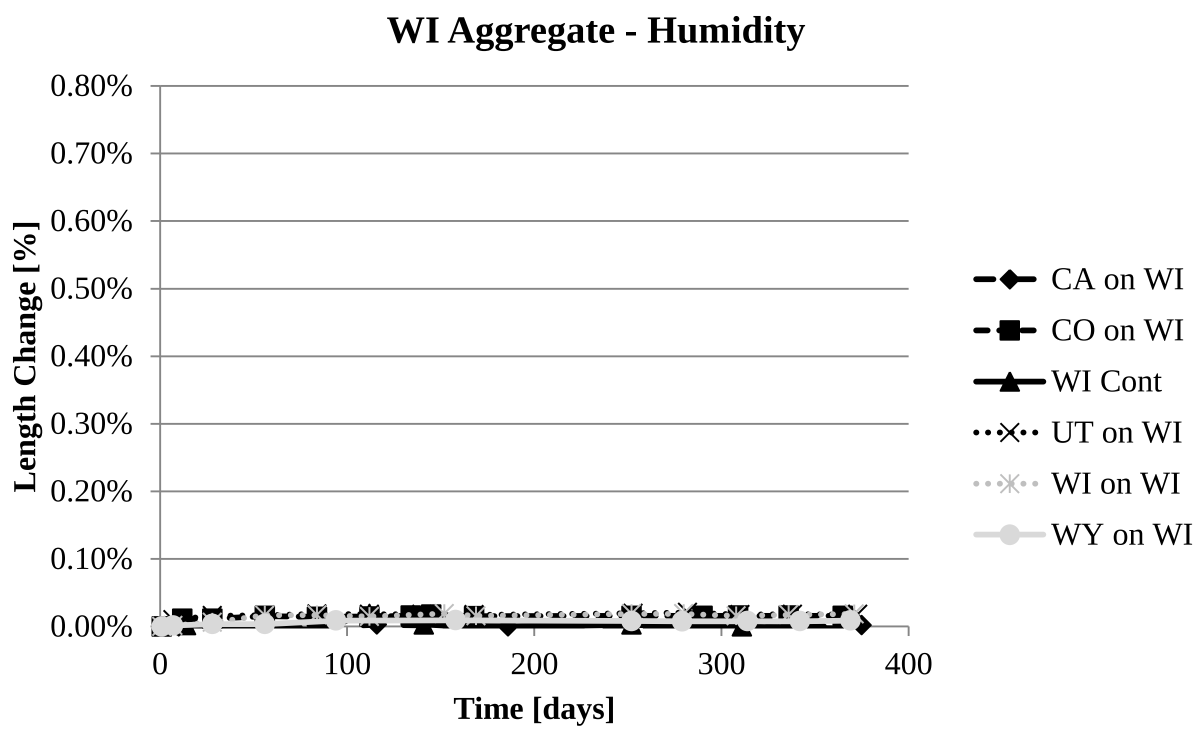

Figure 10 – Length change for C1293-Humid specimens based on Wisconsin aggregate.

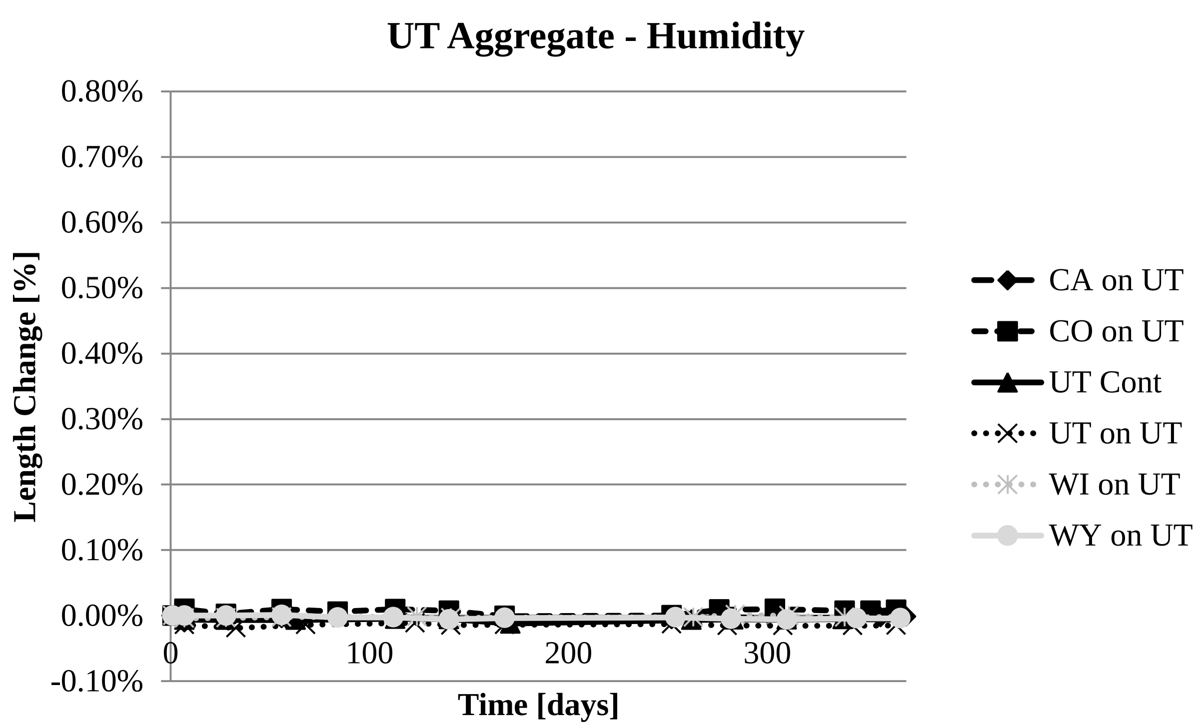

Figure 11 – Length change for C1293-Humid specimens based on Utah aggregate.

Expansion data measured from C1293-Deicer testing are shown in Figure 12 and Figure 13. In the presence of deicer, the expansions become large for those specimens containing microfines composed of 2:1 phyllosilicates. Specimens containing CA, CO, or WY microfines tended to show the largest expansions with both the Wisconsin aggregate and the Utah aggregate. Expansions of specimens with the Utah aggregate tended to be higher than those with the Wisconsin aggregate. Images of the concrete beams from C1293 testing after 1 year can be seen in Figure 14. The cracking seen clearly indicates the specimens exposed to the dicer suffered distress. The concrete has incurred cracking in a map pattern, and it seems there are deposits lining the cracks. This is more evident when UT aggregate was used and CA, CO, and WY microfines. However, expansion did occur in the Wisconsin aggregate specimens despite their unreactive nature. This result is an indication that ASR is not the only degradation mechanism in this C1293-Deicer test.

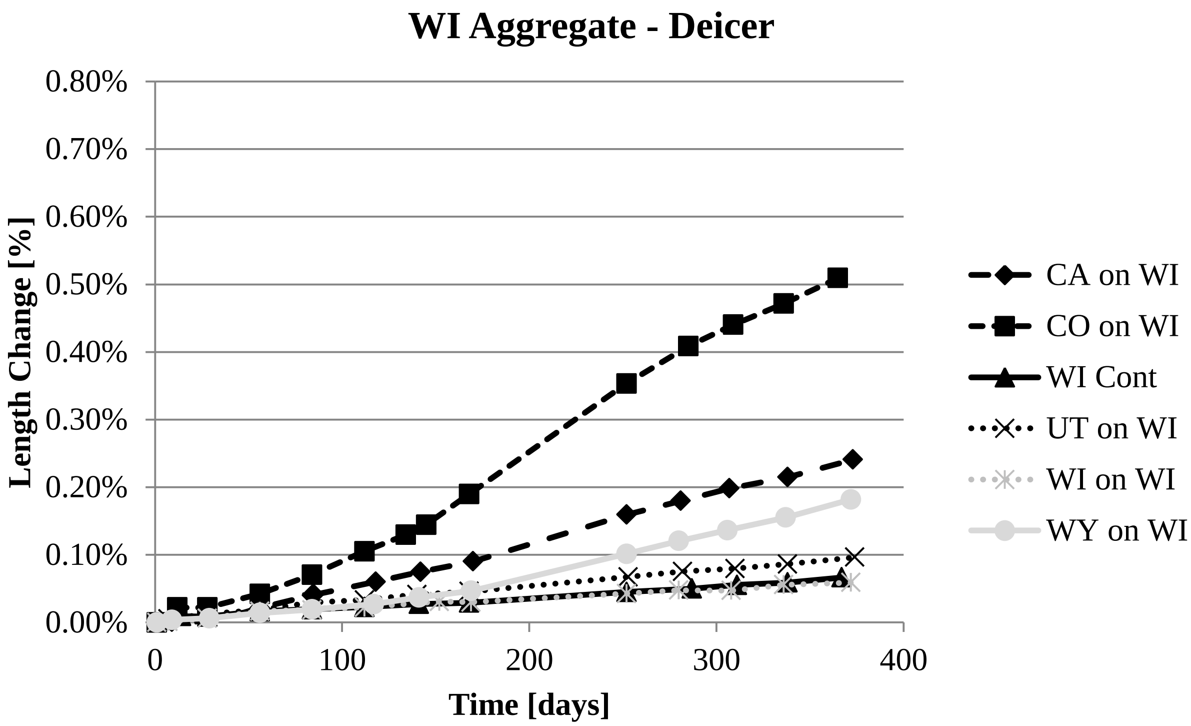

Figure 12 – Length change for C1293-Deicer specimens based on Wisconsin aggregate.

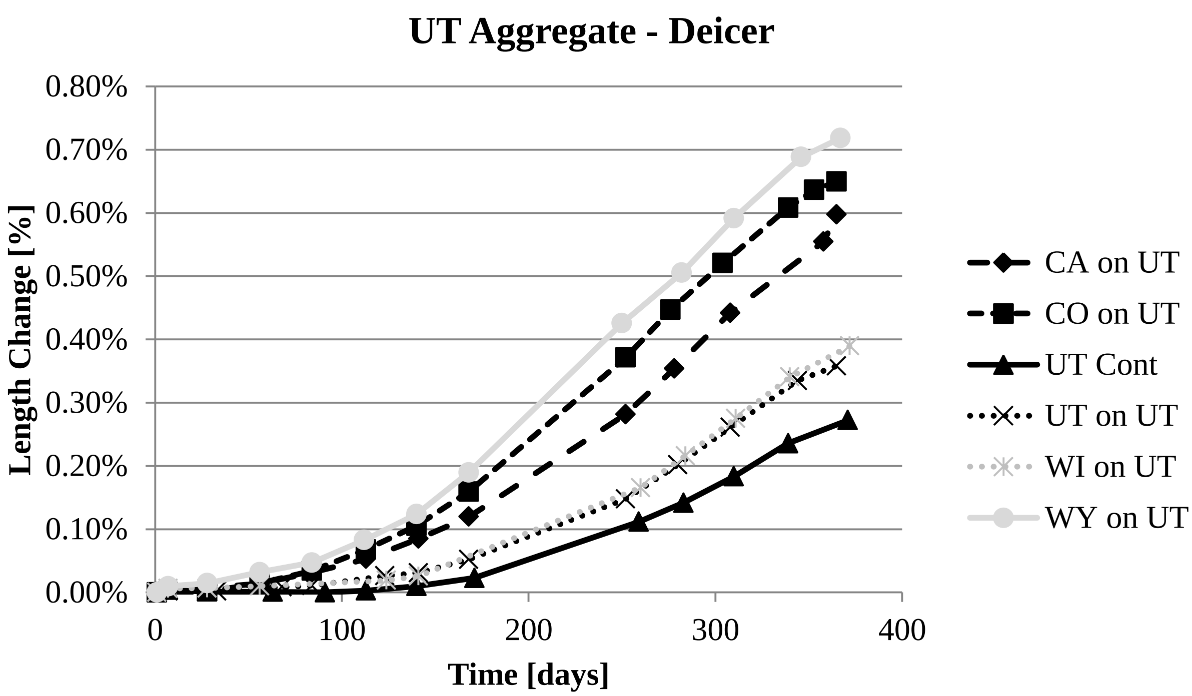

Figure 13 – Length change for C1293-Deicer specimens based on Utah aggregate.

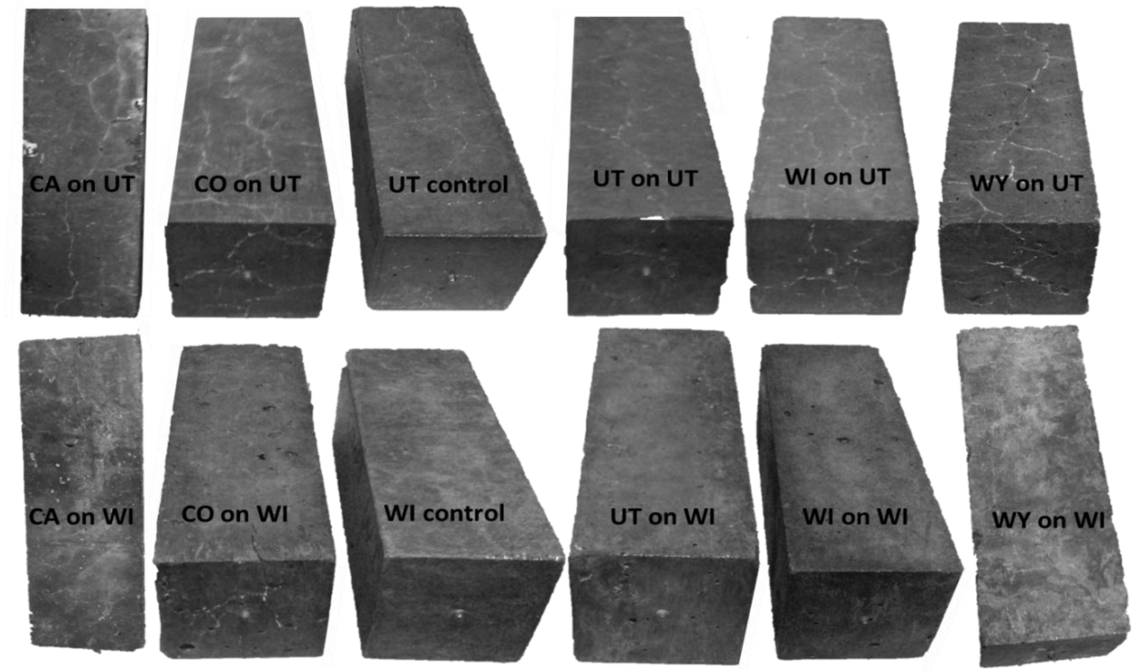

Figure 14 – Degradation of concrete incorporating microfines and submersed in KAc Deicer at 80°C for 1 year.

As mentioned all modified C1293 tests excluded the addition of NaOH typically associated with the ASTM C1293 procedure. In order to gain insight into the possible influence of this intentional omission, a series of modified ASTM C1260 tests were conducted. The results of these tests are shown in Figure 15 (utilizing Wisconsin fine aggregate) and Figure 16 (utilizing Utah fine aggregate). The C1260 results were primarily distinguished by the base aggregate source such that the Utah aggregate specimens showed much larger expansions than those associated with the Wisconsin aggregate. Within a base aggregate set, the largest expansions occurred with the washed control specimens while the microfines appeared to mitigate the expansions. Different behavior was noted between the C1293-Deicer expansions and those of the C1260 tests. In fact, the microfines that provoked the most severe expansions in the C1293-Deicer testing caused the least expansions in the C1260 testing. The presence of microfines, especially those with pozzolanic character (containing clay minerals) contributed to the mitigation of the ASR expansion on the C1260. As reported by Ichikawa, homogeneous mixing of a sufficient amount of very fine siliceous materials in concrete inhibits the ASR by absorbing Ca^{2+} ions for the rim formation.[14]

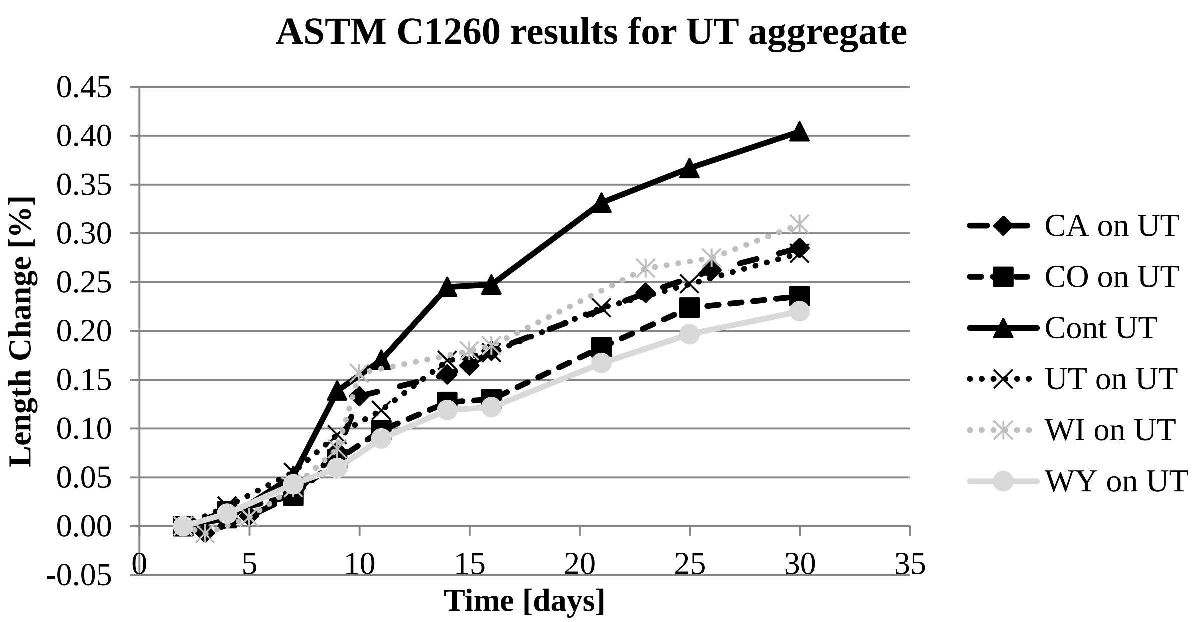

Figure 15 – Modified ASTM C1260 expansion for specimens containing Wisconsin fine aggregate different sources of microfines.

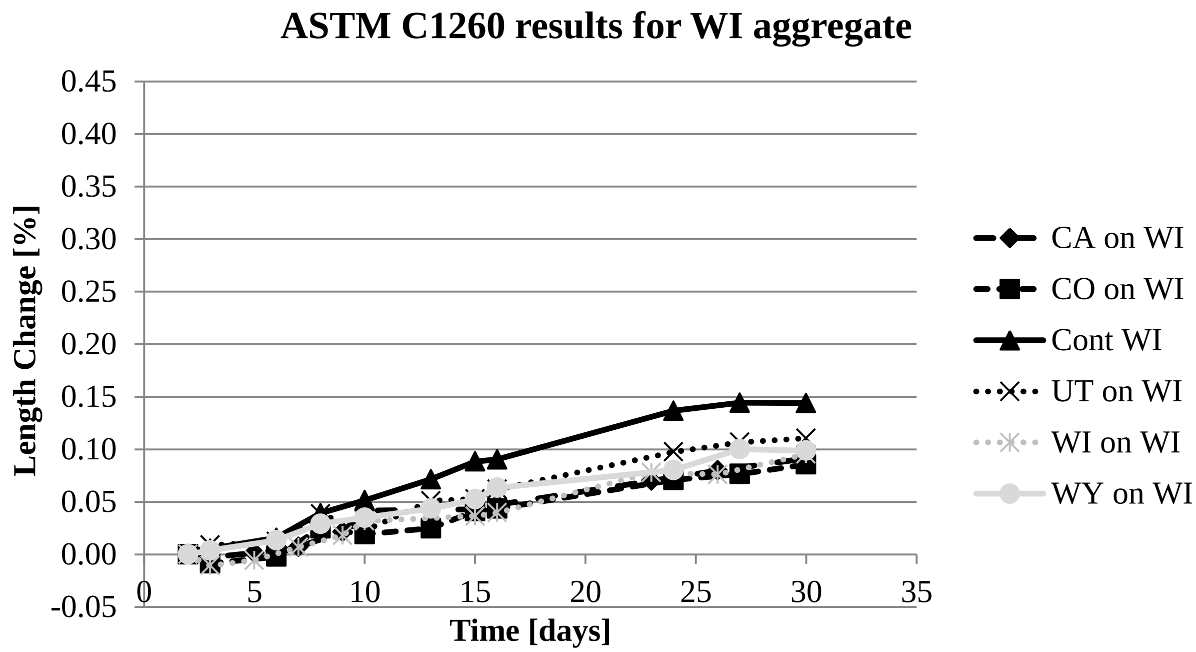

Figure 16 – Modified ASTM C1260 expansions for specimens containing Utah fine aggregate and different sources of microfines.

Freeze-Thaw Durability

The modified ASTM C666 test included measures after every 60 cycles including weight, dimensions, and transverse fundamental frequencies in order to track physical changes and the dynamic elastic moduli. The relative elastic moduli at 300 cycles are shown in Figure 17 and Figure 18 for the Wisconsin and Utah aggregates respectively versus the air content of the corresponding concrete batches. Because of an error made in measuring the initial transverse frequencies, a correction was made to the data such that the relative elastic moduli at 300 cycles are accurate to ± 5%. This correction does not impact the main findings of these tests. As shown in Figure 17 and Figure 18, the degradations at 300 cycles tend to correlate strongly to the level of air content. As indicated earlier, the resulting air content was greatly impacted by the type and amount of microfines in the mix. Weight loss data for increasing freeze-thaw exposure are shown in Figure 19 and Figure 20. These weight loss trends are similar to the relative elastic modulus trends.

The order of the specimen degradation from the largest to the smallest is comparable in the two sets of specimens. The no-microfines controls and the specimens with the Wisconsin microfines degraded the least while Colorado-microfine specimens degraded the fastest followed by the California-microfine specimens. It is interesting to note that the order of freeze-thaw degrade while consistent amongst the two data sets is not identical to the order of C1293-Deicer expansions. However, the similarities within the C666 data and the C1293-Deicer data, suggests that microfines (at these levels) may have a greater influence in durability than the aggregate type.

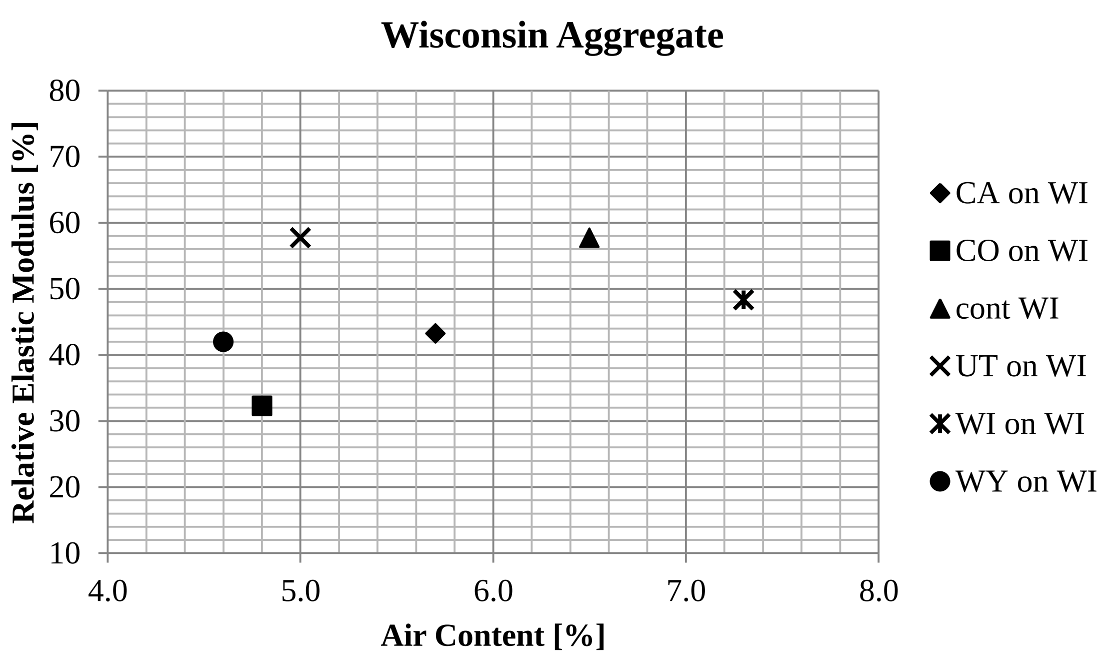

Figure 17 – Relative dynamic modulus for specimens containing Wisconsin aggregate and subject to the modified ASTM C666 protocol versus the corresponding air content.

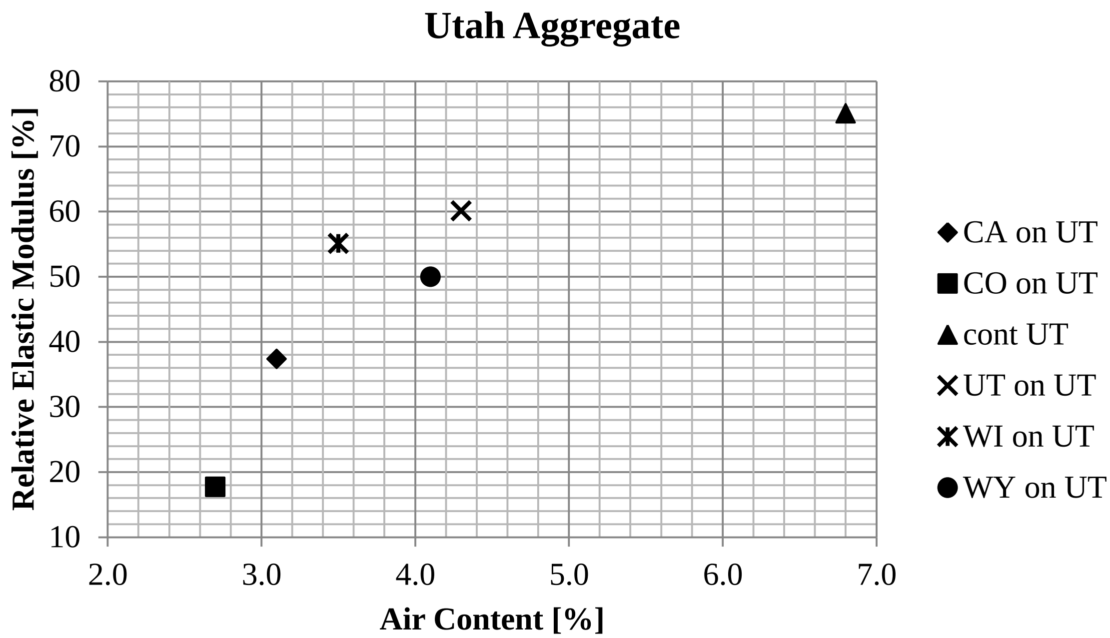

Figure 18 – Relative dynamic modulus for specimens containing Utah aggregate and subject to the modified ASTM C666 protocol versus the corresponding air content.

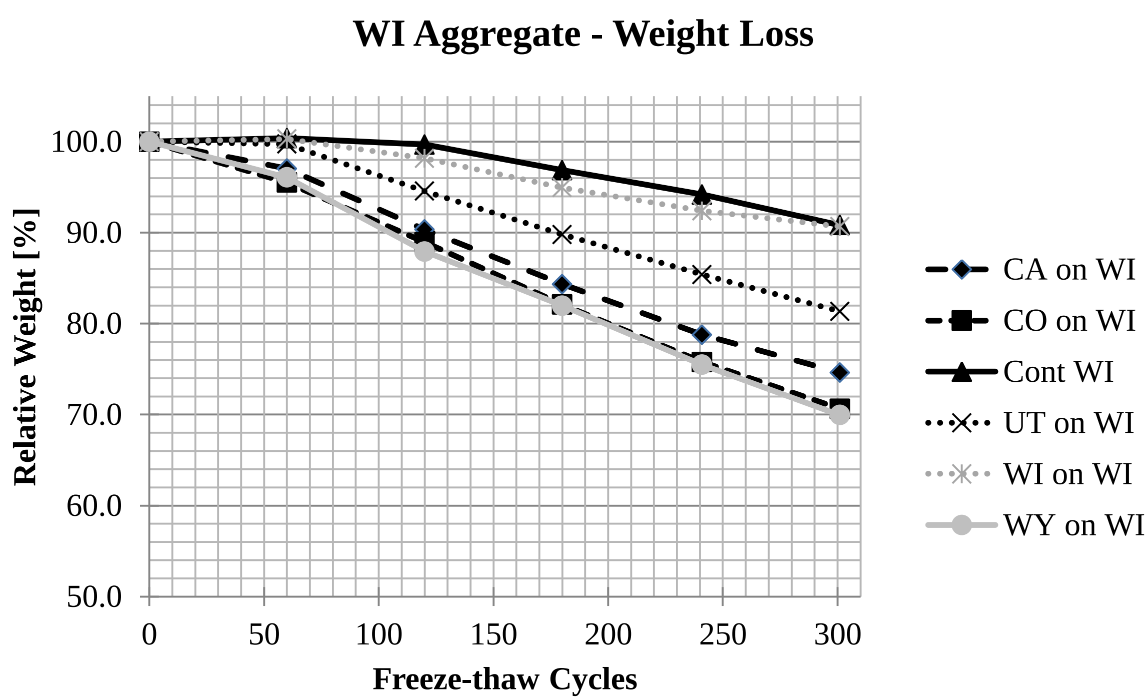

Figure 19 – Relative weight loss of Wisconsin aggregate specimens with freeze-thaw cycles.

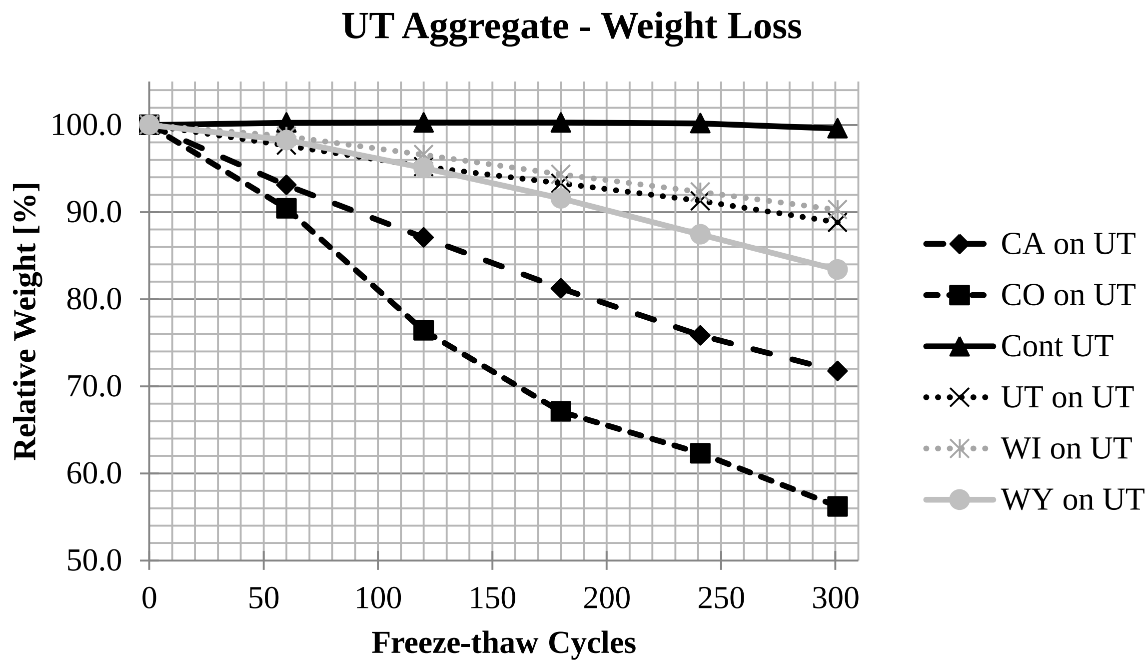

Figure 20 – Relative weight loss of Utah aggregate specimens with freeze-thaw cycles.

CONCLUSIONS

Microfines in quantities used in this research can cause slump loss and render air entrainment admixtures ineffective during concrete mixing. However, assuming those problems can be overcome without compromising the mix, the hardened concrete performed satisfactorily in the absence of potassium acetate deicer exposure. Potassium acetate deicer does induce some expansion and paste degradation even in concrete specimens that do not contain microfines; however, these degradations are not to a level that identifies them as clearly harmful. Previous studies have analyzed the effects of various deicer solutions on concrete material. Our study agrees with Wang et al. that concrete subjected to potassium acetate based solution without additions of microfines caused relatively low expansions and weight changes.[15]

When microfines are present in the concrete specimens and the specimens are exposed to potassium acetate deicer, dramatic deterioration was observed in the form of expansions and reduced freeze-thaw durability. These deteriorations traced in consistent order of severity according to the source microfine present. Microfines with stronger phyllosilicate presence tended to cause the most severe deteriorations. Some microfines in the presence of potassium acetate deicer cause expansions after one year that were 4 to 8 times larger than the control (no microfines present). Expansions were larger with the reactive Utah base aggregate compared to the unreactive Wisconsin base aggregate. However, certain microfines in the presence of potassium acetate deicer caused large expansions even in those containing unreactive Wisconsin aggregate. In modified ASTM C1260 testing of mortar containing the two fine aggregate sources and the different microfines, the microfines actually decreased the expansions. The greatest reduction in expansion in the modified C1260 tests occurred with the microfines that caused the greatest expansions in the modified C1293 tests.

The modified ASTM C666 test protocol with potassium acetate deicer exposure proved to be considerably more severe than the standard C666 test procedure in water. Again, the presence of microfines caused deteriorations whereby relative elastic moduli were 2 to 4 times lower and relative weight losses were 2 to 4 times higher in specimens containing certain microfines as compared to controls (no microfines). Deterioration levels correlated with reduced air contents so it was not immediately evident whether or not these deteriorations were caused by the reduced air contents in those specimens or a more direct degradation from the combined potassium acetate deicer-microfine presence or both.

Considering of all the test data and an examination of the specimens, one concludes that both mechanisms likely contributed to the freeze-thaw deterioration.

ACKNOWLEDGMENTS

The authors would like to thank and acknowledge the Innovative Pavement Research Foundation (IPRF) for their financial support on IPRF Project #01-G-002-06-5 and the project advisory board for their counsel. The authors would also like to recognize Jake Effinger and Ruipeng Li, two graduate students whom aided in concrete mixing and data collection of this research.

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Chapter 4

Chemical Responses to the Interaction of Natural Microfines and Potassium Acetate Deicers

CONCRETE MICROSTRUCTURAL RESPONSES TO THE INTERACTION OF NATURAL MICROFINES AND POTASSIUM ACETATE BASED DEICER

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ABSTRACT

This study investigates the chemical interactions and microstructural changes natural microfines induce in concrete laboratory specimens subjected to potassium acetate deicer. Microfines (material smaller than 75 µm) from 5 aggregate sources around the US were characterized and methodically added to concrete. Microscopy and petrographic testing was conducted with the goal of determining why the combination of the microfines and deicer cause expansion and deterioration of concrete. Microfines containing a high content of phyllosilicates showed the greatest impact on the concrete structure when exposed to potassium acetate deicers. In all cases, formations of potassium sulfate were found in

abundance throughout the system. Alkali-silica gel was not found to be the major form of deterioration although the degradation mechanism mimicked these effects.

Keywords: concrete microstructure; deicer; microfines; ASR; potassium sulfate.

1. INTRODUCTION

Airfield pavements that have been exposed to potassium acetate deicer (KAc Deicer) and containing a high amount of microfines have been linked to deterioration resembling the alkali silica reaction (ASR). (Jack Scott, NWFAA – Personal Communication and Jim Lafrenz, IPRF – Personal Communication). The “dirty aggregates” used in the pavements are acknowledged as aggregates coated with a layer of microfines (particle size smaller than 75 µm). It is generally recognized that, during the mixing of concrete, a layer of microfines that coat the aggregates can totally or partially detach from the aggregate and enter the bulk region of the mortar or remain attached to the surface of the aggregate and form a part of the interfacial transition zone (ITZ) [1]. Based on location, one can imagine two different scenarios by which microfine coatings may affect the quality of concrete; one by changing the chemistry and/or microstructural properties of the mortar, and the other by disrupting the bond between the aggregate and the cement paste [1-3].

Naturally occurring microfines typically exist as stone dust, clay particles, or calcium carbonate [2, 4]. It has been shown that the mineralogy of the material will dictate the changes that may occur within the concrete. [1, 5-8] On one hand, the microfines when mixed with KAc Deicer could in fact induce the ASR as reported. Particularly, Krøyer et al. [9] demonstrated that the presence of blends of kaolin and bentonite induced changes in the calcium silicate hydrate (CSH) structure in cement pastes. Furthermore, Grattan-Bellew [10] claims that when certain types of alkali-bearing clays (such as illites) are present within the matrix of certain rock types, these clays can potentially dissolve upon exposure to alkaline solutions to further augment the alkali levels in the concrete, and thus the potential for developing the ASR process. On the other hand, the microfines could be participating in some other reaction mechanism responsible for the reported deterioration as ASR was not experimentally confirmed in each airfield. In either case, the current purpose of this research was to determine if and how KAc Deicer and microfines interact to cause early deterioration found in pavements.

The overall objective here has been to determine the role that microfines play in the development of concrete deterioration when exposed to potassium acetate deicers. The research involves work predominantly in the laboratory aimed at: 1) determining the potential for deterioration of concrete in the presence of KAc Deicer in the absence and presence of mineral fines; and 2) developing an understanding of the mechanism by which microfines affect the microstructure and hydration products in concrete with fines introduced as coatings on aggregates (“dirty aggregates”). By investigating the deterioration mechanism, mitigation techniques could be more successfully implemented in order to avoid future occurrences of deterioration.

2. MATERIALS AND METHODS

Five different sources of natural microfines were combined with either a reactive or nonreactive aggregate to study a total of twelve combinations of materials. Each of the various combinations can be found in Table 26. Concrete and mortar specimens were formed and subjected to various environments and then analyzed by various means in order to characterize the possible reactions occurring between the microfines and chemical solutions to which they were subjected.

Table 26. Coarse aggregate and microfine material combinations used for test specimens.

Specimen Type	Aggregate type	Aggregate source	Microfine Source					
			CA	CO	UT	WI	WY	control (none)
concrete cylinders	coarse and fine	WI	x	x	x	x	x	x
		UT	x	x	x	x	x	x
mortar cubes	coarse and fine	WI		x	x	x		x
		UT		x	x	x		x
ASTM C1260 mortar bars	fine only	WI	x	x	x	x	x	x
		UT	x	x	x	x	x	x

2.1. Materials

For all specimens in this study, concrete and mortar were made from Type I Portland Cement utilizing two aggregate and five microfine sources. The Type I Portland cement composition is detailed in Table 18 of Chapter 3. The aggregate material came from either Utah or Wisconsin as a known reactive granitic gravel and unreactive dolomitic gravel source respectively. The microfines were extracted from five different aggregate pit-run materials allowing for various mineralogies to be studied in hopes of determining which constituents caused the greatest effect on concrete when exposed to the KAc Deicer. The composition of the microfine material was characterized through the use of X-ray diffraction (XRD) and Thermogravimetric analysis (TG) and the outcomes are summarized in Table 19 of Chapter 3. [11] The concrete and mortar poured in the laboratory from these materials were then subjected to various environments with primary emphasis on the KAc Deicer which consisted of 50% by weight potassium acetate solution in water with a corrosion inhibitor. In the concrete specimens only, one multi component synthetic air entraining agent was employed.

The microfines were extracted from their original pit-run source material in either a washing manner or from dry sieving. In order to make a representative microfine coating, the microfines were recombined in a ratio that matched the original extracted ratio as seen in Table 20 of Chapter 3. From the collected microfines, the “dirty aggregates” were manufactured by submersing, as received washed, dry aggregate in mixtures of water and microfines. Approximately 1.5% ±0.1% (by coarse aggregate weight) microfines adhered to both unreactive Wisconsin (WI) aggregate and reactive Utah (UT) aggregate. The total quantity of microfines consisted of the aggregate coating and additional microfines added to the fine material. (An additional 3.5% based on total aggregate weight was added to the fine material.) Additionally, the microfines naturally incorporated in the plant washed coarse aggregate, was not removed for practical reasons. The Wisconsin fine aggregate contained 0.8% microfines by weight and 1.7% for the Utah fine aggregate.

2.2. Specimens

There were three specimen types incorporated in this study, 1) concrete cylinders, 2) mortar cubes, and 3) modified ASTM C1260 specimens. Concrete specimens were prepared to assess the impact of the microfines in concrete exposed and unexposed to potassium acetate commercial pavement deicer. The concrete mix design is described in Table 21 of Chapter 3. Even with large additions of air entraining agent, there was expected difficulty in achieving the target air content. However, one agent was used for all concrete cylinder specimens with addition levels recorded in Table 27. A total of 24 concrete cylinders measuring four inches in diameter and eight inches in length were formed from the various microfine/aggregate combinations and subjected to two environments. The parameters of the concrete specimens are found in Table 27. One set of each of the twelve combinations of materials were subjected either to high humidity at 80°C or submersed in KAc Deicer solution at 80°C.

Table 27. Mix parameters associated with concrete specimen preparation.

Mix	Adhered Fines [% CA wt]	Total Added Microfines [% total aggregate wt]	Total Added Microfines [% FA wt]	Slump [in.]	Fresh Air Content [%]	ounces AEA per 100 lbs cement
CA on WI	1.6	4.5	11.9	0.75	6.1	3.80
CO on WI	1.5	4.4	11.7	0.375	5.2	4.93
cont WI	0.0	0.0	0.0	9.5	6.9	0.47
WI on WI	1.3	4.3	11.4	2	7.7	0.76
UT on WI	1.4	4.4	11.6	4.5	5.4	1.90
WY on WI	1.5	4.4	11.7	0.75	5.0	3.04
CA on UT	1.4	4.4	11.6	0.25	3.6	4.93
CO on UT	1.4	4.3	11.6	0	3.2	5.69
cont UT	0.0	0.0	0.0	6.25	7.3	0.47
WI on UT	1.3	4.3	11.4	1.25	4.0	0.76
UT on UT	1.5	4.4	11.7	3	4.8	2.66
WY on UT	1.3	4.3	11.4	0.25	4.6	7.59

The mortar cube specimens measured 2x2x2-inch with two ¾-inch microfine-coated stones embedded. Microfines were not added to the bulk of these specimens as in the concrete specimens leaving the total microfine content only that which adhered to the aggregate. Three of the microfine sources underwent testing (see matrix of samples in Table 26) with both types of aggregates; in one cube two non-reactive (Wisconsin) stones and in a second cube two ASR reactive (Utah) stones. Both stones from each cube were coated with microfines except in the case of the control. A depiction of the cubes is displayed in Figure 21. The three microfines were selected based on their unique characteristics. Mortar was mixed in the ratio of 2:1 sand:cement, and 0.45 w/c with no air entraining admixture. The mortar was mixed and poured in two even layers. At each layer, one coated aggregate piece was placed into position. The cubes were cured under wet burlap for 24 hours, submersed in one of three solutions and brought to a temperature of 38ºC or 80ºC. The solutions were 1) water, 2) solution of 0.8M sodium hydroxide (NaOH) and 5M potassium acetate, and 3) 5M potassium acetate. The microstructure of the stone-cement paste interface was analyzed at 4 days and 56 days after casting.

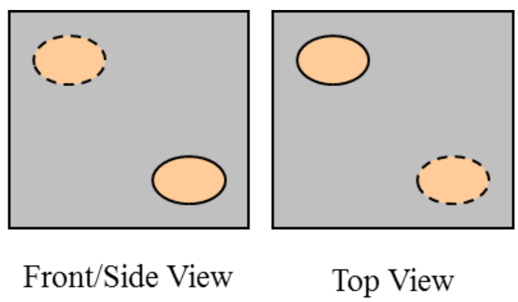


Figure 21. Schematic view of the 2x2x2 in. cement paste cubes with embedded aggregates

Lastly, the modified ASTM C1260 specimens were created according to the standard with the exception of the microfine content. Microfines were added in the same proportion as the concrete specimens (11.6% of the fine aggregate weight) in addition to the required material as identified in the standard. All microfine and aggregate source combinations were evaluated with these specimens as noted in Table 26.

2.3. Methods

The objective of the study was to prepare concrete and mortar specimens containing microfines and evaluate their micro-scale performance under a variety of chemical environments. The objective was tested using two methods. One method utilized concrete to determine if reaction products were found when the microfines act as aggregate coatings and nucleation sites for interactions with KAc Deicer. The second method utilized mortar in order to test a wider variety of conditions than possible with concrete. This mortar was used to determine if differences occurred when ASR was induced by using more standard reaction chemistry for comparison with the naturally occurring reactions in airport pavements represented by the concrete subjected to KAc Deicer. Microstructural alterations were sought in order to determine the reaction mechanisms responsible for deterioration. In this part of the study we tried to resolve the reaction products and associate them with ASR or other reactions. We also searched for damage in the concrete microstructure as a consequence of the presence of both microfines and deicers such as: depletion of $Ca(OH)_2$ concrete reservoirs and/or dissolution of ettringite or monosulfate. Primarily SEM/EDS and petrographic techniques were used in this investigation.

In both the concrete and mortar cube specimens, microfines were placed on the aggregate surface as a coating that concentrated microfines in the ITZ. In this research, the distance from the ITZ starts from the rock surface and moves outward towards the cement bulk. Typically the ITZ is referred to as a distance approximately 40μm to 50μm from the rock surface. [12] In contrast, microfines were dispersed in the bulk of the concrete cylinders and the modified C1260 specimens.

The analysis of the microfine-enfused concrete also included examining the specimen for the presence of hydrated alkali silica gel. As previously presented in this research, the microfines can act as the vehicle for introducing fine materials of diverse mineralogy into concrete. Microfines were a potential source of silica and also alkaline metals, the most important components in the ASR-type reactions. Consideration was given to forming alkali silicates and the appearance of new solid phases that developed. For example, the formation of silicates of the amphibolite family (e.g. tremolite: $Ca_2Mg_5Si_8O_{22}(OH)_2.2H_2O$) by transforming sediments rich in dolomite and quartz has been widely reported. [13] Although, these silicates are not exactly hydrated alkali silicates (ASR products), the slow transformation of well crystalline phases, quartz and dolomite, into a single phase of different density and morphology could well be a very disruptive phenomenon in the microstructure of set concrete.

2.3.1. SEM Analysis

The following procedure was used to prepare the concrete SEM specimens. SEM specimens from concrete were prepared in the same way as the specimens from mortar with the exception of timing and the area of extraction. At 3, 6, and 9 months, a ½-inch thick slice was cut from the concrete specimen. The slice was taken after a ½-inch top layer was removed by wet saw. An aggregate and paste area was selected less than one inch from the outer edge of the cylinder where possible. This area was selected because a previous study found the average deicer penetration to be approximately ¾ to 1 inch in airport pavements. [14] In contrast to concrete specimens, mortar cube specimens were cut at 4 and 56 days from the corner known to contain the aggregate. Lastly, a square cross section was taken from the C1260 test at the conclusion of the data collection period. The SEM samples were processed in a similar manner to that of Muñoz et al. (2010) and Balachandran. [14, 15] The samples were cut and placed in acetone for 5 minutes then dried. The samples were then vacuum-impregnated with Buehler 2 part epoxy. The impregnated specimens were cut using a Buehler lapidary saw with propylene glycol. Afterwards, they were lapped and polished on a Buehler Ecomet 4 Polisher using a series of lapping paper at 330, 400, 600, and 1000 grit, and finishing with 0.05µm micro polish. At this point, each specimen was coated with a thin layer of gold for 80 seconds at 20mV using a Denton Vacuum Desk II sputter coater/etch unit. Each of the samples was examined using a LEO 1530 Scanning Electron Microscope (SEM) in the back scattering electron (BSE) mode using an acceleration voltage of 15 kV.

In order to isolate the impact of microfines in the concrete, this research progressed from examining the simplest to the most complex case. Uncoated aggregate and the microfines were individually studied with the help of SEM and EDS back scattering images. After the base materials were analyzed, concrete specimens exposed to humidity were assessed.

Lastly, the specimens subjected to the KAc Deicer were analyzed. Following the concrete analysis, the mortar examination was conducted in a similar fashion. This allowed us to compare observations from one situation to the next. By using the BSE images and the molar ratios, components in the matrix were identified. When analyzing the concrete containing microfines, the microstructure of standard concrete was used as the baseline for comparison. Calcium silica hydrate (CSH), calcium hydroxide (CH), ettringite, monosulfate, AFm and ADT phases, and hydrogarnet are all normally occurring hydration products. Each of these products can be identified by EDS using the molar ratios of the elements in the analysis. For example, CSH, is associated with a Si/Ca ratio ranging from 0.45 to 0.5 while unhydrated particles of alite have a Ca/Si ratio approximately between 2.5 and 3.

2.3.2. Petrographic analysis

The petrographic analysis was conducted under the supervision of James Schmitt of Schmitt Technical Services. Standard petrographic protocols were followed. [16, 17] Thin sections were created from the concrete samples that were submersed in KAc Deicer after 12 months. Thin section polished surfaces were generated by lapping the concrete with Buehler lapidary papers in the grits of 220, 320, 400, 600, and 1000, ending with a 0.5µm micro polish like the SEM samples. Thin specimens were created with the use of a Buehler Petro Thin® – Thin Sectioning System. Evaluation was made possible by the use of a cross polarizing light microscope with magnification capabilities of 50 to 400x. Using cross polarized light allowed one to identify constituents by assessing birefringence patterns.

Under cross polarized and plain polarized light such things as aggregate type, relic cement grains, crystalline calcium hydroxide, ettringite, and gel material could be identified. [17]

The petrographic analysis included an evaluation of the sulfur content by two methods. X-ray fluorescence (XRF) was conducted to measure elemental sulfur and its oxide form SO_3. AASHTO T290-95 Method A (Standard Method of Test for Determining Water-Soluble Sulfate Ion Content in Soils) was followed to measure the soluble sulfur in SO_4^- form. Both were run according to standard protocol to determine if the microfines contained large amounts of sulfur components.

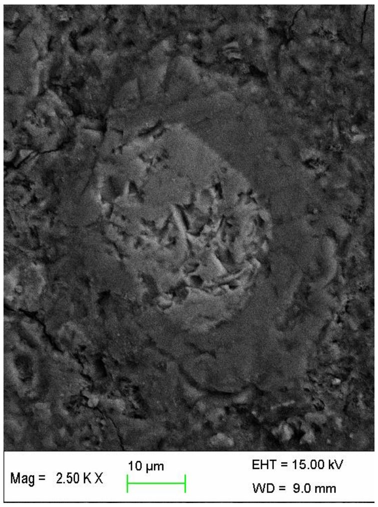
3. RESULTS AND DISCUSSION

From the analysis of the concrete cylinders subjected to high temperatures and humidity, it was found that minimal deterioration occurred in the specimens. In comparison, deterioration unquestionably occurred in the concrete specimens subjected to high temperatures and KAc Deicer.

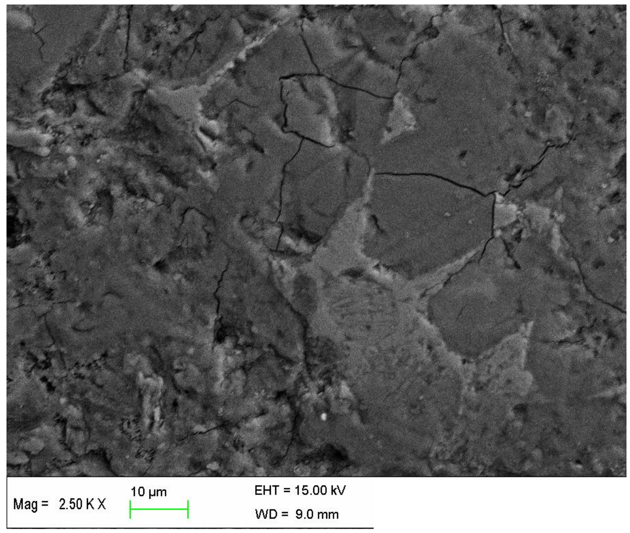
3.1. Results from Scanning Electron Microscopy/Energy-dispersive X-ray Spectroscopy (SEM/EDS)

The SEM analysis identified normal cement components and dense ITZs in concrete specimens subjected to high temperatures and humidity. This established a control baseline of expected microstructure features. Table 28 shows some examples of expected concrete formations present in the specimens.

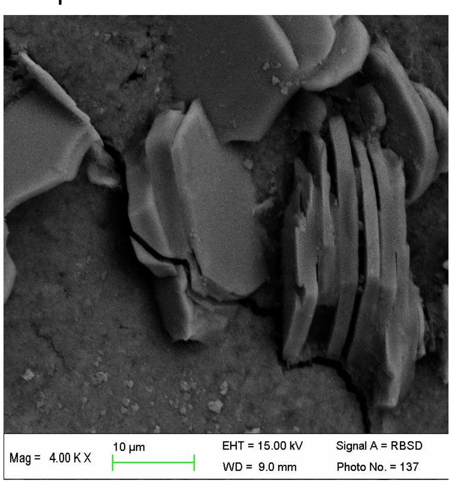
Table 28. Expected cement and hydrated cement compounds



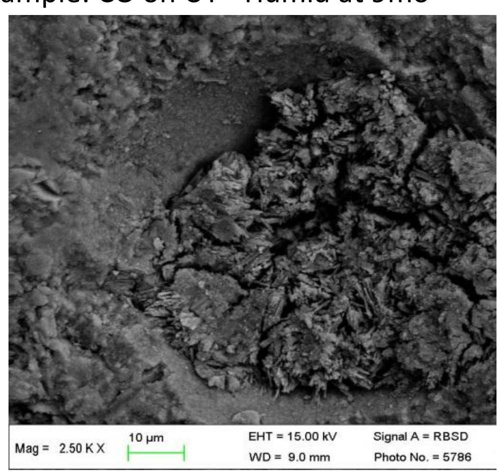
alite cement particle
formula: $3CaO\ SiO_2$
reaction rim Ca/Si = 1.7
unhydrated center Ca/Si = 2.7
sample: CO on UT - Humid at 9mo



belite cement particle
formula: $2CaO\ SiO_2$
reaction rim Ca/Si = 1.7
unhydrated center Ca/Si = 2
sample: CO on UT - Humid at 9mo



calcium hydroxide
formula: $Ca(OH)_2$
Ca/O = 1
sample: WI on UT - Humid at 6mo



ettringite
formula: $3CaO\ Al2O3\ 3CaSO_4\ 32H_2O$
Ca/Al = 2.8; Ca/S = 3.4
sample: CO on WI – Deicer at 3mo

In concrete cylinder specimens subjected to KAc Deicer at elevated temperatures, deterioration of the paste was detected. Deterioration was visually indicated by raveling and increased porosity in later stages of testing. Extreme deterioration of the ITZ was also observed and in most cases the bond between the aggregate and the paste was completely destroyed (see Figure 22).

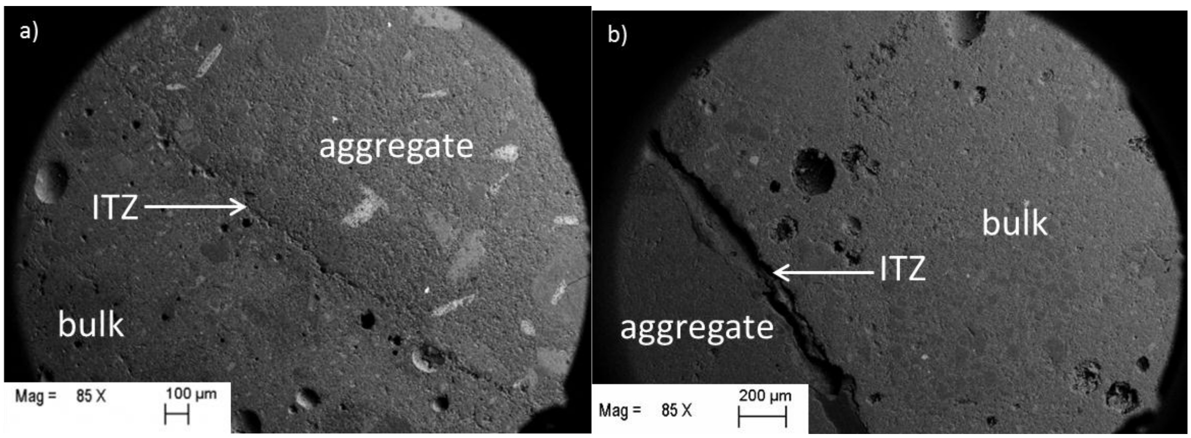


Figure 22. Images showing the deterioration of the ITZ over time; a) WY on UT Humid 3mo b) WY on UT Deicer 9mo

Beyond visual deterioration of the concrete, large areas composed of potassium sulfate crystals (molecular formula K_2SO_4 abbreviated KS) were observed in the ITZ of many of the KAc Deicer treated specimens (Figure 23 and Figure 24). By immersing the fresh concrete specimens (after 24 hours of curing) into the KAc Deicer, penetration was relatively unimpeded as compared to more mature concretes. To understand the observed formation of new products identified as potassium sulfate (KS) complexes, the source of sulfate and its transformation needed to be identified. Typically the sulfate originates from gypsum, and potassium originates from the deicer solution (6.4M KAc). The sulfate in gypsum usually transforms to form ettringite in very early stages of concrete hydration, which eventually transforms to monosulfate. Thus, in order to form these potassium sulfate crystals the sulfate must be extracted from ettringite, monosulfate, or microfines. This transformation is expected to prompt a change in the microstructure of the ITZ and to the adhesion of the cement paste to the aggregate. The formation of KS is not the only chemical reaction that can extract sulfates from ettringite; this also happens in the formation of monosulphoaluminate. The formation of the KS also should limit the carbonation of monosulphoaluminate, which leads to the formation of secondary ettringite. In these concretes secondary ettringite was not observed to line the voids and cracks of specimens.

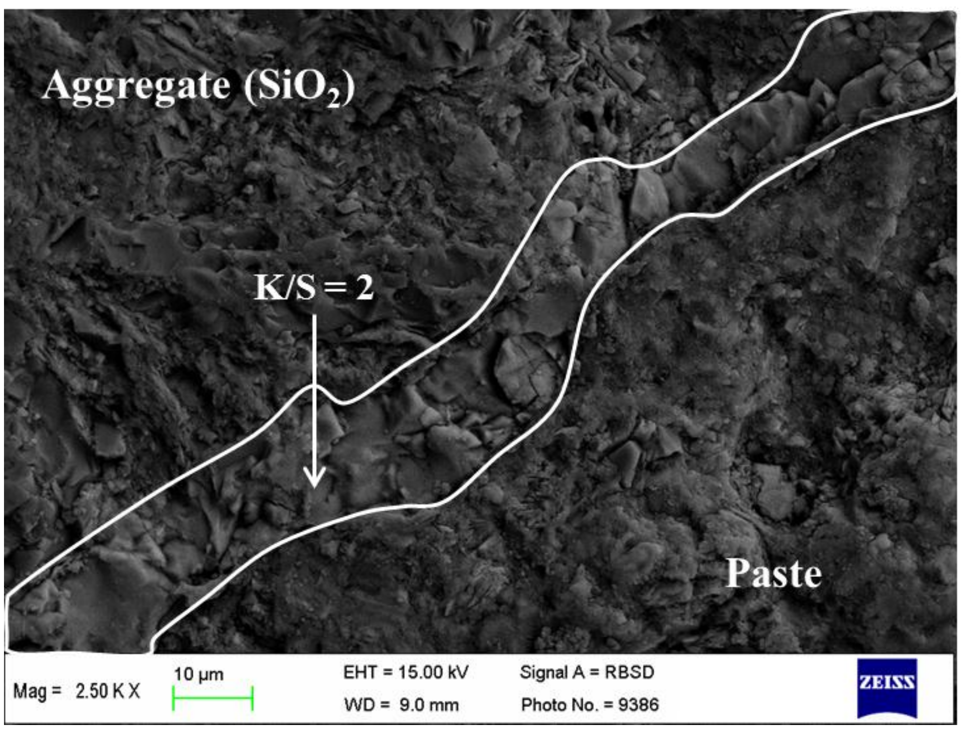


Figure 23. Potassium sulfate complex in CA on UT Deicer specimen after 6 months.

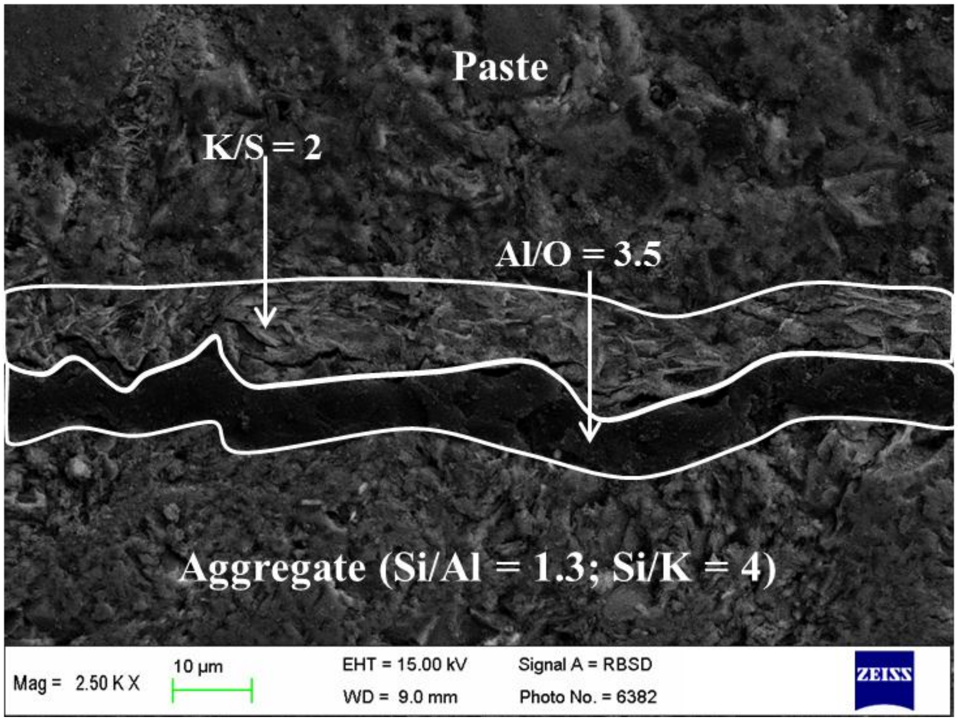


Figure 24. Potassium sulfate complex in CO on UT Deicer specimen after 9 months.

The bulk paste was also examined under SEM, and abundant potassium was observed in the paste. The potassium was further traced to determine if it was paired with the acetate or if it attached itself to some other compound in the bulk matrix. The potassium was observed to exist with varying amounts of carbon and oxygen indicating it may be associated with the acetate. Combinations of Ca, Si, Al, and K in the bulk were clearly observed with the possibility that free potassium ions exist in the pores of the matrix of CSH or CH or the potassium could be combining in at exchangeable sites of the CSH. It is observed that the platy crystals typical of the KS seen in the ITZ are also seen in some cracks and pores of the bulk as in Figure 25.

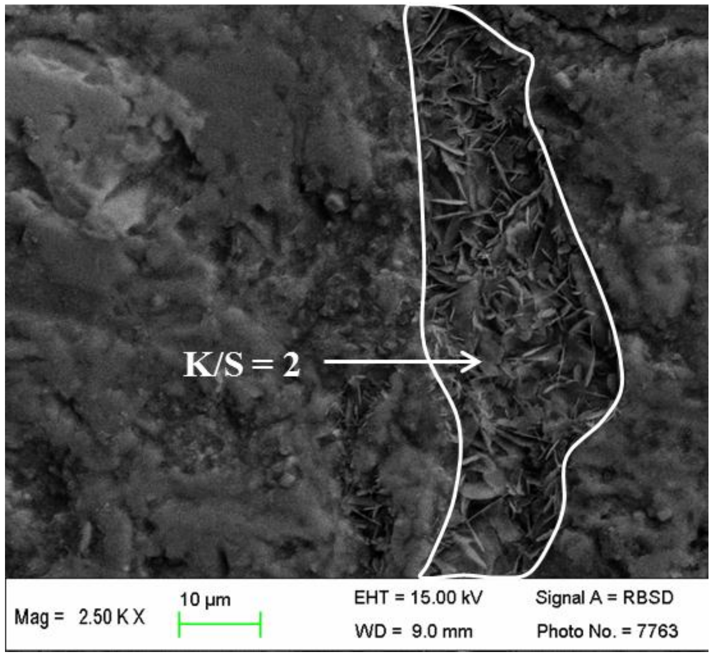


Figure 25. KS complex existing in a void in the bulk.

Thermodynamic simulation using MEDUSA verified that the KS complex gained the sulfur from the ettringite and shows that KS is favored over ettringite and monosulfate. Potassium and sulfate complex formation is favored by increasing pH. Further simulations show that if there are low amounts of potassium, the SO_4^{-2} is free, but if there are high amounts of potassium then KSO_4^- forms. It is important to note that this complex is in solution and not existing as a solid in the form of a crystal. Crystal formation only occurs upon drying or when concentrated. This is important for two reasons, the formation of KS shows the KAc Deicer was chemically attacking the concrete, and the KS formation was not the direct cause of the observed expansions unless dried or concentrated. Additionally, if the normal sulfate bearing compounds are destroyed, the remaining constituents may form other by-product chemical compounds that could cause expansion in the concrete.

Equilibrium diagrams from the MEDUSA predictions indicate that the aluminum ions should be mainly present as a calcium aluminum silicate and/or aluminum hydroxide ($Al(OH)_3$) in a stable phase. The micrograph of Figure 24 shows the presence of a rim of aluminum hydroxide (or oxyhydroxide) particles between the K_2SO_4 crystal formation rim and the aggregate. The simulations also indicate calcium ions should mainly exist as portlandite and calcium aluminum silicates. EDS analysis showed areas in the bulk cement paste that contained peaks in the spectrum of calcium and aluminum. This could be the segregation of the aluminum hydroxide from the ettringite and the calcium forming CSH or portlandite. Areas with the composition of the aluminum calcium silicate predicted by the simulations were also observed in the SEM/EDS analysis. With the introduction of silica from the microfines in the presence of KAc, the system could transform into $Ca_2Al_2Si_3O$ and $CaSiO_2$ or Ca_2SiO_4 (we can see this in the WY on UT deicer specimen.) When $Ca_2Al_2Si_3O$ is formed, the formation of $KAlSiO_3$ as a solid is also predicted from equilibrium diagram simulation when there are low levels of calcium present. This was the case in the UT Control (no microfines) KAc Deicer specimen. The new solid phases could cause expansion as the new formations likely occupy a larger volume than the aggregate. These new formations throughout the system lead to an overall altered paste material which likely differs in properties from normal cement paste.

3.2. Results from Petrographic Analysis

In the petrographic evaluation of the concrete thin-sections, we could find microfines along the aggregate, in the bulk of the concrete, and the porous regions of the concrete as expected and shown in Figure 26. Normal formations of calcium hydroxide were also found in the system. This demonstrates that certain cement hydration products are not likely being attacked as CH is usually the weakest by-product. Also, in general, the paste is not very amorphous. This is important because normally a chemical attack on the paste materials would appear in a petrographic analysis as an amorphous structure and light in color.

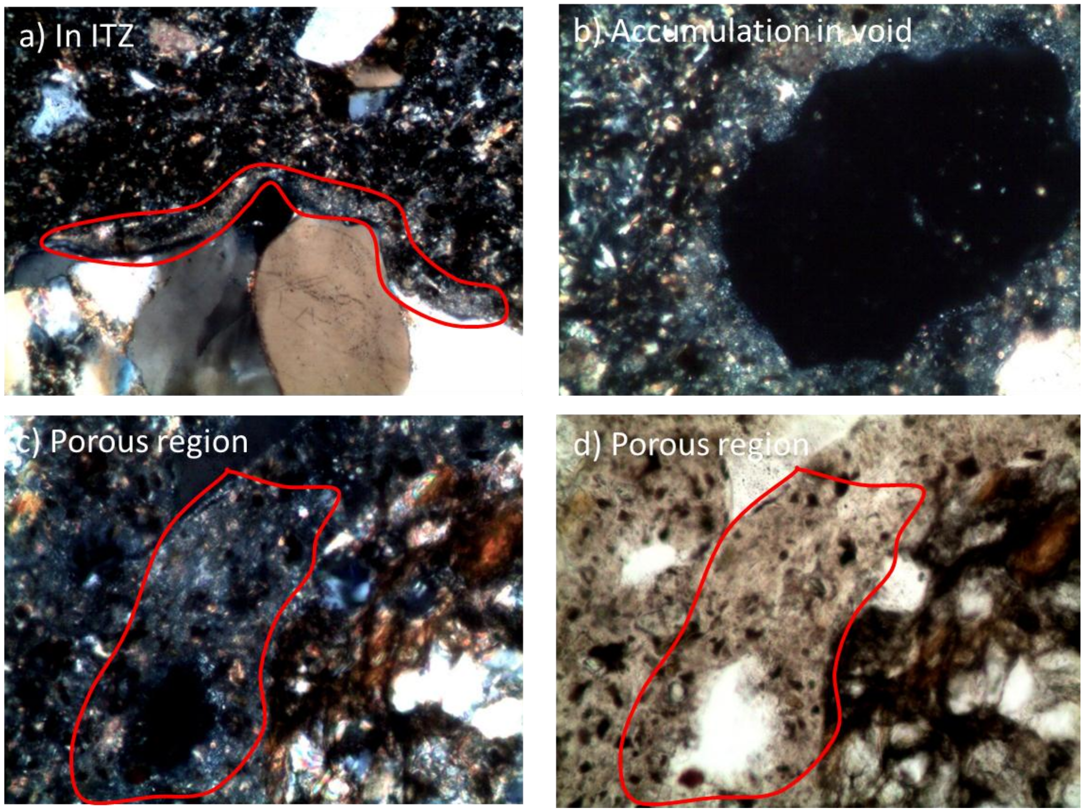


Figure 26. Microfines detected throughout the specimen: a) microfines in the ITZ (aggregate is below the microfines circled in red), b) microfines are seen accumulated around a void, c) microfines are seen in a porous region of the bulk, and d) the same porous region as pictured in c is shown in plain light. (a-c are under cross polarizing light.)

As in SEM, petrographic analysis of the thin sections confirmed potassium based microstructures in overwhelming abundance. The formation was seen in large quantities along the aggregate edges and throughout the paste as depicted in Figure 27. The potassium was identified by its high birefringence pattern and morphology. Upon further evaluation of the samples, we could identify 2 classes of the material, that which projected a high order birefringence pattern and that which displayed a gray pattern. Furthermore, the material was either needle-like in structure or appearing as a platy fiberous format as seen in Figure 28. By examining the specimens, we could determine that the KS material was most concentrated in areas where there were likely accumulations of microfines as indicated by areas of low density, in the ITZ, and in cracks. The formation seems to follow the path of these fines from the aggregate ITZ into the paste or vice versa, possibly following the line of detachment from mixing. This is a predictable location for KS if the KS is extracting sulfur from the microfines. This would appear as a low density region and the new KS material could deposit in place of the microfines. This is also conceivable if the KS is stripping the sulfate from the cement hydration products. From a hydration standpoint, ettringite would be expected to transform into monosulfate, particularly forming in areas containing available water. This normal hydration product would therefore transform into a sulfate-containing material as the normal hydration product is replaced with this new sulfate containing material.

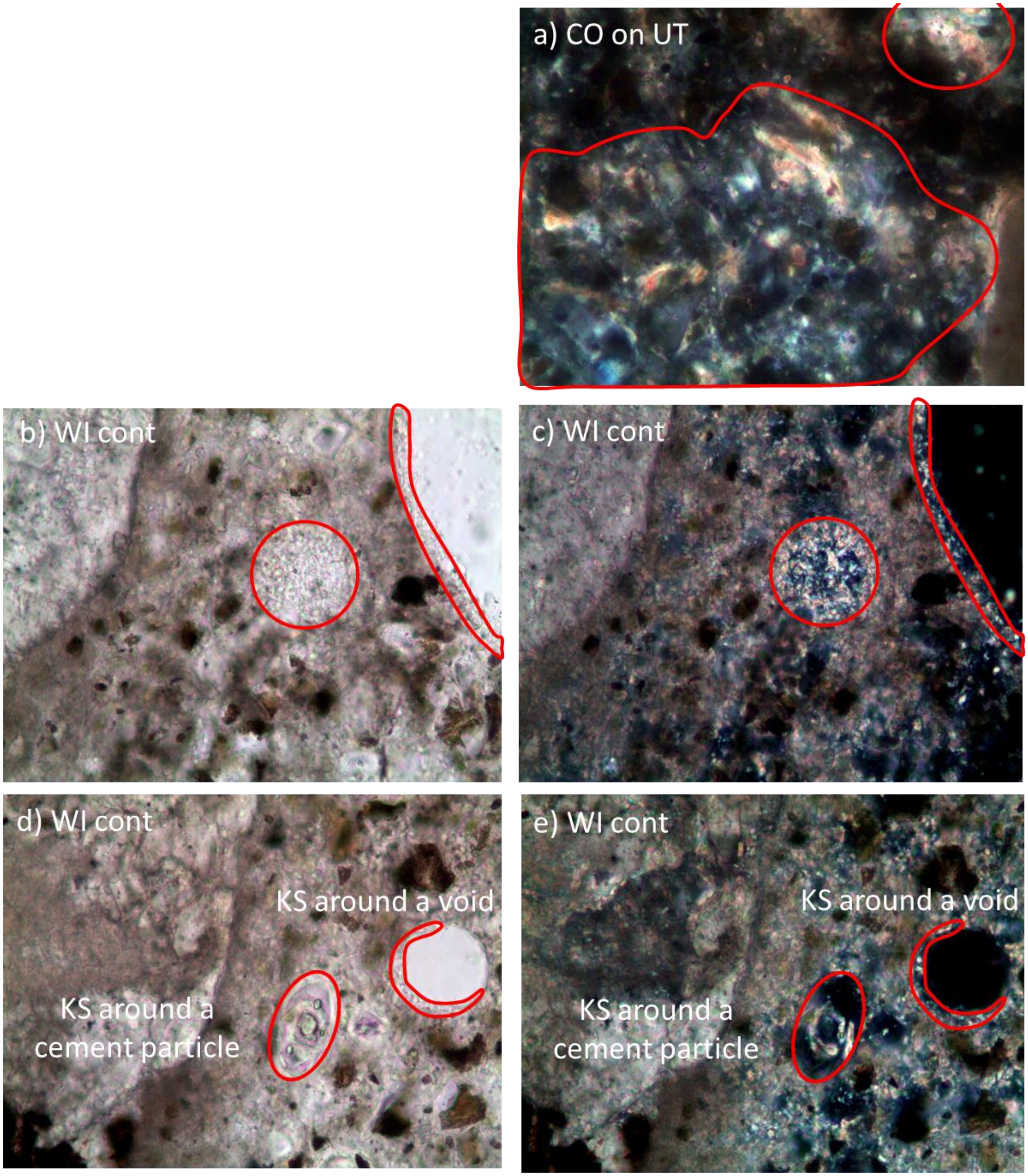


Figure 27. Formations of KS are present throughout the samples: a) KS exists in the bulk, b and c) KS is accumulated in the bulk and in an ITZ, d and e) KS exists around a cement particle and around a void. (a, c, and e are views from cross polarizing light where b and d are views from plain light.)

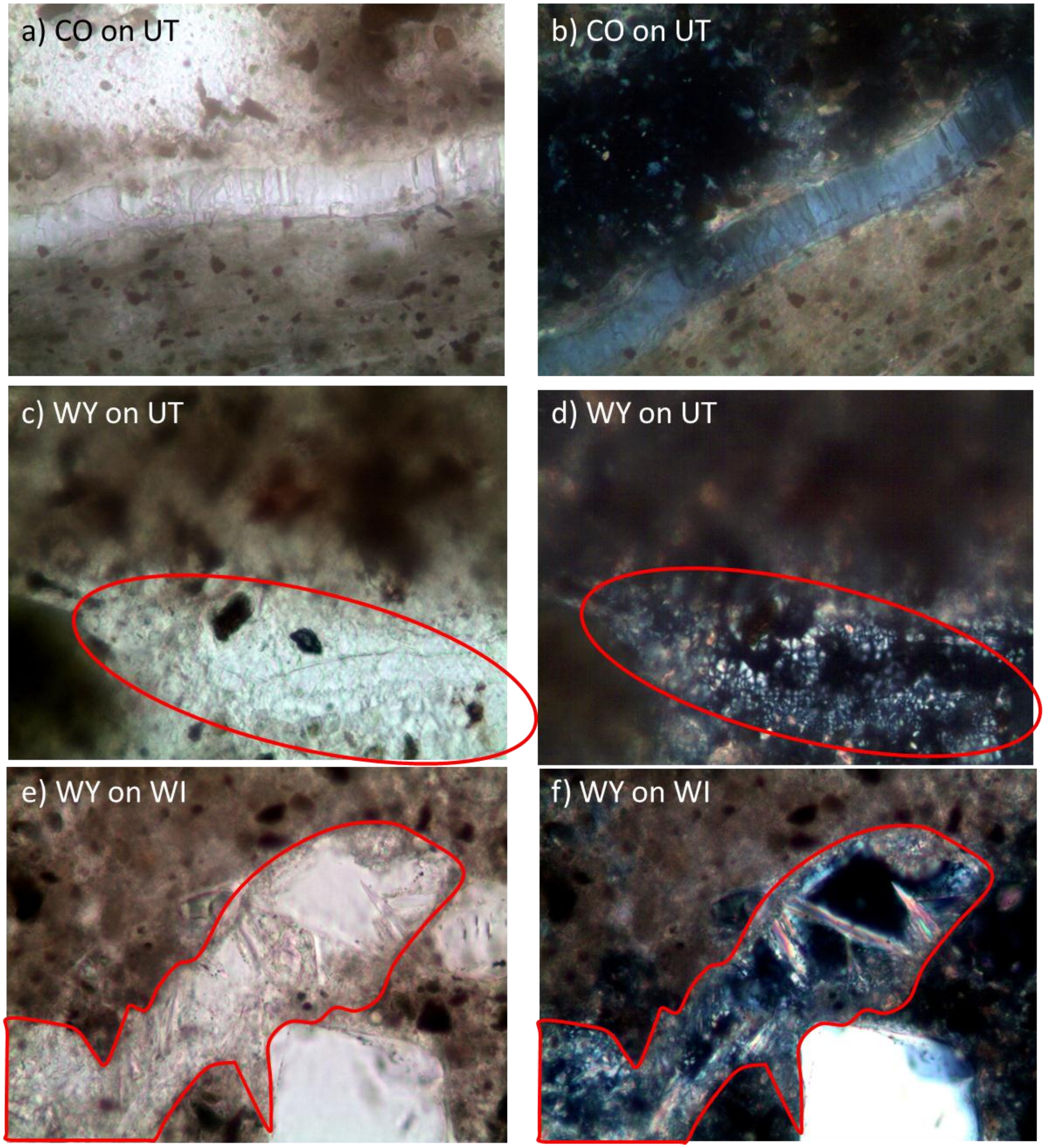


Figure 28. The KS formations are not a gel. The formation has a birefringence pattern indicating its crystal structure. It either exists as a gray structure or emits a high order pattern. Images a and b) show the structure in a ITZ, c and d) show the KS in a bulk void/crack, and e and f show the KS as very crystalline and certainly not a gel.

Results from the petrographic analysis of the sulfate content did not follow the degree of expansion seen in the concrete specimens. Table 29 reports the various forms of sulfur from XRF and AASHTO T 290-6 testing methods. Based on this data set, the quantity of sulfur is not the sole indicator of expansion seen in the concrete or the quantity of sulfur in the microfines would have coincided. Likely, factors exist that dictate the availability of the sulfur to participate in the reactions seen in the concrete studied. It is, however, likely that some sulfur found in the KS formations comes from the microfines.

Table 29. Contents of various forms of sulfur from microfines as tested by XRF and AASHTO T290-95.

	XRF Method		AASHTO T 290-6
Sample	Oxide Content SO_3 [%]	Elemental Content S [%]	Sulfate Ion Content SO_4^- [mg/kg]
CA	0	0	6.847
CO	0.110	0.043	9.047
UT	0.077	0.031	28.842
WI	0.067	0.027	11.952
WY	0.177	0.071	8.134
UT dry*	0.091	0.037	-
UT wet**	0.077	0.031	-
WI dry*	0.059	0.024	-
WI wet**	0.082	0.031	-

Unless indicated, microfines were measured as a mixture of wet and dry extracted microfines as used in concrete

* Microfines separate by sieving only

** Microfines separated by washing only

3.3. Results from the Investigation of Potassium Acetate Penetration

While handling samples for SEM at 3, 6, and 9 months, it was noticed that the specimens saturated with deicer became extremely fragile even at the center of the cylinder. This led to the belief that the KAc Deicer penetration was deeper then 15mm as previously reported. Infrared Spectrometry (IR) was conducted to determine the depth of acetate penetration into the specimens after a period of one year. This test was conducted on concrete samples with the following four microfines and aggregate combinations: CA on UT, CO on UT, WI on WI, and WY on WI. From each specimen, a slice was taken at three inches from the finished cylinder surface. Samples from this slice were taken in at least three locations using a 5/32 hammer drill bit, at incremental intervals from the surface. First, the center was analyzed and then a comparison was taken from the edge to determine if acetates had reached full strength in the core of the piece. If it had not, then pulverized samples were available for analysis heading towards the edge to determine the depth of penetration.

When analyzing the IR spectra results, each spectrum was subtracted from controls which were concrete specimens in a humid environment that had no exposure to deicer, but the same composition. To standardize the intensity, both spectra were normalized with respect to the quantity of concrete seen by the IR by using a peak at 1813 cm^{-1} as it is sharp and independent of the quantity of acetate in the specimens. Subtraction of these spectra rendered a clearer signal for the absorption bands of acetate, otherwise buried under the stronger absorption bands of other species in concrete. The peak at 1578 cm^{-1}, due to the asymmetric stretching of acetate, is compared to determine if acetate had penetrated into the concrete samples and how far.

It was determined that in all cases, the acetate had penetrated to the core of the samples after one year. The method of examination is qualitative and therefore did not allow a precise measure of the quantity of acetates that had penetrated. It was also deduced that the acetate in the system is likely complexed with calcium. It should be recognized that the specimens were subjected to constant soaking in KAc Deicer after only 24 hours after mixing and subjected to heat, so this is an accelerated progression of acetate into the concrete.

3.4. Results of Investigating ASR Deterioration of the Samples

One of the objectives of this research was to determine if potassium acetate deicer and microfines promote ASR. ASR is the combination of silica with alkali ions commonly in the form of calcium silicate with sodium and potassium ions. In the concrete systems studied in this research, silicates are readily available from some of the aggregates and all of the microfines. There is also silica in the system from the paste although it is more difficult to liberate the Si from hydrated particles in the form of CSH. Thermodynamically, the silica from the aggregates will be soluble silicates in high concentrations at a pH of 12.5 and higher. The CSH will not be destroyed until the pH rises above 13.5 where in the silica becomes $SiO_2(OH)_2^{-2}$. The alkali ions originate from the microfines, or the pore water with counter ions as hydroxide or in this case could be as acetate. The conditions of the concrete exposed to the KAc Deicer are thus favorable to ASR. Gels containing silica, calcium, potassium, and sodium would be indicators of this reaction.

Figure 29 shows various possible gels seen in the KAc Deicer concrete specimens. The structures are composed of Ca, Si, and K. The data shows there was potential for ASR and some species resembled this type of reaction. Typical deterioration would be visible as distressed aggregates and gel expanding into the paste. However, these indicators of distress were not observed in our research specimens. Conditions were favorable for ASR and some ASR was present. However, from the SEM analysis of the specimens subjected to deicer only, we feel that the ASR reaction was not a significant cause of deterioration in concrete subjected to KAc Deicer exposure.

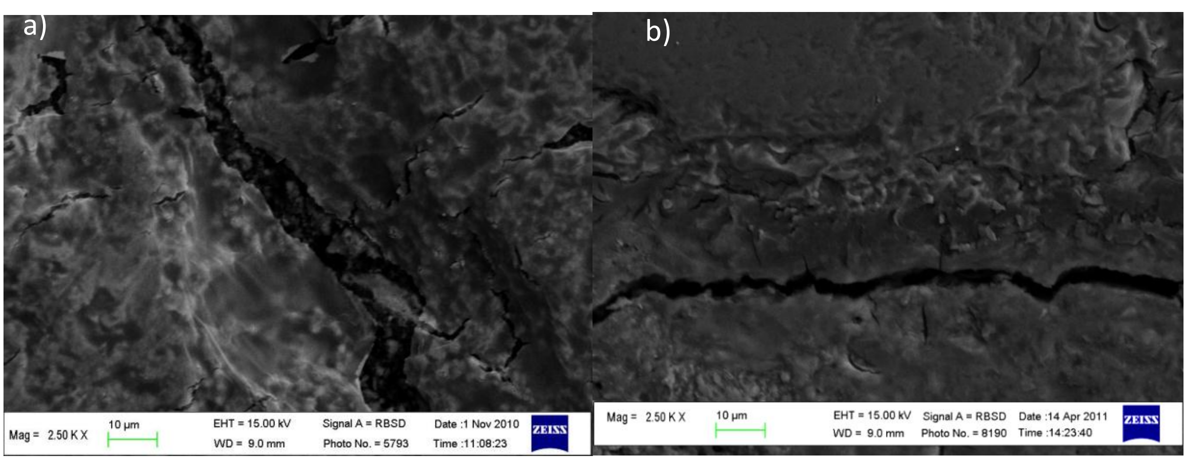


Figure 29. a) A sheety, gel material, composed primarily of calcium and silica, found in the CO on WI Deicer species after 3mo, and b) gel material, composed primarily of calcium and potassium, found in the UT control deicer species after 9mo.

The two-inch cubes of mortar containing two coated coarse aggregate pieces were also evaluated for ASR. This testing protocol had a high potential for ASR as the various submersions included NaOH, a known ASR inducer. When the hydroxide is free and migrating in the pore solution, it will deteriorate the aggregate or any mineral containing silica. As a result, sodium and potassium ions will combine with free calcium and silica in the pore solution to form a gel.

In the mortar specimens subjected to NaOH and KAc, a formation of a potassium silicate was observed. Some thermodynamic simulations were conducted to determine why potassium silicate was present here and not in the samples with only KAc Deicer. It was found NaOH provided a more basic condition than in the case of the KAc only. This means the aggregates and microfines were being attacked to a greater degree thereby freeing more silica than when only subjected to KAc. Thermodynamically there could be three solid phases, $Si_3Al_1K_1O_8$, $K_1Al_1Si_2O_6$, and SiO_2 and these phases were all observed in these samples. When the cubes were subjected to only KAc, they produced similar results to the concrete in KAc Deicer. When the mortar cubes were subjected to both KAc and NaOH, the NaOH overwhelmed the system producing different results then with only KAc Deicer.

Lastly, parts of the modified ASTM C1260 specimens were analyzed under SEM. In this case, where only NaOH was present as a soak solution, different compounds were seen which were more characteristic of ASR reactions particularly in the samples containing the reactive Utah fine aggregate. Unlike the samples from concrete cylinders soaking in KAc Deicer, a gel composed of Si, Na, and Ca was found despite the source of microfines. See Figure 30 displaying the gel in the matrix of the UT on UT specimen.

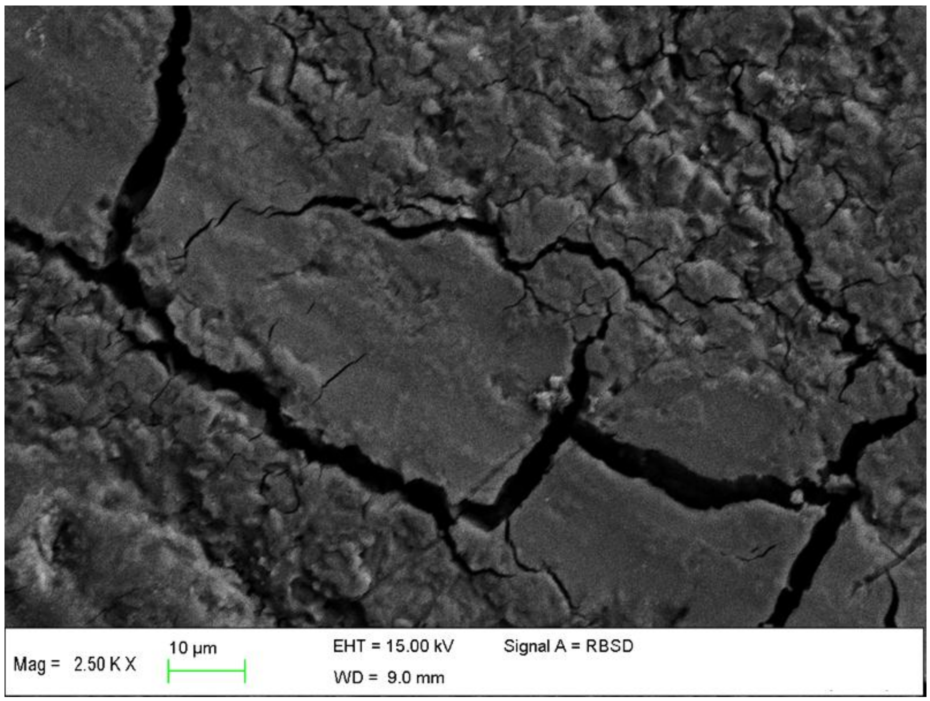


Figure 30. Gel in UT on UT mortar ASTM C1260 specimen exposed to NaOH which has a composition of alkali silica gel consisting of Si, Na, and Ca.

ASR gel was also not found to be prevalent in the petrographic examination. The material lining the cracks of the matrix was not seen to fill the aggregate cracks and spew into the bulk area typically seen in ASR reactions. There were small amounts of gel found in one case, but not in quantities or in a pattern indicating major deterioration through an ASR mechanism. (See Figure 31 showing one occurrence of a gel in the CO on UT specimen).

Also, the KS material was seen in one case to be in an aggregate, but was in a cleavage line so was not likely causing major alkali aggregate deterioration. See Figure 32.

Figure 31. Plane light image of a rare gel structure in bulk of concrete CO on UT specimen.

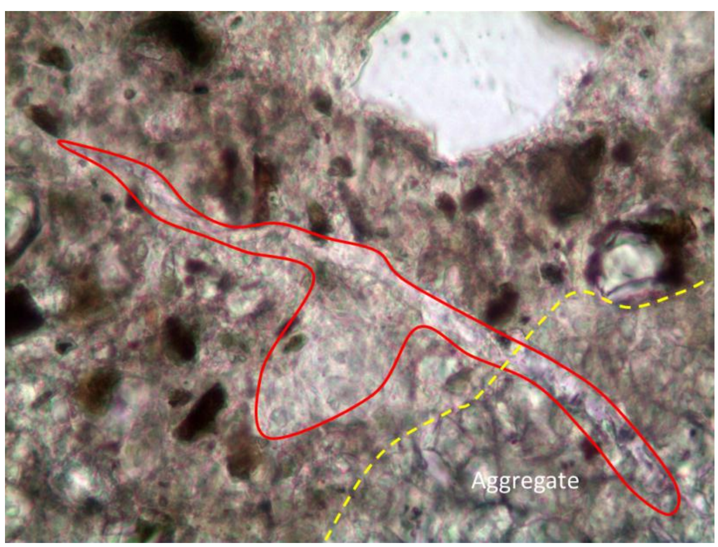


Figure 32. Plane light image of a rare finding of the KS material within an aggregate cleavage line and a bulk concrete crack of a WY on WI deicer specimen.

3.5. Results of Expansion Observations

The chemical degradation discussion has been centered on the formation of new mineral phases in the form of large crystals including K_2SO_4. Expansion can occur from the precipitation of various salts when the pore water becomes concentrated upon drying. It may be that the molar volumes of the new phases are larger than that of the parents or the pore volume. With this in mind, the pore water in these specimens had a high ionic strength. This condition further alters the solubility of species normally found in the cement paste.

Expansion data collected from the concrete submersed in KAc Deicer indicated that specimens containing different microfines and different aggregates expand in distinguishable amounts. This leads us to believe that the microfines and aggregates react with the potassium acetate or the concrete distinctly. As stated before, the specimens that were subjected to the KAc Deicer contained KS. Potassium is most obviously coming from the KAc Deicer while sulfur originates from the cement or microfines. Since KS was present even in the control specimens, the formation of KS was from the cement and likely also due to the presence of microfines as specimens with microfines expanded to a greater degree. Expansions from microfines in concrete not subjected to KAc Deicer did not occur in the one year timeframe of this research. The most likely contribution from the microfines was the introduction of highly reactive silica or sulfates that created new phases in the concrete. While the clays presented the ability of some physical expansion from their individual behavior this was not observed in the humidity specimens and unlikely to be the major contributor to expansions that distinguish the KAc Deicer test results.

4. CONCLUSIONS

A series of microstructural investigations were undertaken on the concrete specimens to determine if any chemical and/or microstructural changes could be associated with the deteriorations reported in the field. Scanning Electron Microscope (SEM) analyses were conducted on concrete specimens that were exposed to 38°C and either humid or KAc Deicer environments. By using SEM, we could better examine the fate of the microfines introduced as coarse aggregate coatings in cured concrete. In addition, this technique allowed us to examine how the microfines reacted with the KAc Deicer in the cement paste. By using SEM back scattering we could image the cement aggregate interface and by employing EDS we could determine the mineralogical makeup of the microstructure. Thermodynamic simulations were used to complement these results. Infrared Spectrometry (IR) analysis was used to establish the penetration levels of the potassium acetate. This allowed us to show that potassium acetate had penetrated to the core in distressed concrete specimens. From this we conclude that distress was associated with the direct presence of the potassium acetate, derivative forms of potassium complexes, and chemical/physical transformations of the microfines.

Based on the microstructure analysis, it was concluded that the potassium acetate causes the structure of the paste to transform and increases the pH by freeing vast quantities of hydroxide. This effect has some similarities to the chemical effect of saturating concrete systems with sodium hydroxide. The potassium appears to transform over the exposure period from potassium acetate to calcium-potassium compounds and finally to potassium sulfate. Large areas of potassium sulfate crystals were observed in the interfacial transition zone (ITZ) in regions where one would expect to see ettringite crystals or monosulfate. The sulfate found in the new potassium sulfate complex was drawn from monosulfate and/or ettringite and likely from the microfines. The increased pH prompted a transformation of silica in the matrix into new species. These changes resulted in degradation and the formation of less dense and larger volume products that appear to be responsible for deterioration and expansion. These reactions were not what are traditionally viewed as an alkali silica reaction (ASR) and they occurred both in specimens containing the unreactive Wisconsin aggregates and in specimens containing the reactive Utah aggregate. Evidence of reaction rims around aggregates was not present, and behaviors observed in C1260 mortar specimens that specifically tested for ASR were significantly different than those observed in the concrete specimens. By examining the C1260 specimens we could detect the presence of alkali silica gel. A small amount of alkali silica gel was found in the concrete specimens submersed in KAc Deicer but not in significant amounts. However, there appears to be similarities to the ASR in that the KAc Deicer promotes the occurrence of highly alkaline solutions that react with the silica and other elements in the microfines. These reactions were not confined to the reactions around the aggregates but occur both around the aggregates where some microfines were concentrated and in dispersed areas throughout the cement matrix where additional quantities of microfines were dispersed. Expansions in the concrete specimens were somewhat larger in the specimens containing the reactive Utah aggregate.

The testing and analysis performed under this study has demonstrated that specific combinations of naturally occurring aggregate microfines and KAc Deicer are deleterious to the durability of Portland cement concrete systems. The degree of distress depended on the mineralogical and chemical nature of the microfines, their quantity, and the degree of penetration of the potassium acetate into the concrete material matrix. The laboratory tests conducted in this research that form these conclusions are likely worst-case scenarios that may not frequently occur in the field. None-the-less, combinations of these materials induce chemical and physical changes that even in field concretes under less severe conditions are likely to take a toll over time. The microfines often included 1:1 and 2:1 phyllosilicates, which in some cases can have positive and negative pozzolanic attributes, and are highly reactive. In addition, it was observed that microfines containing 1:1 and 2:1 phyllosilicates are not easily removed from coarse aggregates during washing. While some microfines are more reactive than others, none examined in this study were considered inert. Microfines fall on a differential scale of likely impact on concrete systems and with some microfines inducing impacts that can be many times greater than that of other microfines present in similar concretes at similar levels.

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Chapter 5

Summary and Conclusions

1. OBJECTIVE

The objective of this research was to identify the roles that aggregate-based microfines may play in the durability of airport concrete exposed to potassium acetate-based deicers. Microfines in this study were defined as those particles below 75 microns ranging to smaller than 10 microns. Particular emphasis was placed on the potential for the alkali silica reaction (ASR) and similar deleterious chemical reactions. In pursuit of this objective, a laboratory study was conducted that examined the nature and chemical reactivity of microfines associated with alluvial deposits of aggregates from select locations across the western half of the United States.

2. MICROFINE CHARACTERIZATION AND REACTIVITY

Microfines were characterized and it was ultimately determined that California and Colorado microfines contained significant quantities of 1:1 and 2:1 phyllosilicates. All sources included significant quantities of silica in various forms and were categorized by their potential to cause deleterious reactions in concrete. Overall, this work showed that the microfines are highly reactive and are likely to impact the hydration process and the microstructure of concrete.

3. MICROFINE AND POTASSIUM ACETATE EFFECTS ON MECHANICAL PROPERTIES OF CONCRETE

Concrete specimens were prepared to assess the impact of the microfines in concrete exposed and unexposed to the potassium acetate commercial pavement deicer. In order to determine the impacts of the microfines and potassium acetate deicer (KAc Deicer), two modified ASTM C1293 length-change protocols and a modified ASTM C666 freeze-thaw durability protocol were followed. In order to distinguish between ASR that maybe forming and other reactions, a comparison test -following ASTM C1260 was performed.

From the concrete specimens prepared, it was determined that microfines in the quantities used caused slump loss and rendered air entrainment admixtures ineffective during concrete mixing. Despite these problems, concrete was cast and it was found that the concrete performed satisfactorily in the absence of KAc Deicer exposure. It should be noted that KAc Deicer does induce some expansion and paste degradation even in concrete specimens that do not contain microfines. However, these degradations are not to a level that one can identify as being harmful. On the contrary, when microfines were present with KAc Deicer, large expansions were measured and deterioration was observed in reduced freeze-thaw durability. These deteriorations traced in consistent order of severity according to the source of microfine present. Microfines with a stronger phyllosilicate presence tended to cause the most severe deteriorations, and, in some cases after one year, expansions were 4 to 8 times larger than the control (no microfines present). As expected, the concrete incorporating the reactive base aggregate incurred larger expansion as compared to the unreactive base aggregate. However, it was the microfine type that was most concerning as certain microfines even in the Wisconsin aggregate specimens caused large expansions in the presence of KAc Deicer.

Based on the modified ASTM C1260 results, the deterioration seen is not likely to be caused by ASR. In modified ASTM C1260 testing, the microfines actually decreased expansions. The greatest reduction in expansion in the modified C1260 tests occurred with the microfines that caused the greatest expansions in the modified C1293 tests. These results indicate a different reaction mechanism than the ASR induced by this test.

In the modified ASTM C666 test protocol with KAc Deicer exposure, again the presence of microfines caused deterioration. In the concrete containing microfines, relative elastic moduli were 2 to 4 times lower and relative weight losses were 2 to 4 times higher as compared to controls (no microfines). Considering all the test data and examination of the specimens, one concludes that both reduced air contents due to the microfines and the KAc Deicer interactions likely contributed to the freeze-thaw deterioration.

Lastly, Infrared Spectrometry (IR) analysis was used to establish the penetration levels of the acetate. The IR spectra analyses revealed that the acetate had penetrated to the core in distressed concrete specimens. From this we conclude that distress was associated with the direct presence of the KAc Deicer, derivative forms of potassium complexes, and chemical/physical transformations of the microfines.

4. MICROSTRUCTURAL INVESTIGATIONS

The microstructure of the concrete was analyzed to determine if the deterioration could be linked to a chemical or microstructural change in the concrete. Based on the microstructure analysis, it was discovered that transformations had occurred likely because vast quantities of hydroxide were being freed causing an increase in pH which in turn affected the bulk matrix. The transformation appears to occur in steps starting as potassium acetate then transforming to calcium-potassium compounds and finally to potassium sulfate. Large areas of potassium sulfate crystals were observed in the interfacial transition zone (ITZ). The sulfate is drawn from monosulfate and/or ettringite and likely somewhat from the microfines as well. The increased pH prompts a transformation of silica in the matrix into new species. These changes result in degradation and the formation of less dense and larger volume products that appear to be responsible for deterioration and expansion.

It was also discovered that these reactions are not what is traditionally viewed as an alkali silica reaction (ASR). The new formations occurred in specimens utilizing the unreactive aggregates and the reactive aggregate. Evidence of reaction rims around aggregates was not present. However, insignificant amounts of the alkali silica gel were found in the modified C1293 specimens. One should note that there appears to be similarities to the ASR in that the KAc Deicer promotes the occurrence of highly alkaline solutions that react with the silica and other elements in the microfines but that these are NOT ASR. These reactions seem to primarily occur where microfines were present, in the ITZ and throughout the paste.

Petrographic analysis confirmed the results found in the SEM analysis. Areas of potassium sulfate crystallization were seen throughout the concrete matrix. A few areas of ASR were detected, but not in the formation likely to cause major expansions. Rather small amounts of the gel were found in the matrix not found to be forcing aggregate cracking. The microfines also underwent testing to determine the levels of various types of sulfur (SO_3^-, SO_4, and S). The levels did not exactly coincide with the expansions seen so either the sulfur is not always accessible to the reaction or other mineralogical components are more important than the direct quantity of sulfur.

5. SUMMARY OF MAJOR FINDINGS

The testing and analysis performed under this study has demonstrated that specific combinations of naturally-occurring aggregate microfines and potassium acetate deicer are deleterious to the durability of Portland cement concrete systems. The degree of distress depended on the mineralogical and chemical nature of the microfines, their quantity, and the degree of penetration by the KAc Deicer into the concrete material matrix. The laboratory tests conducted in this research that form these conclusions are likely worst case scenarios and they may not always occur in the field. None-the-less, combinations of these materials induce chemical and physical changes that even in field concretes with less severe conditions are likely to take a toll over time. While some microfines are more reactive than others, none examined in this study was considered inert.

Combinations of microfines at less than 5% of the total aggregate weight and KAc Deicer exposure caused significant deterioration of concrete that may be mistaken for ASR cracking and expansion. However, our analyses suggest it was not ASR, at least as traditionally diagnosed through the presence of alkali silica gels and reaction rims around aggregates. In summary, the following conclusions were made:

- Expansions in modified ASTM C1293 produced expansions from 0.05% to 0.70% at one year depending on the type of microfine. Expansions of specimens containing microfines but not exposed to KAc Deicer produced negligible expansion.
- Expansions were larger with base aggregate known to be prone to ASR, but significant expansions (up to 0.50% at one year) also occurred in specimens with unreactive aggregates.
- Degradation combined with the reduction in entrained air content led to dramatic loss of freeze-thaw durability. These degradations were associated with specific mineralogical profiles of microfines in the presence of potassium acetate and these profiles consistently were associated with corresponding levels of degradation.
- The KAc Deicer transformed in the concrete pore solutions to form potassium sulfate and calcium-bearing potassium sulfate compounds. During the transformation of the potassium acetate the level of hydroxide increases dramatically in the pore solution and can lead to reformation of silica species released by the microfines and the aggregates. While these reactions do not appear to be the classical alkali silica reaction, they may exhibit some similarity and create an environment where expansion internally within concrete leads to deterioration.