INFLUENCE OF ROCK SALT IMPURITIES ON LIMESTONE AGGREGATE DURABILITY

by

JONATHAN VARNER

B.S., Kansas State University, 2011

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Civil Engineering
College of Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2013

Approved by:

Major Professor
Dr. Kyle Riding

Copyright

Abstract

Some limestone coarse aggregate in concrete pavement can break down under repeated freeze-thaw cycles. Application of rock salt may increase the severity of exposure conditions because of trace compounds, such as calcium sulfate, in rock salt. Subsequently, limestone aggregate in concrete was subjected to freeze-thaw cycling in two methods: salt-treating the aggregate before batching concrete, and half-immersing concrete specimens in rock salt solution during freeze-thaw cycling. Concrete and saw-cut limestone specimens were also subjected to wet-dry cycles in varying salt solutions to examine the influence of trace compounds in rock salt. Freeze-thaw test results indicate that the test methods used were not severe enough to determine if a limestone aggregate was durable or not. The wet-dry testing was also not severe enough to determine the effects of trace compounds in salt solution.

Table of Contents

List of Figures

List of Tables

Acknowledgements

I would like to thank my advisor, Dr. Kyle Riding, for his guidance and support in this project. I would also like to thank Dr. Mustaque Hossain and Dr. Robert Stokes for serving on my advisory committee.

Thanks also to Joshua Welge and other KDOT personnel for providing aggregate samples as well as information on standard procedures such as salt application practices of various districts.

Thanks also to David Berger for aid in modifying the operation of the freeze-thaw machine for freeze-thaw testing.

Thanks also to Ryan Benteman for his aid in troubleshooting various parts of the project.

Thanks also to various graduate and undergraduate students who have assisted at one time or another, including Amir Momeni, Jose Donjuan, Feraidon Ataie and Sean Tomlinson.

Finally, thanks to Tamara Robinson for assistance in copy-editing.

Chapter 1 - Introduction

Background

Concrete pavement can be subjected to cyclic freezing and thawing, often in the presence of deicers compounds used to keep the pavement surface clear for traffic. However, deicers increase the severity of the freeze-thaw exposure conditions. Rock salt, which can contain substances other than sodium chloride, is a common deicer containing impurities that may increase severity of pavement exposure conditions.

These exposure conditions are common in Kansas, causing concrete pavement deterioration, especially if non-durable limestone coarse aggregate is used.

Problem Statement

Certain limestone aggregates in concrete pavement degrade under freeze-thaw action. Deicing salt application increases the severity of exposure conditions and severity may be further increased by the presence of impurities in deicers. Thus, certain limestone aggregates in concrete may degrade with deicer application, causing premature deterioration of concrete pavement.

Objectives

1. Determine if a concrete freeze-thaw test using impure rock salt can separate durable and non-durable limestone aggregates.
2. Determine the effects of impure rock salt on limestone aggregate without freeze-thaw action.
3. Analyze rock salt for the presence of potentially deleterious substances.

Study Method

Various experiments were conducted to examine the influence of rock salt impurities, as summarized in Figure 1.1. Concrete containing limestone aggregate was subjected to two methods of freeze-thaw testing: treating coarse aggregate with impure rock salt prior to casting concrete and half-immersing concrete specimens in impure rock salt during freeze-thaw cycling.

Wet-dry testing of both saw-cut limestone prisms and concrete containing limestone aggregate in impure rock salt was also conducted.

The chemistry of rock salt was studied using inductively coupled plasma analysis and X-ray diffraction. Rock salt samples from individual storage sheds throughout Kansas were analyzed for composition variations.

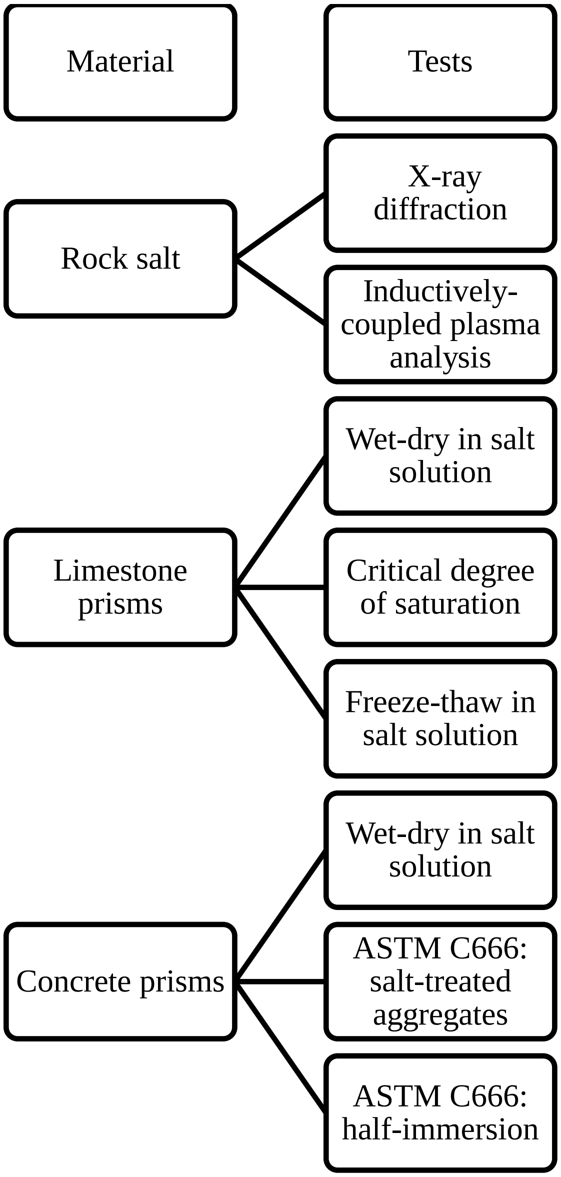

Figure 1.1: Test Method Flow Chart

Chapter 2 - Literature Review

Frost durability of stone for use as concrete aggregate or dimension stone has been extensively studied. Durability is not “an intrinsic property” of the material and depends on the exposure conditions (Pigeon and Pleau 1995).

D-Cracking

The quality of coarse aggregate influences the frost durability of concrete pavement. D-cracking results from the use of frost-susceptible aggregate that degrades under freeze-thaw conditions and damages the surrounding cement paste. Pavement cracks appear on the surface parallel to joints, generally preceded by cracking at the bottom of the slab. The aggregate must be sufficiently saturated with water for damage to occur (Koubaa, Snyder, and Janssen 2002).

Kansas Department of Transportation Practices

The Kansas Department of Transportation (KDOT) extensively uses limestone coarse aggregate in concrete pavement. This practice has led to deterioration of concrete pavement under freeze-thaw conditions, shown by the appearance of D-cracking (McLeod 2012). KDOT also applies deicing salt on roads, which is held to increase the D-cracking problem (Crumpton, Smith, and Jayaprakash 1989).

KDOT Aggregate Specifications

KDOT tests frost durability of limestone coarse aggregate with the use of KTMR-21: Soundness and Modified Soundness of Aggregates by Freezing and Thawing, and KTMR-22: Resistance of Concrete to Rapid Freezing and Thawing. The latter test is a modification of ASTM C666 which specifies limits on the durability factor and percent expansion, classifying passing limestone as “Class 1” or “Class 2.” Aggregate must meet these specifications for use in “on-grade concrete” (McLeod 2012).

KDOT Deicing Salt Practices

KDOT divides Kansas into six districts that use varying methods of salt application and salt sources. District 1 uses magnesium chloride ($MgCl_2$) in Topeka and Kansas City metro areas as well as sodium chloride (NaCl) in solid form or in brine. Other parts of the district use NaCl in either form. Brine concentration is 23% salt as measured by a hydrometer. Salt used by District 1 comes from Hutchinson Salt, Independent Salt, Cargill, or Central Salt (Jaci Vogel, KDOT District Maintenance Engineer, personal communication October 27, 2011).

District 2 also applies NaCl as brine (23% salt solution) or solid form with salt originating from Independence Salt or the Hutchinson Salt Company (James Roudybush, KDOT District Maintenance Engineer, personal communication November 2, 2011). The KDOT highway maintenance manual describes salt application for various conditions based on temperature and precipitation. The amount of salt, either in brine or solid form, applied per lane mile increases with increasing severity of a freezing event (KDOT 2009).

District 3 uses a “salt sand mix,” pretreats with salt brine, and purchases salt from Hutchinson, Kan. (Joseph Finley, KDOT District Maintenance Engineer, personal communication, November 4, 2011). District 4 uses NaCl brine for pre-treatment and deicing and purchases “medium graded salt” from the Cargill or Hutchinson salt companies (John Hrenak, KDOT District Maintenance Engineer, personal communication November 2, 2011). District 5 also uses NaCl in a 23% salt brine and purchases salt from the Hutchinson salt company or from Cargill’s mine in Lyons, Kan. (Scott Koopmann, KDOT District Maintenance Engineer, personal communication November 2, 2011). District 6 uses NaCl in a 23% brine solution with salt from Central Salt in Lyons, Kan. and Hutchinson Salt Company in Hutchinson, Kan. (Ron Hall, KDOT District Maintenance Engineer, personal communication November 2, 2011).

Deicing Salt Impurities

Rock salt applied to Kansas roads is not pure NaCl but the composition varies based on the salt source. For example, one chemical analysis showed salt to be 98.7% NaCl in addition to sulfate, calcium, magnesium, and sodium ferrocyanide decahydrate, also called yellow prussiate of soda (Lloyd Cady, QA mine manager for Cargill, personal communication December 1, 2011). Another analysis found the salt to be 95.25% NaCl with varying amounts of impurities, such as calcium or sodium sulfate and magnesium (Todd Hamer, Area Sales Manager for Central Salt, personal communication November 17, 2011).

Frost Damage to Concrete

Crystallization Pressure Theory

Scherer and Valenza (2005) state ice crystallization pressure causes internal frost damage. Ice crystals form within pores and are separated from pore walls by a narrow film of liquid. The film arises because of repulsion between the crystal and pore wall which allows the crystal to grow toward of the pore wall, exerting pressure. The resulting pressure causes damage in the material surrounding the pore. In mortar, entrained air voids counteract this pressure by nucleating ice in the air voids which causes removal of water from the pore network. Sun (2010) also discusses frost damage in the presence of entrained air voids. Ice forms in the air voids, drawing water out of the capillary voids and causing contraction.

Critical Degree of Saturation of Concrete

Frost damage to concrete requires sufficient saturation (Li et al. 2012). Li et al. studied air-entrained mortar in freeze-thaw and moisture sorption tests. In moisture sorption tests greater air content increased the amount of water absorbed but reduced the degree of saturation reached due to additional volume provided by the air entrainment. Samples were also subjected to freeze-thaw tests at varying degrees of vacuum saturation. Damage, measured by changes in the relative elastic modulus using active acoustic emission, decreased as saturation was reduced. The critical degree of saturation was determined as 88%, which Li et al. (2012) state "appears to be independent of the air content." Accordingly, greater air content does not change the critical degree of saturation but increases the time required for critical saturation to occur as there is more total volume to be filled with water. Li et al. (2012) also noted that greater air content did not prevent damage above the critical degree of saturation.

Frost Damage to Aggregate

Hydraulic Pressure Theory

Verbeck and Landgren (1960) studied effects of aggregate on concrete frost durability based on the hydraulic pressure theory which states that damage occurs from water movement caused by ice formation. They investigated the time needed to reach critical saturation of the aggregate and resulting behavior once saturated. Aggregates require time to saturate sufficiently for frost damage to occur based on pore size distribution and porosity. With a greater amount of smaller pores, the required time to critical saturation decreases as moisture is both absorbed and retained more readily at lower relative humidity levels compared to a pore system with larger pores. The time to critical saturation for a given pore size distribution increases with greater porosity. Properties of the paste surrounding the aggregate also influences the time to critical saturation by increasing the time with decreasing permeability and increasing cover thickness. Verbeck and Landgren (1960) also examined instantaneous freezing of a critically saturated aggregate, but this is unlikely to occur in concrete outside the lab.

Damage during freezing of a critically saturated aggregate can be a function of aggregate size (Verbeck and Landgren 1960). At lower freezing rates, ice formation causes water movement through the aggregate. The resulting pressure depends on freezing rate and porosity, size, and permeability of the aggregate. "Critical size" refers to the aggregate size below which hydraulic pressure can be sustained by the aggregate. The combination of "moderate" porosity and low permeability can lead to a lower critical size value. Expulsion of water from the aggregate can also damage the surrounding paste. The amount of water expelled into the paste increases with increasing aggregate size and porosity, subsequently increasing the volume of air-entrained paste needed to "accommodate" the expelled water. Increased entrained air content can reduce the required paste volume. Verbeck and Landgren also note that the freezing point is lowered if the pore solution contains "water-soluble salts and cement alkalies." Ice formation is also reduced if water is adsorbed or in very fine pores. The lower freezing point or decreased ice formation reduces hydraulic pressures.

Aggregate Pore Size Effects

The size of an aggregate's pores influences its durability (Hudec 1987). Hudec states that "The shape of the pore is not as important as the size of the shortest direction. It determines most of the properties of that pore space." Hudec (1987) also notes that capillary transport can cause expansion or contraction, depending on pore size. Very small pores ($<4\text{x}10^{-5}$ in.) can lead to expansion from osmosis between the pores and external water. Contraction can occur in stones containing capillary pores ($4\text{x}10^{-5}$ – 0.04 in.) due to capillary tension, but the stone may return to original size upon full saturation. Deicing salt leads either to contraction by increased capillary tension or expansion due to osmosis if the external solution becomes more dilute than the pore solution. As a result of these effects, wetting and drying may be sufficient to break down the stone, particularly for stones containing mostly pores smaller than $4x10^{-5}$ in. Adsorption also affects pore solution as bound water will have a lower vapor pressure. Dissolved ions in the pore solution tend to increase adsorption effects.

Hudec (1987) also notes that pore size affects response to freeze-thaw. If pores are smaller than $4x10^{-5}$ in., freezing in the pores will not occur due to lower vapor pressure of the adsorbed water. Subsequently, damage appears to be caused by osmosis, as described above. In stones containing mostly capillary pores ($4x10^{-5}$ – 0.04 in.), water super-cools and then rapidly freezes. If pores are small ($4x10^{-5}$ – $2x10^{-4}$ in.), less ice forms but the stone is less durable due to sorption effects. For stones containing larger pores (>$2x10^{-4}$ in.), Hudec notes that damage occurs in accordance with hydraulic pressure theory and that water super-cools a few degrees before freezing. Hudec also notes that osmotic effects from deicing salts are likely the cause of increased damage in freeze-thaw in salt solution.

Collins (1988) also found small pores to be detrimental, though the size of frost-susceptible pores differs from Hudec's results mentioned previously described. He studied aggregate durability by freeze-thaw testing of concrete, mercury porosimetry and optical petrography. Comparison of aggregate freeze-thaw performance, porosity, and strength showed that pore size distribution and strength are related to durability. Frost susceptibility was greater as the amount of pores smaller than $8x10^{-6}$ in. increased. The author also noted that the effect of smaller pores could be offset by a sufficient volume of pores larger than $8x10^{-6}$ in. For a given pore size distribution, increased strength resulted in greater durability. However, the author noted limitations to mercury porosimetry, which Pitt et al. (1987) also describes as the “ink bottle” effect. In the case of a large pore with a narrow entry, mercury porosimetry categorizes the pore according only to the radius of the entry. Collins (1988) also used petrography to study the aggregate, identifying larger pores as well as various durable attributes of the stone. Collins also observed that a relatively impervious matrix could surround susceptible elements in the aggregate.

Combined Effect of Pore Network and Mineralogy

Hudec (1987) notes that stone mineralogy also has a significant influence on durability since some minerals, such as clays or chert, are more active than others and cause increased adsorption within aggregate pores.

Dunn and Hudec (1966) studied durability of carbonate stone based on its clay fraction, noting that stone durability depends on porosity and mineralogy. Stones reaching the lowest degree of vacuum saturation after 24 hours immersion were more durable. Differential thermal analysis indicated that less water froze in non-durable stones to the extent that no freezing was detected in some stones, even at temperatures as low as -40°F. This result was attributed to water binding to clay minerals. The authors noted that damage may occur from expansion of this unfrozen water as temperature decreases. Clay distribution within the stone also affects durability, as concentrated and water-accessible clay could make a stone non-durable. The authors noted that dolomite may not bind to clay during stone formation, leading to concentration of clay and reducing durability. Conversely, calcite may bind to clay, causing clay dissemination throughout the stone and no durability reduction.

Influence of Salt on Concrete

Salt Crystallization Pressure

Damage to porous masonry can occur from crystallization of salt, as described by Scherer (2004). First, salt crystals are precipitated from solution. Crystal growth exerts pressure against pore walls because a $4\text{-}8\times10^{-8}$ in. layer of solution exists between the crystal and pore wall, allowing the crystal to grow toward the pore wall. Crystal formation requires super-saturation of the solution, and the location of super-saturation depends on solution movement through porous material.

Moisture Transport of Salt Solutions in Concrete

Salt affects moisture transport in concrete. Spragg et al. (2011) measured moisture sorption and desorption of concrete and mortar in dilute and concentrated solutions of NaCl, $MgCl_2$ and calcium chloride ($CaCl_2$). Concrete samples were immersed in the solutions according to ASTM C1585. Results are shown in Figure 2.1. Dilute NaCl solution (0.7%) slightly increased the amount of fluid absorbed, but other salt solutions, including 23% NaCl, decreased the amount of fluid absorbed compared to deionized water. The absorbed amount varied based on salt type, but increasing the salt concentration reduced absorbed fluid for all salt types. Reduced absorption in salt solution was attributed to increasing viscosity (η) and surface tension (γ) occurring from increased salt concentration. Spragg et al. used "the square root of the ratio of surface tension and viscosity of the fluid $((\gamma/\eta))^{(1/2)}$" to compare water and salt solutions. As the $((\gamma/\eta))^{(1/2)}$ value of a salt solution decreases relative to water, the relative absorption also decreases.

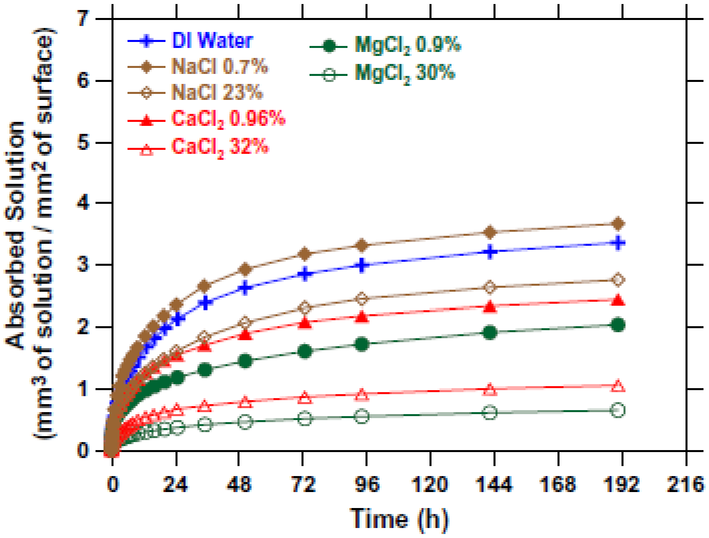

Fig. 3. Volume of deicing solutions absorbed by concrete as a function of time (typical standard deviation less than 0.1 mm^3/mm^2).

Figure 2.1: Concrete Absorption of Salt Solution (Spragg et al. 2011, with permission from Elsevier)

Following solution absorption Spragg et al. (2011) then dried the samples at 50% relative humidity (RH) and 73°C. Samples containing salt solutions lost less water, particularly those treated in concentrated solution, compared to deionized water. Increased salt concentration increased disparity, but the 0.7% NaCl solution increased water loss. The rate of moisture loss during drying was slower than the rate of moisture uptake during wetting. The authors noted, therefore, “concrete is more likely to become preferentially increasingly wet over time.”

Absorption of deionized water into the samples was then measured (Spragg et al. 2011). Again, treatment with salt solution reduced the amount of water absorbed compared to deionized water, even for 0.7% NaCl. However, the absorbed fluid amount increased for all samples as compared to the initial sorption test, even when deionized water was used for both tests. Spragg et al. also conducted ASTM C1585 on concrete stored in various states ranging from oven-dry to vacuum saturated. The drier the storage environment, the more moisture was absorbed.

Spragg et al. (2011) also measured mass during drying of mortar saturated in concentrated solutions of NaCl, $CaCl_2$, and $MgCl_2$, as well as deionized water. RH of the drying environment was gradually reduced from 97.5% to 0%. The salt-treated samples gained mass at the first step (97.5% RH) and then gradually lost water as RH was decreased. Sample mass dropped below initial saturated weight only when RH dropped below the equilibrium RH of the salt solution.

Frost Damage to Concrete in Salt Solution

Litvan (1976) studied cement paste in freeze-thaw in various concentrations of NaCl. Length change measurements showed an increased net expansion in dilute solutions that decreased as solution concentration increased. The author used differential thermography that showed ice formed at the freezing point of the "eutectic" solution and the salt solution. The eutectic solution consistently froze at approximately -8°F, and was preceded by freezing of the salt solution at a higher temperature. The difference between the two temperatures decreased as salt concentration increased. Differential thermography showed ice formation at one point for specimens in water or 26% NaCl.

Dunn and Hudec (1966) also subjected various stones to freezing in NaCl solution. Differential thermal analysis showed freezing point depression, slower freezing rate and reduced ice formation compared to freezing in water.

Shi et al. (2010) tested non-air-entrained concrete in freeze-thaw cycles in de-ionized water and various dilute (approximately 3%) solutions of deicers. Samples were tested according to SHRP H205.8 using concrete samples placed on a sponge immersed in various solutions subjected to 10 freeze-thaw cycles. The 3% by mass NaCl solution significantly increased mass loss of the concrete sample compared to deionized water. Chemical alteration of the paste was also observed by SEM/EDX methodology. The authors stated, "We hypothesize that the exposure of the cement paste to sodium chloride led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of calcium sulfate ($CaSO_4$) from AFm and AFt phases." Effects of dilute deicers other than NaCl varied; some of the deicers caused more mass loss than NaCl and other deicers less.

Sodium Salt Attack of Concrete

Haynes et al. (2008) observed salt weathering of concrete exposed to sodium sulfate (Na_2SO_4), using river gravel for coarse aggregate and Type II cement with 5% tricalcium aluminate. Cylinders were partially immersed in a 5% by mass solution of Na_2SO_4, tap water, or kept dry. Exposure conditions varied to include constant temperature and relative humidity as well as cyclic exposure varying temperature and/or relative humidity. Samples were kept in the exposure conditions for approximately three years, although one and one-half years in relative humidity levels were reduced to increase damage. Damage was thought to occur primarily from salt crystallization rather than chemical sulfate attack, although some chemical sulfate attack was observed. Loss of scaled material primarily occurred below the evaporation front and above the solution level. The authors attributed salt damage to formation of mirabilite, the hydrous form of Na_2SO_4, rather than anhydrous thernardite. The authors observed mirabilite crystallization in environmental conditions where thernardite only was expected. The authors also noted that alkali-silica gel appeared, though they did not list it as a primary cause of damage.

Haynes et al. (2010) also researched the effect of sodium carbonate (Na_2CO_3) and NaCl on concrete, using the same concrete and environmental conditions as the study published in 2008. NaCl was found to be less destructive than Na_2CO_3 and both were found to be less destructive than Na_2SO_4. NaCl caused negligible scaling when compared to the other two salts. Damage from NaCl and Na_2CO_3 was primarily due to salt crystallization, in particular the formation of hydrous Na_2CO_3, according to the authors. Chemical alteration of the paste occurred with sodium carbonate and NaCl leading to slight depletion of sulfur dioxide and increased sodium oxide levels near the solution level. The authors also noted that symptoms of alkali-silica reaction appeared for specimens treated with Na_2CO_3, which may have contributed to damage.

Concrete Durability in Wet/Dry Cycles in Salt

Darwin et al. (2007) subjected concrete prisms to cyclical of wetting and drying in deicing salt solutions. NaCl, $MgCl_2$, $CaCl_2$, and calcium-magnesium-acetate (CMA) were used in 1.06 and 6.04 molal concentrations, as well as air and distilled water for control specimens. The NaCl grade was not explicitly stated, but since distilled water was used to make the solutions it is probable that the NaCl was either technical or reagent grade. Damage was monitored by relative dynamic modulus of elasticity, referred to as $P_{w/d}$, similar to measurements used in ASTM C666 freeze-thaw testing. The results of the specimens subjected to concentrated deicers are given in Figure 2.2 (Darwin et al. 2008). The dilute and concentrated NaCl solutions initially increased the $P_{w/d}$, which was attributed to moisture absorption or pore filling by salt. After reaching a maximum value, $P_{w/d}$ decreased over time in the concentrated NaCl solution, but did not appreciably decrease for dilute NaCl. The time to reach the maximum $P_{w/d}$ was greater for concentrated NaCl than for dilute NaCl. Surface scaling was noted in concentrated NaCl and "few signs of damage" were noted for specimens in dilute NaCl (Darwin et al. 2007).

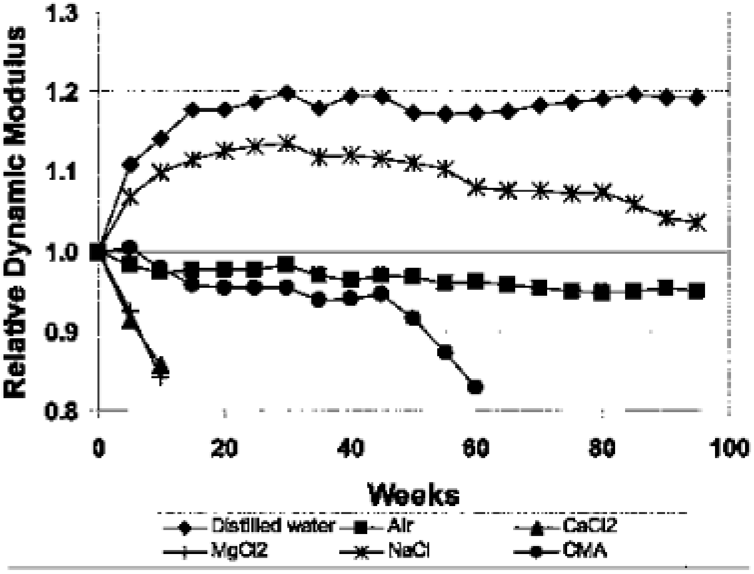

Fig. 1—Relative dynamic modulus of elasticity (wet-dry) $P_{w/d}$ versus number of weekly wet-dry cycles for specimens exposed to 6.04 molal ion concentration deicer solutions.

Figure 2.2: Relative Dynamic Modulus of Concrete Exposed to Various Deicer Salts (Darwin et al. 2008, with permission from American Concrete Institute)

Wang et al. (2006) tested paste and concrete samples subjected to wet/dry cycles in deicing salt solutions, including NaCl and distilled water as a control. Freeze-thaw cycles were also conducted using these solutions. In wet/dry cycles, mass change was similar when samples were immersed in NaCl or water. Scaling was also negligible for samples in both solutions, though in NaCl solution compressive strength decreased slightly as the number of wet/dry cycles increased. In freeze-thaw cycles scaling was slightly more severe for NaCl than water.

However, with increasing freeze-thaw cycles, compressive strength increased slightly for samples in NaCl as compared to an initial increase followed by a slight decrease for samples in water.

Chemical Attack on Concrete from NaCl

Sutter et al. (2008) conducted an extensive study of concrete durability, examining chemical attack and scaling resistance in various concentrated deicers. Various test methods were employed, including ASTM C666 method A with 3x3x11 in. concrete prisms in concentrated salt solutions. In almost all of the tests, NaCl was found to be relatively benign to concrete (corrosion was not considered), although NaCl affected concrete chemistry through formation of Friedel's salt and depletion of calcium hydroxide. The exception was a non-standard freeze-thaw test including oven-drying and exposure to deicing solutions. Increased damage was attributed to physical effects of the salt, including increased moisture retention, salt crystallization, and thermal expansion. Food grade NaCl was used in the study, although if different grades were used in various tests, it was not stated. An analysis of the NaCl solution showed trace amounts of sulfur and other ions in addition to sodium and chloride.

Salt Impact on Aggregate Frost Durability

Effect of Deicing Salt on Aggregate

Crumpton et al. (1989) conducted a study on concrete "cups" made by taking concentric cores of field concrete, some with the inner core off-center to create variable thickness. These cores were filled with a 15% salt solution made with "standard Kansas deicing salt," indicating impurities were present in the NaCl. The cups were then subjected to a number of wetting and drying cycles and damage was assessed by observation. The hygroscopic nature of the salt solution was observed by the cups adsorbing sufficient water to keep the exterior damp at high humidity. The authors noted that "On days when it was raining outdoors, the moisture buildup on the outside of the cups was often great enough to dissolve some of the salt deposits." Capillary sorption was also noted as the tops of the cups became coated with salt although the solution level was approximately one half-inch below the top of the cup. Salt crystallized on the cup exterior most rapidly in cracks (including those in the aggregate) and then aggregate-paste boundaries. The rate of moisture transport through individual aggregates varied, and was more rapid in aggregates that became coated in salt.

Concrete performance varied in the study (Crumpton et al. 1989). In several cups the paste was scaled more than the aggregate but in other cups aggregate scaled more than the paste. The authors described scaled material of paste or aggregate as "oatmeal-sized" flakes, although one aggregate lost "a bean-shaped flake" 0.6 in. long. The authors also tested a sealer that led to cup cracking after the first cycle, indicating lower durability since the cups without the sealer did not crack even after 12 cycles (a cycle was 14 days). The authors also included "clinical observations" of field performance of aggregate as influenced by deicing salt, such as increased severity of alkali-aggregate reaction. Other observations included salt deposits in limestone and chemical degradation of aggregate leading to formation of sulfate salts.

Chemical Attack in Salt Solution

Gillott (1978) examined a number of quartzite and limestone samples for length change in continuous immersion in water and salt solutions. Limestone composition varied in amount and formation of dolomite or calcite as well as grain size range. Dilute and concentrated solutions of NaCl, $CaCl_2$ and magnesium sulfate ($MgSO_4$) were used. Length change varied based on stone composition, occurring for some stones only in sulfate solutions but in other stones only noticeably in chloride salt solutions. Electron micrographs of limestone before and after testing showed rounding of surfaces, indicating stone damage. Scaling or dissolution of the stones occurred, limiting observation of a consistent location over time using an electron microscope. The author noted that chemical attack from salt solutions occurred particularly at discontinuities in the stone matrix, such as cleavages or grain boundaries.

Gillott (1980) used scanning electron microscopy to study additional stones subjected to immersion in salt solutions of $CaCl_2$ and $MgSO_4$. He noted the carbonate fraction of the stones was most susceptible to salt attack. Damage effects were scaling and disintegration.

Interaction of Deicing Salt and Carbonate Stones

Hudec (1980) reported results of two studies examining carbonate stones for length change and absorption, testing stones that had been dried after immersion in 3% NaCl. More silica (mostly clay and chert) in the stone corresponded to increased absorption and increased loss in a freeze-thaw test of bare aggregate and $MgSO_4$ soundness test. NaCl treatment increased absorption at 92% RH for stones with low absorption, although absorption decreased or was unchanged for stones of high absorption. At 45% RH, NaCl treatment had little effect on absorption. Stone expansion during absorption was also measured; showing NaCl treatment increased expansion in stones of low expansion without NaCl and decreased expansion when the expansion was high without NaCl. The author also noted that "Expansion of some rocks upon wetting is equivalent to thermal expansion of over 212°F." An initial contraction was observed during wetting attributed to "capillary contraction."

Comparison of Frost Durability in Water or Salt Solution

Hassan et al. (2002) conducted freeze-thaw testing in deicing solutions of unconfined coarse aggregate in a study of asphalt concrete pavement. Limestone and quartzite aggregates were tested in distilled water and solutions of varying deicers including NaCl, referred to as road salt. The NaCl grade used was not explicitly mentioned, but the reference to road salt indicated impure NaCl was used. Comparison of solution concentrations indicated the most mass loss occurred when the concentration was 2% "relative to a fully saturated solution of each deicer." The mass loss of both aggregates was approximately 10% after 30 freeze-thaw cycles in distilled water. In NaCl, this value increased for both aggregates, especially quartzite. However, during the first 10 cycles, limestone mass loss was less in NaCl compared to water. It was also observed that "Limestone aggregates broke along definite planes into two or three particles, while quartzite particles were practically pulverized." The authors attributed variable aggregate performance to differing "microstructures and contact area subjected to the deicing solution" rather than differing aggregate chemistry.

Pétursson and Schouenborg (2004) also subjected aggregates to freeze-thaw cycles in either water or salt solution. Numerous aggregate types from various countries, including limestone and basalt, were tested. Freeze-thaw testing was done according to the European test EN 1367-1, and the test was run on unconfined aggregate in water or 1% NaCl solution. Average mass loss of all stones in water was 2% or less without salt. NaCl addition increased severity of the test even though the mass loss reading for some aggregates did not increase significantly. In other aggregates mass loss increased noticeably with the addition of salt; in one case, the salt test increased loss from 2% to more than 30%.

Effect of Salt Impurities on Concrete

Pitt et al. (1987) conducted a series of experiments examining the effect of deicing salt impurities on concrete frost durability. Samples were treated in various ways with saturated salt brines containing NaCl and comparatively small amounts of gypsum and then subjected to freeze-thaw testing.

Pitt et al. (1987) first tried four ways of applying salt brine to mortar cylinders over a 28 day period and then subjected the cylinders freeze thaw testing according to ASTM C666 method A. None of the four methods caused noticeable damage without freeze-thaw testing. The first ("Method 1") and most damaging method was to immerse the cylinders halfway in salt solution for 28 days. The second method filled an indentation in the cylinders. The third method alternated between four days total immersion in solution followed by three days drying. The last method was total immersion. During freeze-thaw testing samples that were half-immersed in solutions containing 1.57 and 3.10% gypsum by weight of solute cracked below solution level. These samples, as measured by "pulse velocity ratio" according to ASTM C597, were the only cylinders to deteriorate significantly during freeze-thaw testing. Half-immersion in salt solution also reduced splitting tensile strength, even in samples immersed only in NaCl. Loss for treatment with NaCl alone was approximately 10% and gypsum addition caused greater loss. Mercury porosimetry was used to compare samples treated in NaCl with samples treated with NaCl solution containing 3.1% gypsum. The addition of gypsum increased porosity at the solution level and reduced porosity above and below the solution level. The authors noted reduced pore size could have led to increased freeze thaw damage. Chemical tests run on the samples showed that the addition of gypsum had a varying effect on chloride and sulfate contents, depending on the gypsum amount added and location of the sample tested. For example, chloride content increased below solution level but decreased at the sample midpoint with the addition of gypsum.

Pitt et al. (1987) ran a further set of experiments on samples exposed to freeze-thaw cycles while half-immersed in salt brines containing NaCl and varying amounts of gypsum. Half-immersion during freeze-thaw increased the rate of damage and reduced the number of cycles. Below the solution level, cracks "perpendicular to the longitudinal axis of the cylinders" were initially observed but became more disordered with time. The authors observed a pessimum effect of gypsum content as the damage measured by pulse velocity ratio increased and then decreased with increasing gypsum content. However, brine composition data indicated that while gypsum content increased, NaCl content decreased, indicating an overall drop in solution concentration. Tensile strength of samples subjected to freeze-thaw cycles was determined and varied with increasing gypsum content in a manner similar to that observed for pulse velocity ratio readings. Mercury porosimetry indicated pore filling with the addition of NaCl and gypsum, the extent of which increased then decreased with increasing gypsum content, similar to results of tensile strength and freeze-thaw testing. X-ray diffraction data indicated that treatment with NaCl solution without gypsum led to increased formation of ettringite as well as formation of Friedel's salt. Gypsum addition increased formation of ettringite and Friedel's salt, thus causing pore filling. The authors also indicated that Friedel's salt, which "does not contain the sulfate radical found in ettringite," is more responsible than ettringite for pore-filling due to decreased sulfate concentrations in freeze-thaw treated samples. The authors noted less than 0.5% sulfate (by weight of solute) influenced mortar durability, and the primary damage mechanism was pore filling by Friedel's salt and possibly ettringite.

Pitt et al. (1987) also examined cores of concrete from an intersection of two roads, one heavily salted and the other not. Away from the intersection on the un-salted road the chloride concentration decreased and the sulfate concentration increased slightly, correlating with laboratory testing. Chloride concentration was also higher at joints and lower at mid-points of slabs.

ASTM C666 using Salt Solutions

Salt solutions have been used to modify the ASTM C666 test method. Results and methods of a number of modified ASTM C666 tests are described.

Iowa DOT Salt-Treated Aggregates Study

Dubberke and Marks (1985) tested aggregate durability by salt treating coarse aggregate used to make concrete tested by ASTM C666 method B with a 90 day moist curing time. NaCl was used because of reduced field performance of aggregate as the amount of deicing salt applied on roads increased. Aggregate was oven-dried at 230°F for 24 hours and then soaked in a saturated solution of NaCl for 24 hours with the solution dumped over the aggregate upon removal from the oven. The process was repeated five times and the aggregate rinsed before mixing. Salt-treatment increased test severity. A reduction in "initial sonic modulus" was noted, indicating some damage occurred to the concrete before testing. However, test results correlated well with field performance. Durable aggregates were relatively unaffected by the test, lasting 300 freeze-thaw cycles with slight reduction in durability factor (DF) compared to the test run on untreated aggregate. Non-durable aggregates were severely impacted by salt-treatment and failed the test within 100 cycles. Untreated, DF of the non-durable aggregates after 300 cycles was greater than 90. The effect of salt-treatment on a non-durable aggregate is shown in Figure 2.3, where “NaCl only” refers to the salt-treatment method. One aggregate, “a low-porosity, fine-grained Farmington Stone,” was severely damaged by the salt-treatment, with cracking in the aggregate that was not present without salt-treatment. The authors pointed out possible mechanisms for the severity, including retention of water due to the salt, depressed freezing point, or salt crystallization. Aggregate chemistry was also examined, showing that increased sulfur content correlated to reduced durability, “especially when magnesium is present.” Iron content could also be a factor, as the authors noted the possibility of a deleterious reaction in concrete when a “porous pyritic dolomite” is used as aggregate. The grade of NaCl used was not mentioned (i.e., rock salt, food, or reagent grade).

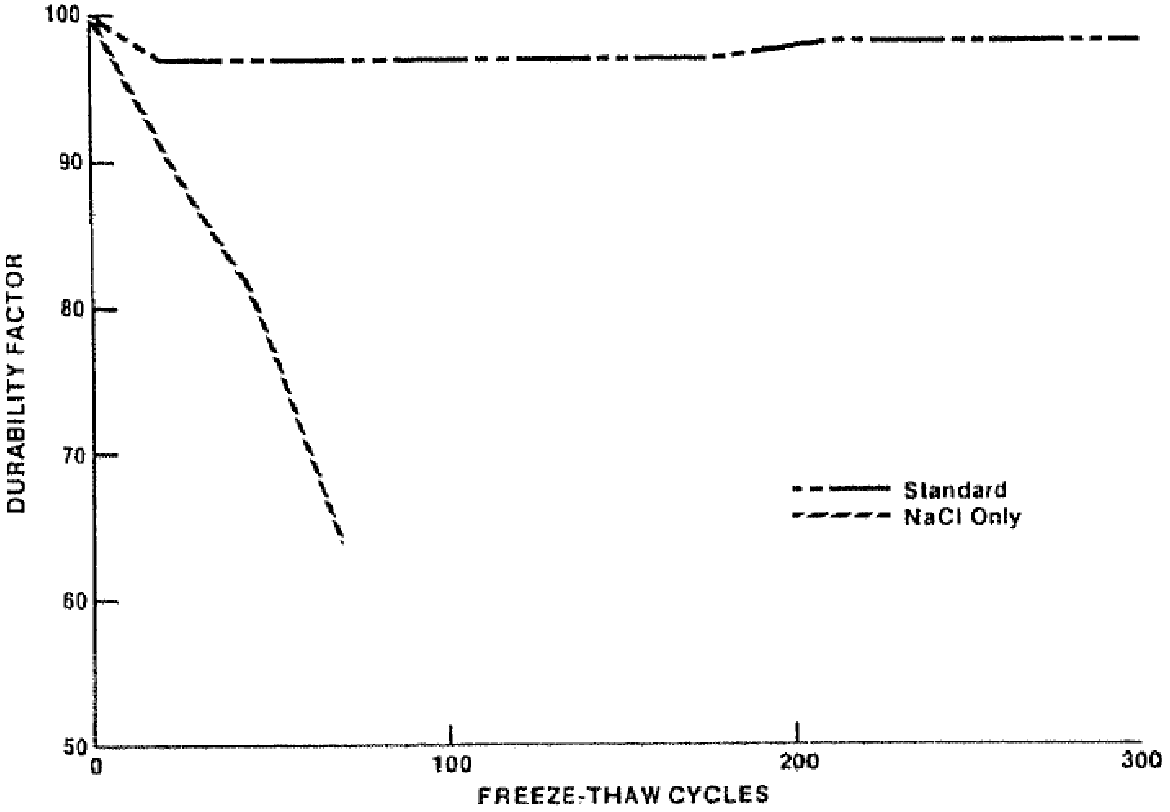

FIGURE 5 Smith durability factors.

Figure 2.3: Iowa DOT Salt-Treated Aggregate Results (Dubberke and Marks 1985, with permission from the Transportation Research Board)

Further ASTM C666 Testing Using Salt-Treated Aggregates

Koubaa and Snyder (1996) evaluated aggregate durability using three variations of ASTM C666 method B, the Washington hydraulic fracture test, and the Virginia Polytechnic Institute single-cycle slow-freeze test. The three ASTM C666 method B variations were, in order of increasing severity: unmodified, prisms wrapped in cloth, or salt-treated aggregate. In this study, “durable” and “marginal to non-durable” aggregates were not significantly impacted by salt-treatment. Non-durable aggregates were affected, with lower DF values and greater expansion than unmodified procedure B method. Not all non-durable aggregates were equally affected, as the drop in DF varied between seven and 73. A similar pattern held for increased expansion, although a slight reduction in DF did not necessarily correspond to a minimal increase in expansion. The authors noted that the salt-treated aggregate procedure correlated best with field performance. Koubaa, Snyder, and Peterson (1997) also published this data in greater detail in a report for the Minnesota DOT.

Koubaa, Snyder, and Janssen (2002) also used the salt treated coarse aggregate test method to assess frost durability of several coarse aggregates using various mitigation measures. Some measures included reducing water to cement ratio, blending durable and non-durable aggregates, and reducing coarse aggregate size. Alternative test methods such as VPI single-cycle slow-freeze test were used, although the unmodified ASTM C666 method B was not used.

Virginia DOT ASTM C666 Testing in Salt Solution

The Research Council of the Virginia Department of Highways and Transportation (VDH&T) compared results of ASTM C666 method A using water or NaCl solution (Newlon 1978). The concrete was moist-cured for 14 days and then dried for seven days in the lab with a relative humidity between 35 and 45% prior to testing. Salt solutions of 2, 3 and 4% were used to study the effect of solution concentration on test results. Durable aggregates were used in the study and air content and cementitious material were varied. The average DF of concrete with air content of 3.5 and 8% decreased with the addition of salt solution but did not drop below 95 regardless of concentration. Variability increased as indicated by larger standard deviations. Without air entrainment, the average DF was 5.8 in a 2% salt solution. Type II, IP, and I cement with fly ash were used as replacement for type I Portland cement and were moist-cured for 67 days without a drying period prior to testing (due to equipment failure). DF values for alternate cementitious materials were lower even in water. The addition of salt solution to the test reduced DF slightly except for the batch containing fly ash, in which the average DF increased by approximately 12. However, variability with fly ash when tested in water was high as the standard deviation was approximately 14.

ASTM C666 Testing in Salt Solution Containing Gypsum

Detwiler and Powers-Couche (1999) tested concrete according to ASTM C666 procedure A in 3% salt solution. The solute was NaCl or NaCl with 5% replacement with gypsum. Specimens were also examined by petrography and a scanning electron microscope was used to observe ettringite formation in air voids. Concrete was made using siliceous river gravel and varying cement types. Gypsum was added to the cement for some batches. Concrete fresh air content (by ASTM C231) was about 2 or 4%. In concrete with low air content ettringite formation was not observed in air voids, but with higher air content, ettringite and/or calcium hydroxide formation was noted in air voids. For type I cement, ettringite formation occurred earlier when gypsum was present in the salt solution compared to only NaCl. When gypsum was added to type I cement ettringite formation was limited to near the surface. For type II cement in NaCl solution, ettringite was observed near the scaled surface and in small air voids near the surface of the concrete, although calcium hydroxide formation was more prevalent. These effects were not appreciably affected by gypsum addition to NaCl solution. The authors noted freeze-thaw action was the primary damage mechanism and ettringite formation was an effect.

Variations in ASTM C666 Testing Between State Agencies

Vogler and Grove (1989) surveyed ASTM C666 test methods used by various state transportation departments to evaluate coarse aggregate durability. Both procedure A and B of ASTM C666 were used. Test procedures varied between states in numerous ways, including batch proportions, curing, and number of cycles. Pennsylvania and Vermont were also found to use a 3% NaCl solution for the freezing medium in method A.

Dimension Stone Durability

Dimension stone performance under freeze-thaw action or salt weathering cycles has been extensively studied.

Correlation of Durability to Material Properties of Stone

Goudie (1999) subjected a variety of limestone samples to salt weathering in Na_2SO_4 and compared measured material properties to durability. He found that high modulus of elasticity, low absorption, and high density generally indicated good durability, but exceptions to this trend occurred. Goudie (1999) also mentioned that a low saturation coefficient, ratio of voids filled with water to total void volume, may indicate a durable stone even without some of the aforementioned properties.

Stone Response to Freeze-Thaw Testing

Ingham (2005) studied a number of stones in freeze-thaw cycles but determined the test method was misleading as it showed some durable stone to be non-durable and non-durable stone to be durable. Stone durability was classified by historical performance in the United

Kingdom. Following testing thin sections of the stones were examined under a microscope showing crack progression was influenced by stone morphology. Cracks were observed "parallel to the bedding" as well as "exploiting" weaker areas of the stone.

Ruedrich and Siegesmund (2006) measured length change of stone samples in freeze-thaw cycle of both "capillary-saturated" and dry samples. Dry samples linearly contracted during cooling and expanded during heating with little residual strain. The capillary saturated samples showed an expansion at a temperature slightly below freezing followed by contraction. This subsequent contraction was influenced by pore size distribution of the samples. Samples with pores generally larger than $4x10^{-5}$ in. contracted similarly to the dry samples. Saturated samples with pores generally smaller than $4x10^{-5}$ in. contracted appreciably more than when dry. The authors noted that the latter samples also contained large amounts of clay which possibly caused negative pressure in the pores, leading to increased contraction. Effects of the cooling rate and saturation level were also examined. Increased cooling rates reduced maximum contraction but increased residual strain. The saturation level was examined using vacuum-saturated samples dried to various degrees of saturation. Deviation from linear contraction of the dry samples was noted for 20% saturation, although residual strain occurred starting at 80% saturation. Comparison to capillary saturated samples indicated that water distribution within the pores also influences sample length change during freezing based on the difference between a capillary saturated sample and one 80% vacuum saturated, both containing approximately the same amount of water. In the vacuum-saturated sample, expansion continued after an initial sharp expansion attributed to ice formation, whereas the capillary-saturated sample contracted following ice formation expansion. The length change variation was attributed to vacuum-saturation filling different size pores in the stone.

Ruedrich et al. (2011) conducted a similar length change procedure on additional stone types with results showing a similar relationship between pore size distribution and length change pattern. The authors also subjected stones to 1,400 freeze-thaw cycles showing different degradation patterns. One stone experienced appreciable mass loss and did not complete all the cycles, but the other three continued to the end with little mass loss. However, of the three stones that completed all the cycles, one showed a continuous decline in elastic properties whereas the elastic properties of the other two stones remained approximately the same following an initial drop. The limestone tested was found to be somewhat susceptible to residual strain from temperature cycles as calcite thermally expands in one direction and contracts in another during heating.

Critical Degree of Saturation of Building Stone

Chen et al. (2004) examined a welded tuff for critical degree of saturation using a freezing rate of 59°F/h. Samples were saturated by immersion “in distilled water under vacuum condition for 72 h.” After one freeze-thaw cycle, compressive strength, P-wave velocity, and change in porosity were measured. The critical degree of saturation was determined to be 70%, the lowest saturation level in which loss of compressive strength and P-wave velocity were observed. Increased porosity was observed beginning at a 70% saturation level. Above 78% saturation, surface cracks appeared, increasing in width with increasing saturation level. Two saturated samples were also examined for water movement during the test. One sample was frozen by immersion in liquid nitrogen, and the other frozen in a chamber at 0°F. In the nitrogen-frozen sample saturation was comparatively consistent between the surface and center of the specimen, but for the sample frozen at 0°F the saturation level was higher towards the sample exterior. The authors noted the results indicate water movement towards the specimen surface during freezing.

Stone in Freeze-Thaw in Salt Solution

Wessman (1996) studied the effect of salt on frost durability of stone, observing the critical degree of saturation and length change based on salt type and concentration. Wessman found the critical degree of saturation to be approximately 90%, regardless of salt type or concentration. Sodium sulfate slightly increased deformations between 100 and 90% saturation levels when compared to NaCl. Deformation at 100% saturation in salt solution was approximately equal regardless of salt type or concentration, although the addition of salt increased the deformation in comparison to water. However, only 1 and 0.5% salt solutions were used in the study.

McGreevy (1982) subjected limestone to freeze-thaw cycles in water, NaCl, $MgSO_4$, and Na_2SO_4 solutions of varying concentrations. The author found that increased concentration reduced mass loss, although the use of dilute NaCl increased the damage compared to water. The author also compared solution uptake of limestone in water and in salt solutions showing that limestone absorbed less salt solution.

Stone Response to Alternating Freeze Thaw and Salt Weathering Cycles

Warke and Smith (2007) used varying combinations of sodium sulfate weathering and freeze-thaw cycles to compare stone durability, using a standard sodium sulfate test for reference. Modified tests showed that more freeze-thaw cycles increased mass loss of some stones while reducing mass loss for others. The authors also noted that accelerated tests can be overly severe and damage can also be exaggerated by use of small specimens since 1.6 in. cubes were used for the standard test and 3 in. cubes for modified tests. Permeability measurements showed that mean low permeability did not necessarily indicate that the stone was durable and, for a given mean permeability, lower durability corresponded to a higher range of permeability values.

Salt Influence on Drying

Goncalves et al. (2007) used magnetic resonance imaging (MRI) to observe moisture movement during drying of masonry with and without NaCl. The samples used were made of plaster, mortar and stone. Drying occurred initially from the sample surface, but over time the evaporation front progressed into the sample interior. The addition of salt decreased the overall evaporation rate of the samples thereby, maintaining an evaporation front at the sample surface for more time. Reduced evaporation in salt solution was attributed to the influence of equilibrium RH (RH_{eq}) of the salt solution as it decreased the "driving RH gradient for vapour transport," with the evaporation rate decreasing as salt concentration near the surface increased during the drying period. The authors also noted subsequent salt crystallization at the surface may impede evaporation as well.

Temperature Influence on Salt Crystallization

Angeli et al. (2010) subjected a limestone to wet/dry cycles in Na_2SO_4, varying salt concentration and temperature. Damage was attributed to salt crystallization, the location of which depended on where the solution in the stone became super-saturated. Theoretically, super-saturation is a function of temperature, occurring at lower salt concentrations with lower temperature. Damage, expressed in terms of amount and size of particles lost from the stone, was a function of temperature and concentration. Mass loss was greater at lower temperatures. For a given temperature, higher salt concentration induced super-saturation deeper in the sample, increasing scaled particle size. Larger scaled particles increased variability of results between samples for a given temperature and concentration since natural variations within the stone governed size and location of particle loss.

Comparison of Salt Type in Stone Weathering

Benavente et al. (2004) studied crystallization of salt in pores, comparing NaCl and Na_2SO_4, the latter of which caused more stone damage. NaCl crystallized at the stone surface, whereas hydrous and anhydrous forms of Na_2SO_4 crystallized into within the stone. Crystallization was also observed in glass capillary tubes, showing that NaCl formed at the water/vapor interface and Na_2SO_4 formed below the interface. Rodriguez-Navarro and Doehne (1999) also noted these effects in their glass capillary tube experiment.

Ruiz-Agudo (2007) conducted a salt comparison study of Na_2SO_4 and $MgSO_4$ in limestone. Location of salt crystallization varied for the two salts as solution uptake was slower for $MgSO_4$ compared to Na_2SO_4. $MgSO_4$ crystallized deeper within the stone and caused cracking, whereas Na_2SO_4 crystals formed underneath the surface and caused scaling. However, both salts produced hydrated and anhydrous forms so it was unclear precisely how salt crystallization produces damage.

Cardell et al. (2008) studied the influence of dilute and concentrated solutions of calcium, magnesium, potassium, and sodium sulfates as well as various combinations of these salts. Moisture transport was more rapid with dilute solutions, though concentrated solutions led to more damage. Increased viscosity of concentrated solution slowed capillary rise, moving the evaporation front within the stone and causing salt crystallization. Damage was observed as limestone dissolution and formation of "microfissures." Furthermore, calcium and magnesium carbonate formation at the surface from dissolved constituents was noted. Salt type also altered damage symptoms because sodium solutions led to scaling, whereas magnesium solutions generated cracks. The authors also reported that mixing salts reduced damage.

Influence of Evaporation Rate on Sodium Salt Crystallization

Rodriguez-Navarro and Doehne (1999) found that salt crystallization is influenced by the salt type and environment, specifically RH changes. NaCl crystals formed in drops of salt solution showed different NaCl crystals based upon location within the drop. Reducing the RH only reduced the "number of well developed crystals" since the relative location of crystal morphologies remained the same. Salt crystallization within limestone showed that NaCl mostly formed efflorescence at the surface with minor scaling occurring under the efflorescence at low RH. These results were attributed to an increased evaporation rate allowing damaging crystal formation within the stone. Small pores were filled with NaCl, hindering capillary rise of the salt solution. The authors noted that NaCl crystal formation was slower compared to Na_2SO_4, which may have reduced damaging crystallization pressure.

Variations in Stone Permeability During Salt Weathering

McCabe et al. (2011) studied permeability of stone subjected to salt weathering in a combined solution of NaCl and $MgSO_4$. The authors used geostatistics to plot variation in permeability values over the stone surface over the course of the experiment. Permeability measurements were taken from numerous points on the sample surface. Permeability measurements reflected the influence of salt deposition, as permeability decreased due to salt crystallization in surface pores and then increased when salt removed material from the surface, exposing pores not yet filled with salt. This process occurred non-uniformly over the stone surface, which the authors explained using the concept of "dynamic instability," or when initial material variations are "exploited" by the weathering process causing variable rates of decay over the stone surface.

Buj et al. (2011) used similar methods on two limestone types subjected to salt weathering in NaCl or $MgSO_4$ solutions. The authors noted that differences in stone morphology govern the weathering process, relating high or low permeability values to particular features of the stone. The authors also noted that salt crystallization can reduce permeability by pore filling yet also increase it by expanding or creating cracks.

Summary

Durability of an aggregate depends heavily on its mineralogy and size and distribution of pores. Smaller pores are typically more detrimental, either from generating increased hydraulic pressure during freeze-thaw action or osmotic and sorption effects. The presence of certain minerals, such as clay or chert, may indicate greater susceptibility to deterioration. Exposure conditions also affect durability, as deicer application can increase damage during freeze-thaw exposure. Effects of deicers include depression of the freezing point, increased moisture retention, or generating osmotic effects. Deicing salts can also degrade concrete due to chemical attack or salt crystallization, depending on salt type. When rock salt is used, the sulfate content may damage concrete more than pure NaCl due to increased formation of ettringite or Friedel's salt.

Chapter 3 - Materials

Aggregates

Various limestone coarse aggregates, all provided through KDOT, were the principal object of study. Only one fine aggregate sample was used for all concrete batching.

Fine Aggregate

Kaw River sand was used as the fine aggregate in all concrete samples. The sand is the same type used by KDOT to assess coarse aggregate durability in the KTMR-22 testing procedure (KDOT 2006). The fine aggregate specific gravity (SPG) and absorption were determined according to KT-6: Specific Gravity and Absorption of Aggregate (KDOT 2007). To determine SPG, mass of a volumetric flask is measured when empty, filled with water, and filled with water and saturated-surface-dry (SSD) fine aggregate. Absorption is determined by comparing the oven-dry mass and SSD mass of the fine aggregate sample. The cone test was used to determine when the fine aggregate was at SSD. The bulk specific gravity was determined to be 2.61 and the absorption was 0.5%.

Coarse Aggregate

Six limestone coarse aggregate samples were examined. All but one limestone sample were from sources that typically pass KDOT specifications for aggregate durability. The low grade limestone sample was from the Plattsmouth ledge of Hamm’s Lawrence quarry (Joshua Welge, KDOT Engineer of Tests, various personal communications between 2011 and 2013). Designations and sources of coarse aggregate samples are given in Table 3-1. The designation L1 was used for sample of Hamm’s Lawrence Toronto ledge limestone that was used only to make saw-cut limestone prisms.

Table 3-1: Coarse Aggregate Designations and Sources

Rock Type	Designation	Source
Limestone	L2	Hamm’s Lawrence Plattsmouth ledge
Limestone	L3	Zeandale
Limestone	L4	Severy
Limestone	L5	Desoto
Limestone	L6	LeLoup
Limestone	L7	Coffeyville

The SSD SPG, bulk SPG and absorption of the coarse aggregates were determined according to KT-6 (KDOT 2007). Results are given in Table 3-2.

Table 3-2: Coarse Aggregate Properties

Aggregate	SSD SPG	Bulk SPG	Absorption (%)
L2	2.56	2.49	2.6
L3	2.60	2.54	2.3
L4	2.57	2.50	2.7
L5	2.60	2.55	1.9
L6	2.61	2.55	2.3
L7	2.53	2.44	3.8

Cement

Monarch type I/II cement was used in all concrete samples, as stipulated by KTMR-22. KDOT uses this cement when batching concrete for ASTM C666 testing (KDOT 2006).

Concrete Admixtures

Air-entraining admixture (AEA) was the only concrete admixture used in the concrete samples. The type used was Daravair 1000, a “saponified rosin formulation” (W.R. Grace & Co. 2009). The exact amount varied as a new sample of the admixture was used after batching some of the earlier concrete samples.

Rock Salt

Rock salt samples from 13 storage sheds in Kansas were provided by KDOT. These samples were subjected to Inductively Coupled Plasma (ICP) analysis by KDOT as well as X-ray diffraction. One large sample from a storage shed in the Manhattan, Kan. area provided the rock salt to make all the rock salt brine used in testing of limestone or concrete specimens.

Limestone Prisms

Large rock samples of limestone, provided by KDOT, were used to make 2x2x9 in. stone prisms subjected to various testing methods. The prisms were cut to within ±1/16 in. of stated dimensions using a slab saw. The prisms were generally cut with the long dimension approximately parallel to the bedding, though as-received rocks were cut to maximize the number of samples that could be cut out of the rock, resulting in several prisms cut perpendicular to the bedding. Prism dimensions were determined based on the maximum length that could be cut and size of rock samples.

Limestone came from three quarries, but one quarry provided limestone from two different ledges so that samples were treated as coming from four separate sources. Quarries were located near Lawrence, Severy and Zeandale, Kansas and provided coarse aggregate for use in concrete samples. The Lawrence quarry provided material from the Toronto and Plattsmouth ledges though only the Plattsmouth ledge provided additional concrete coarse aggregate. Designations and sources for the different limestone sources are given in Table 3-3 (Joshua Welge, KDOT Engineer of Tests, various personal communications between 2011 and 2013).

Table 3-3: Limestone Prism Designations and Sources

Rock Type	Designation	Source
Limestone	L1	Hamm’s Lawrence Toronto ledge
Limestone	L2	Hamm’s Lawrence Plattsmouth ledge
Limestone	L3	Zeandale
Limestone	L4	Severy

Batch Design

The batch design specified in KTMR-22 was used for all concrete samples in this project. Cement content was 601.6 lbs/yd^3 and the water to cement (w/c) ratio was 0.39. Design air content was 6.0%. Aggregate proportions were determined by the absolute volume method, using fine aggregate to fill 50% of aggregate volume and coarse aggregate the remaining 50%. Varying SPG values of coarse aggregates caused slight variations in batch weights. Specified slump and fresh air content values were 2 ± 1/2 in. and 6.0 ± 1.0%, respectively. In compliance with KTMR-22, coarse aggregate was split evenly into two size fractions before batching: -3/4 in. + 1/2 in. and -1/2 in. + 3/8 in. Separate fractions of the coarse aggregates were immersed in water for 24 hours and towel-dried to SSD before batching (KDOT 2006).

Theoretical mixture proportions, using SSD coarse aggregate and oven-dry fine aggregate SPG values, are given in Table 3-4 and Table 3-5 for salt-treated aggregate and half-immersion methods, respectively. AEA amounts varied as a result of switching to a new container of the same admixture over the course of batching. Batch designations were based on aggregate type and treatment method, using the first term to reference aggregate source and the second term for test method. The "STA" designation refers to salt-treating the aggregate before batching concrete, and "IS" refers to batches to be half-immersed in salt solution during ASTM C666 testing.

Table 3-4: Salt-Treated Aggregate Mixture Proportions

Batch Designation	Cement (lbs/yd^3)	Water (lbs/yd^3)	Fine Aggregate (lbs/yd^3)	Coarse Aggregate (lbs/yd^3)	AEA (fl. oz./yd^3)
L2-STA	602	235	1511	1480	6.8
L3-STA	602	235	1511	1504	6.8
L4-STA	602	235	1511	1489	6.8
L5-STA	602	235	1511	1505	7.4
L6-STA	602	235	1511	1510	7.4
L7-STA	602	235	1511	1464	7.4

Table 3-5: Half-Immersion Mixture Proportions

Batch Designation	Cement (lbs/yd^3)	Water (lbs/yd^3)	Fine Aggregate (lbs/yd^3)	Coarse Aggregate (lbs/yd^3)	AEA (fl. oz./yd^3)
L2-IS	602	235	1511	1480	6.7
L3-IS	602	235	1511	1504	6.7
L4-IS	602	235	1511	1489	6.3
L5-IS	602	235	1511	1505	6.7
L6-IS	602	235	1511	1510	6.7
L7-IS	602	235	1511	1464	6.7

Mixture proportions for concrete prisms subjected to wet-dry cycling are given in Table 3-6. Prisms from these batches were individually labeled according to solution used in the wet-dry test.

Table 3-6: Wet-Dry Test Mixture Proportions

Coarse Aggregate Used	Cement (lbs/yd^3)	Water (lbs/yd^3)	Fine Aggregate (lbs/yd^3)	Coarse Aggregate (lbs/yd^3)	AEA (fl. oz./yd^3)
L3	602	235	1511	1504	6.5
L4	602	235	1511	1489	5.8

Chapter 4 - Methods

Chemical Analysis of Rock Salt Samples

Rock salt samples received were analyzed using X-ray diffraction and ICP analysis. ICP analysis was conducted by KDOT.

X-Ray Diffraction of Rock Salt

For each rock salt sample, a small amount of rock salt was finely crushed using a mortar and pestle. The salt was then placed in a glass plate and placed in the X-ray machine.

Rock salt was analyzed in a Rigaku Miniflex II diffractometer. Samples passed through the diffractometer at 30mV 15mA with a scanning speed of 3.5 seconds per 0.02° two theta.

Fifteen salt samples were analyzed. Thirteen samples were rock salt from various samples sent by KDOT. Another sample of USP grade NaCl was also crushed and analyzed. The last sample was made from leftover residue after making a trial brine batch. The brine was made using approximately an equal amount of salt from all salt samples, except for the Manhattan sample, which had not yet been delivered. A residue sample was taken and dried at 80°C for several days. The sample was then ground and analyzed similarly to the other samples.

Inductively Coupled Plasma Analysis of Rock Salt

Twelve of the rock salt samples were subjected to ICP analysis by KDOT. The percentage amounts of sodium, chloride, magnesium and calcium were determined. The percentage amounts of sodium and chloride forming NaCl were also determined (Joshua Welge, KDOT Engineer of Tests, personal communication, December 22, 2011).

Rock Salt Brine Production

The process of making rock salt brine roughly simulated field production. The brine was made by filling a 5-gallon bucket with distilled water while leaving enough space so that stirring would not cause the brine to overflow. Rock salt was then added and stirred until most of the rock salt dissolved. Stirring continued until the concentration reached 23% based on the salt hydrometer reading. In all cases, the brine contained small amounts of insoluble material that could be temporarily brought into solution but would settle out of solution. In suspension, the insoluble material caused the brine to take on a dark gray color.

For the salt-treated aggregate ASTM C666 test procedure, three individual batches of brine were made at a time. This quantity was sufficient to salt-treat three coarse aggregate samples. Approximately equal proportions of each brine batch were combined to make the brine used to treat one coarse aggregate sample. This procedure was done to reduce the influence of a single batch of brine in C666 testing.

Length Comparator Measurements

Length comparator measurements were taken for various tests. Each time before measurements were taken, the comparator was reset using an invar rod. Samples were then placed in the comparator and rotated slowly and the lowest value taken as the reading. Samples were placed in the comparator with a consistent orientation, with one sample end taken to be the "top" and one longitudinal face the "front."

Wet-Dry Testing in Salt Solution

Concrete Prism Wet-Dry Test

Concrete prisms were subjected to isothermal cycles of wetting and drying in salt solutions. Prisms were 3x3x11 in. and made using concrete batch proportions from KTMR-22 (2006). Two sets of eight prisms each were made varying only the limestone coarse aggregate. The first set was made with Zeandale quarry limestone (L3) and the second set was made with Severy quarry limestone (L4). Prisms were cured in molds for 24 hours, followed by 13 days wet curing in a fog room, and then dried in a shrinkage room maintained at 50% RH and 73°F for seven days before starting the wet/dry test.

Four prisms, two containing L3 and two containing L4 aggregate, were placed in each of four different solutions, using a separate container for each solution and each aggregate type for a total of eight containers. All solutions were prepared using distilled water. The following solutions were used: distilled water, 23% by weight USP-grade NaCl, 23% by weight USP-grade NaCl with 3% solute weight replaced with ACS grade gypsum, and rock salt brine. Respectively, the solutions were referred to as: water, NaCl, gypsum, and brine. The solutions were replaced every 10 cycles. The rock salt brine contained particles that settled out of solution, and the brine was stirred before returning samples to the brine. Upon removal from rock salt brine the top of the samples retained some settled particles during the drying stage of the cycle.

The wet-dry test took place in a shrinkage room maintained at 50% RH and 73°F. Prisms were immersed in solution for 96 hours and dried for 72 hours. Prisms were measured for length change, mass, and relative modulus within the last two hours of the drying period.

Limestone Prism Wet-Dry Test

Saw cut limestone prisms were also subjected to isothermal cycles of wetting and drying in salt solutions. Gauge pins were inserted into the prism ends for length comparator measurements. To insert the pins, holes were drilled into the ends of the limestone. The interior of the holes were then roughened up with steel wool and cleaned with compressed air. Gauge pins were then placed into the holes using epoxy to secure them.

Prisms were oven-dried at 122°F until constant mass and stored in an environmental chamber maintained at 73°F and 50% RH for nine days before starting the wet-dry test. Prisms were placed in the same four solutions as the concrete wet-dry test. Forty-eight prisms were subjected to the test with three different prisms from each of the four limestone sources for each solution. For the first 25 cycles, the wet-dry cycles consisted of 24-hour immersion followed by 24 hours of drying. The duration of the wetting and drying periods were respectively changed to 96 and 72 hours for the next 25 cycles, as the first 25 cycles produced negligible damage. The solution was replaced after the first 25 cycles were completed and then replaced after every 10 cycles. Similar to the concrete test, the rock salt brine contained particles that settled out of solution. The brine was stirred at the start of the wet stage of the cycle, causing particles to be retained on top of limestone prisms during the drying stage.

Limestone Prism Freeze-Thaw Tests

Two freeze-thaw test procedures were attempted using limestone prisms.

Limestone Prism Critical Degree of Saturation

Limestone prisms were vacuum-saturated, dried to varying degrees of saturation, and exposed to freeze-thaw cycles after the manner of Li et al. (2012). Prisms were oven-dried at 176°F until constant mass and then stored at 73°F and 50% RH for 24 hours. At this time, the prisms were measured for oven-dry mass and relative modulus. The prisms were then placed in a vacuum desiccator maintained at 0.6 psi for three hours to draw air out of the prisms. Distilled water was introduced into the desiccator while maintaining vacuum. When the prisms were completely immersed, the water flow into the desiccator was stopped. Vacuum pressure in the desiccator was maintained for an additional 24 hours before introducing air back into the desiccator.

After saturation, prisms were towel-dried to SSD and measured for mass. Based on this measurement, prisms were allowed to dry at 73°F and 50% RH until the appropriate degree of saturation was reached. Prisms at the higher degrees of saturation (e.g. 95) very rapidly dried so were stored the lab room containing the desiccator. When the appropriate degree of saturation was reached, the prisms were wrapped in plastic wrap and sealed in plastic tubing to prevent water loss. Prisms were then subjected to 10 freeze-thaw cycles in which the prisms were placed in a 0°F freezer for 12 hours, followed by 12 hours in a shrinkage room maintained at 73°F. At the end of the last freeze-thaw cycle, the prisms were removed from plastic and oven-dried at 176°F. Prisms were then stored at 73°F and 50% RH for 24 hours after which time final mass and relative modulus readings were taken.

Limestone Prism Freeze-Thaw Test in Salt

The second freeze-thaw test procedure subjected prisms to freeze-thaw cycles while immersed in 1% by weight rock salt brine. Ten L4 limestone prisms were oven-dried at 176°F then stored in a desiccator containing a silica desiccant packet at room temperature until the test was started. Prisms were placed on a plastic grid (cut from a plastic light diffuser) in a five-gallon bucket and then enough salt solution to completely immerse the prisms was added to the bucket. The bucket was sealed and placed in the solution for 24 hours at 73°F before starting freeze-thaw cycles. Prisms were subjected to five freeze-thaw cycles alternating between 48 hours at 0°F and 48 hours at 73°F.

Concrete Batching

Concrete was batched using a pan mixer with a capacity of two cubic feet. For consistency, fine aggregate was oven-dried and coarse aggregate towel-dried to a saturated-surface-dry condition before batching. The batch water amount was adjusted based on the aggregate moisture conditions. The batching procedure followed the steps of ASTM C192 (2008a). Batching proceeded as follows:

1) Air-entrainment agent added to the mixing water.
2) Coarse aggregate added to the mixer

3) Began mixing
4) Fine aggregate added
5) Cement added
6) Mixing water added
7) Concrete mixed for three minutes
8) Mixing stopped for three minutes
9) Concrete mixed for two minutes

Except for the L4 wet-dry prisms which were consolidated by using a vibrator, concrete samples were consolidated by rodding. After casting, samples were moist cured in prism molds for 24±4 hours by covering the prisms with a layer of damp burlap and a plastic sheet. Prisms were then de-molded and placed in a fog room for moist curing.

ASTM C666 Testing

Freeze-Thaw Machine

The freeze-thaw machine used to conduct freeze-thaw testing had a capacity of twenty 3x4x16 in. concrete prisms in either method A or B of ASTM C666. For both methods, the chamber was free of water during the freeze stage of the cycle and flooded with water during the thaw stage. To run ASTM C666 method A, concrete prisms are placed in plastic sample containers designed to surround 3x4x16 in. prisms with a water layer between 1/32 and 1/8 in. thick (ASTM 2008b). The containers are open at the top so when the chamber is flooded with water during the thaw stage, the thaw water mixes with water in the sample containers.

The chamber contained 20 sample slots, two containing samples with embedded thermocouple wire to control chamber operation. All slots were filled for either testing method. When half-immersed samples were placed in the chamber, all samples were half-immersed. If sufficient test samples were not available, old test specimens were inserted to maintain consistent chamber conditions.

Data Measurement

Freeze-thaw prisms were measured for mass, expansion, and transverse frequency to monitor deterioration. Expansion was measured by comparator measurements, using an invar reference bar. Transverse frequency was measured using a James E-Meter Mk II.

Data Calculations

Transverse frequency of freeze thaw prisms was used to calculate the relative modulus and durability factor according to equations in ASTM C666 (2008b). The relative modulus was calculated according to Equation 1.

$$Relative\ modulus\ (\%) = \frac{({n_x}^2)}{({n_i}^2)} * 100$$ **Equation 1**

Where: n_x = Transverse frequency at freeze-thaw cycle x

n_i = Initial transverse frequency

Durability factor was calculated according to Equation 2.

$$Durability\ Factor = \frac{RM}{M} * N$$ **Equation 2**

Where: RM = Relative modulus after the last freeze-thaw cycle

N = Total number of freeze-thaw cycles completed

M = Specified number of freeze-thaw cycles for the test

Prisms were subjected to 300 freeze-thaw cycles, which was the value used for M. N was considered to be 300 cycles or the cycle at which the relative modulus dropped below 60%. Linear interpolation was used to calculate the relative modulus at exactly 300 cycles or the cycle at which the relative modulus was 60%.

Length change was calculated according to Equation 3 from ASTM C666 (2008b).

$$Length\ Change\ (\%) = \frac{(l_x - l_0)}{(l_g)} * 100$$ **Equation 3**

Where: l_x = Comparator reading at cycle x

l_0 = Initial comparator reading

l_g = Gauge length

Gauge length was 14 inches as the prisms were cast in 3x4x16 in. molds using recessed gauge pins.

Curing Procedure of Concrete Freeze-Thaw Specimens

Per KTMR-22, concrete prisms were cured for 90 days prior to the start of freeze-thaw cycling according to ASTM C666. Prisms were moist-cured for one day in molds and then for

66 days in a fog room. Prisms were then placed in a shrinkage room maintained at 73°F and 50% RH for 21 days, followed by full immersion in room-temperature water for 24 hours and an additional 24 hours in approximately 40°F water. Initial prism measurements were taken and the prisms were subjected 300 freeze-thaw cycles (KDOT 2006).

Salt-Treated Aggregates

Coarse aggregates were subjected to five cycles of wetting and drying in salt solution before use in concrete prisms similar to the method of Dubberke and Marks (1985). Cycles consisted of 24-hour immersion in salt solution, followed by 24 hours of drying in an oven at approximately 230°F. Rather than using saturated NaCl solution, 23% rock salt brine was used to determine if impure salt had a noticeable influence on the ASTM C666 results. After the salt-treatment, aggregates were placed in a wire basket through which water was run for 30 seconds. The wire basket was agitated while rinsing to ensure all aggregates were washed. Following rinsing, coarse aggregates were towel-dried to SSD.

Concrete prisms for ASTM C666 method B testing were then cast, using the mix design in KTMR-22, as given in Table 3-4 (2006). Prisms were cured as described in "Curing Procedure of Concrete Freeze-Thaw Specimens" and then subjected to freeze-thaw cycling according to ASTM C666 method B for approximately 300 freeze-thaw cycles (ASTM 2008b). The freeze-thaw machine was set to conduct one freeze-thaw cycle in three hours, lowering sample temperature from 40°F to 0°F in 110 minutes and raising the temperature back to 40°F in 70 minutes.

Half-Immersion in Salt Solution

In the half-immersion method concrete prisms were cast and cured according to standard KTMR-22 procedure (2006). These prisms were subjected to ASTM C666 freeze-thaw testing while half-immersed in 3% by weight salt solution. Time and temperature profile of the freeze-thaw chamber was determined according to ASTM C666 method A requirements (2008b).

Salt solution

The salt solution used in the test was made by diluting 23% by weight rock salt brine down to 3% by weight. The 23% brine was made with distilled water according to the procedure previously described and its concentration was verified using a salt hydrometer. Distilled water and 23% brine were combined to form a 3% by weight solution, determining the concentration by measurement with the salt hydrometer. The solution was stored in a sealed five gallon bucket and stored in a chest freezer maintained at approximately 40°F so solution replacement would not raise concrete prism temperature.

Prism immersion

Prisms were placed in plastic sample containers provided by the manufacturer of the freeze-thaw machine. Containers were designed for the 3x4x16 in. prisms for use in ASTM C666 method A (2008b). Prisms were placed in these containers and salt solution added to approximately mid-height on the prisms. The solution was replaced whenever the prisms were removed from the plastic containers for measurement.

Sample sealing

The freeze-thaw machine used in the study flooded the chamber containing the concrete prisms with water during the thaw stage and then drained the water so that the chamber was water during the freeze stage. To prevent dilution of the salt solution surrounding the prisms as well as prevent the salt solution from corroding elements of the freeze-thaw machine, samples were sealed with plastic for approximately the first 60 freeze-thaw cycles.

Plastic tubing was used to create a water-proof top on the container. The base of the tubing was attached to the container using tape. Two layers of tubing were used in case of leaks. This method proved cumbersome, particularly for thermocouple blocks, due to the added difficulty of creating a leak-proof seal around the thermocouple wire. This method was abandoned in favor of raising the top of the samples above the water level during thawing.

Raising samples

After consulting with David Berger (ScienTemp Production Engineer, personal communication, May 2013), it was determined that raising the samples would prevent the salt solution from mixing with thaw water without sealing the tops of sample containers. The metal frame holding the concrete samples was raised such that the water level during the thaw stage remained below the top of the plastic sample containers. This was accomplished by inserting small pieces of solid plastic beneath the metal frame corners. Raising the samples eliminated the need to seal containers with plastic.

Leaving the sample containers open allowed evaporation of salt solution. Evaporation was noticeable in the thermocouple blocks since initially additional solution was not added to these samples every time the freeze-thaw chamber was opened for sample measurement. When solution evaporation from thermocouple samples was noted, additional solution was added. No obvious drop in solution level for the test specimens was observed, but this was not measured. The open container also allowed the top of the specimens to dry out, possibly reducing damage in the un-immersed portion of concrete samples.

Time and temperature profile

The half-immersion method deviates from the standard ASTM C666 procedures and required adjustment to machine operation to reach a time and temperature profile that would subject the prisms to the correct thermal variations (2008b). The first successful profile required nearly five hours to complete a freeze-thaw cycle. Through program adjustments this was reduced to four and one-half hours. David Berger of the freeze-thaw chamber manufacturer gave essential aid in formulation of a correct program (ScienTemp Production Engineer, personal communication, May 2013).

The time and temperature profile are given in Figure 4.1. Temperatures are the program set-points to which the machine is programmed in order to adjust the concrete sample temperature to reach throughout one freeze-thaw cycle. The machine was designed to freeze with the thaw water drained, so for the machine was set to drain thaw water from the chamber during the last 15 minutes of the thaw cycle (David Berger, ScienTemp Production Engineer, personal communication, May 2013).

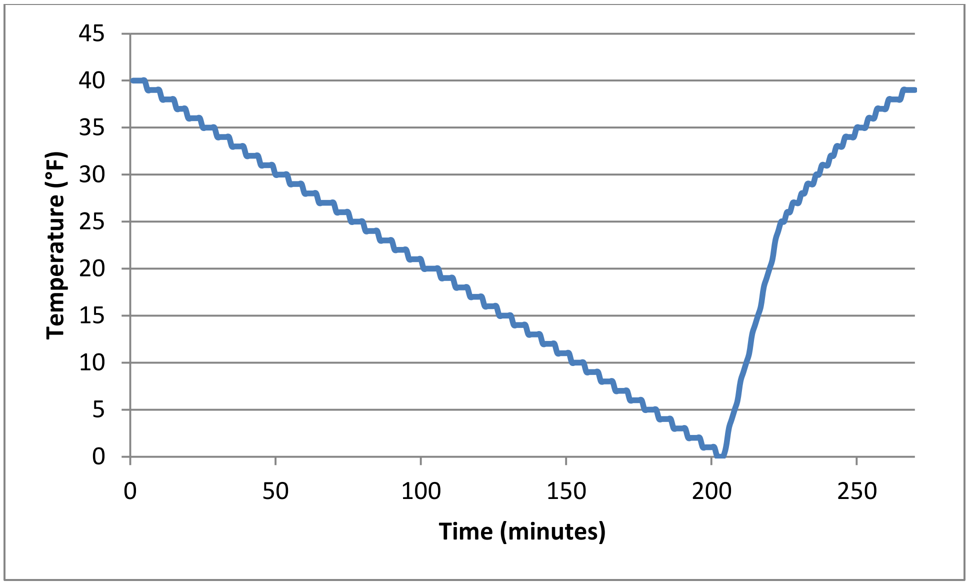

Figure 4.1: Time and Temperature Profile for ASTM C666 Method A

Initial test conditions

The first six sets of half-immersion prisms, consisting of L2, L3, L4, L5, L6, and L7 prisms, were subjected to freeze-thaw cycling of various durations. Prisms were subjected to the 300 freeze-thaw cycles where low and high temperature points were reached, but they were also subjected to additional cycles where either low or high temperature points were not reached. These additional cycles were the result of a trial and error process used to develop the final time and temperature profile. L5, L6, and L7 prisms were added two days later than L2, L3, and L4 prisms, so exposure conditions were not entirely uniform for both aggregate sets, though the difference was slight. Also, for approximately the first 60 freeze-thaw cycles, L2, L3, L4, L5, L6, and L7 prisms were sealed in plastic as described in “sample sealing,” therefore, results comparison with other samples is questionable due to exposure conditions during freeze-thaw testing.

Chapter 5 - Results

Rock Salt Analysis Results

Rock Salt X-ray Diffraction Patterns

X-ray diffraction patterns of various samples are shown in Figure 5.1 which shows the intensity in counts per second (cps) vs. 2θ angle. Patterns generally are similar to the USP grade NaCl sample, though variations in size and distribution of peaks indicate the presence of impurities. Of particular interest is the pattern labeled “Brine Residue.” This pattern departs significantly from the USP grade sample and may indicate that impurities in the rock salt are more apt to stay in residue than to dissolve into brine.

Proprietary PDXL analysis software package controlling the diffractometer was used to analyze patterns for phases present. The software package automatically searches for compounds that may be present in a sample based on comparison of stored diffraction patterns. The software assigns a Figure-of-Merit (FOM) value for each phase, indicating quality of match. The lower the FOM, value the more likely it is that the phase is present in the sample. For sample analysis, the software was used to search for inorganic compounds potentially in the sample containing one or more of the following elements: sodium, calcium, magnesium, hydrogen, sulfur, oxygen, and chloride. This search generated a list of possible phases in each sample. Theoretical peak patterns of possible phases were then visually compared to the sample pattern to verify quality of the match.

Halite (NaCl) was present in all samples. A calcium sulfate phase was also indicated by the software as a possible phase in all samples except the Independence, Manhattan, Phillipsburg, Pratt, and ACS grade NaCl samples. Theoretical peak pattern for anhydrite ($CaSO_4$) indicated its principal peak is around 25.5 degrees two theta. A peak exists at that location for all rock salt samples tested, though its prominence varies. This particular peak is most prominent in the brine residue sample and least prominent in the Belleville sample.

Other phases such as hydrogen chloride or sodium chlorate (VII) were generated by the software as potential phases, typically with higher FOM values than NaCl or $CaSO_{4,}$ indicating a less likely match. Phases other than NaCl or $CaSO_4$ were determined to not be present as the principal peaks were either not present in the sample pattern or they lined up with peaks found in the NaCl or Ca_2SO_4 pattern.

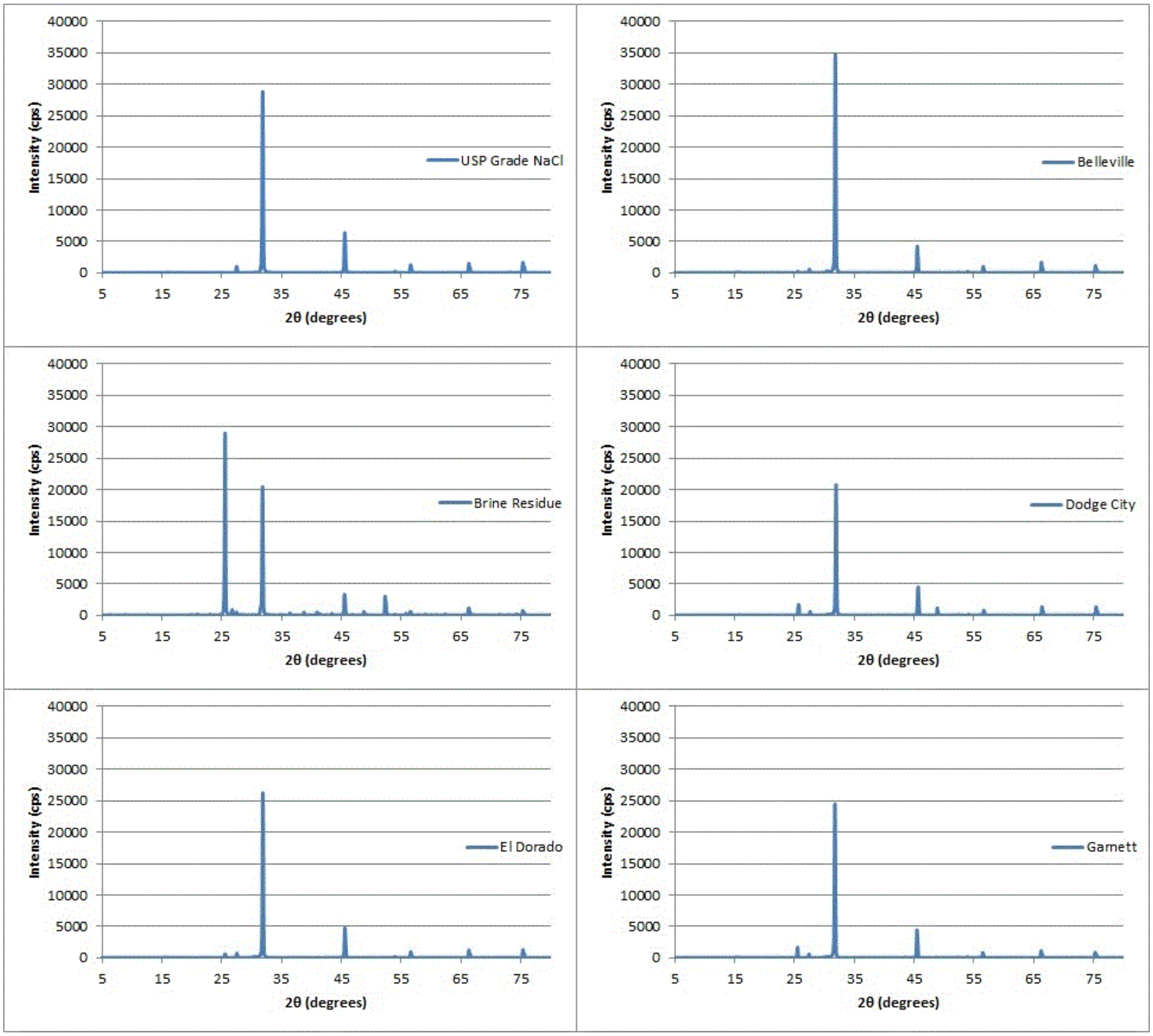

Figure 5.1a: First Six Rock Salt Diffraction Patterns

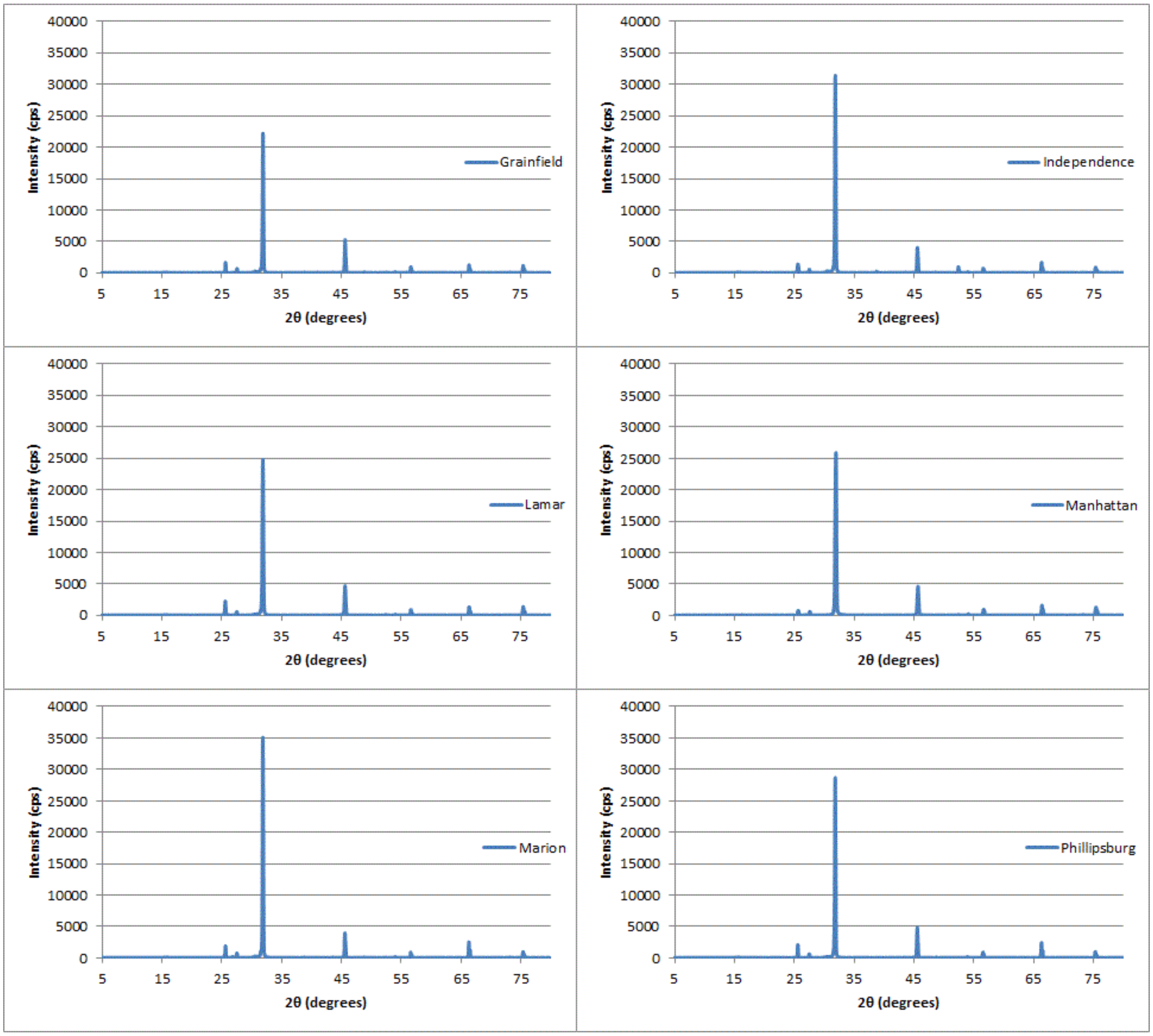

Figure 5.1b: Second Six Rock Salt Diffraction Patterns

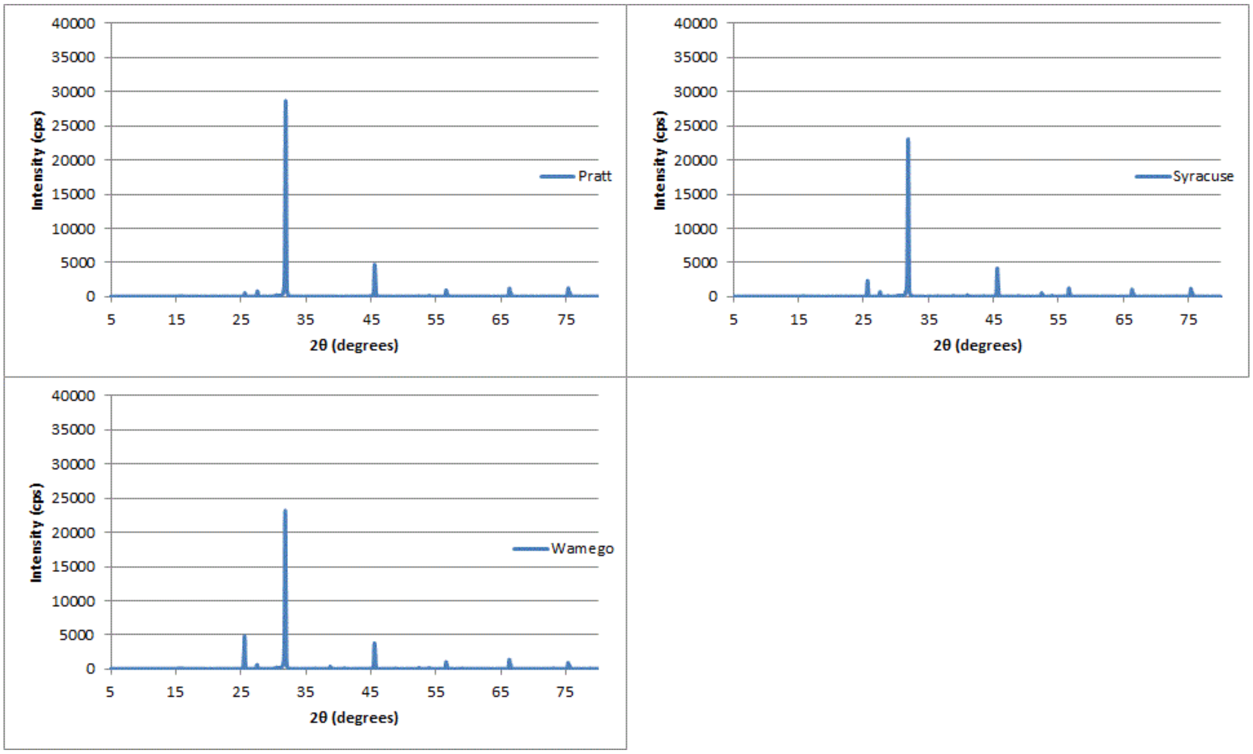

Figure 5.1c: Last Three Rock Salt Diffraction Patterns

ICP Analysis Results

Results of KDOT's ICP analysis of rock salt samples are given in Table 5-1. These results show varying amounts of sulfur, calcium, and magnesium in the salt and the variation is less than 1% between all samples. The Independence sample contained almost 1% magnesium, though XRD analysis only identified NaCl in the sample pattern. In this case, XRD analysis software search for the Independence sample did not generate other potential phases.

Table 5-1: KDOT ICP Analysis Results

Source	Chloride (%)	Chloride as NaCl (%)	Sodium (%)	Sodium as NaCl (%)	Sulfur (%)	Calcium (%)	Magnesium (%)
Belleville	57.70	95.08	37.45	95.19	0.58	0.65	0.12
Dodge City	55.62	91.66	36.26	92.18	1.31	1.45	0.14
El Dorado	57.83	95.30	37.75	95.96	0.79	0.91	0.04
Garnett	56.33	92.83	36.64	93.15	1.11	1.25	0.10
Grainfield	56.98	93.90	37.28	94.76	0.76	0.87	0.11
Independence	57.41	94.64	37.12	94.36	1.00	0.99	0.99
Lamar	56.79	93.61	36.94	93.90	0.81	0.92	0.16
Marion	56.91	93.79	37.30	94.82	0.89	1.02	0.10
Phillipsburg	57.02	93.97	36.86	93.69	0.74	0.84	0.12
Pratt	56.83	93.65	37.24	94.66	0.86	0.97	0.14
Syracuse	54.72	90.18	35.87	91.18	1.20	1.32	0.26
Wamego	56.48	93.08	38.03	96.68	0.92	1.05	0.13

ICP results were theoretically compared to the sulfate exposure categories of ACI 318 (2008) based on the amount of sulfate in rock salt solutions of varying concentrations by weight. Sulfur concentrations, given in Table 5-1, were converted to sulfate by multiplying sulfur concentration by the molecular weight ratio of sulfate to sulfur. The sulfate concentration was then multiplied by the amount of solute theoretically in each salt solution, giving sulfate content in grams. Sulfate content in grams was then converted into parts per million (ppm) by dividing the sulfate mass by the total mass of solution and multiplying by 10^6. Results are given in Table 5-2. The assumption that all sulfur in each rock salt sample is present as the sulfate ion may be overly conservative but allows for comparison of rock salt from various locations in Kansas.

According to ACI 318 (2008), moderate sulfate exposure occurs if the water soluble sulfate concentration is between 150 and 1500 ppm and severe exposure occurs between 1500 and 10,000 ppm. Table 5-2 shows that one-third of the rock salt samples contain enough sulfate content to generate a moderate sulfate exposure in a 0.5% by weight rock salt solution. At a 1% rock salt solution, all the samples generate a moderate sulfate exposure. At 23%, all rock salt samples generate a severe sulfate exposure.

Table 5-2: Theoretical Sulfate Content in Rock Salt Solutions of Varying Concentration

Source	Sulfate concentration (%)	Sulfate Content in 23% Solution (ppm)	Sulfate Content in 3% Solution (ppm)	Sulfate Content in 1% Solution (ppm)	Sulfate Content in 0.5% Solution (ppm)
Belleville	1.74	3996	521	174	87
Dodge City	3.92	9026	1177	392	196
El Dorado	2.37	5443	710	237	118
Garnett	3.33	7648	998	333	166
Grainfield	2.28	5236	683	228	114
Independence	3.00	6890	899	300	150
Lamar	2.43	5581	728	243	121
Marion	2.67	6132	800	267	133
Phillipsburg	2.22	5099	665	222	111
Pratt	2.58	5925	773	258	129
Syracuse	3.59	8268	1078	359	180
Wamego	2.76	6339	827	276	138

Wet-Dry Test Results

Wet-dry test results showed noticeable surface damage to specimens in salt, though internal damage to the specimens was not observed in length change measurements in concrete or limestone prisms. Relative modulus measurements of concrete prisms also did not indicate internal damage.

Concrete Wet-Dry Test

Concrete prisms made using L3 and L4 coarse aggregates were subjected to 40 wet-dry cycles in salt solutions. Photographs of the prisms before and after testing are shown in Appendix B. The average relative modulus, length change, and mass change of L3 concrete prisms during cycling are given in Figure 5.2, Figure 5.3, and Figure 5.4, respectively. The average relative modulus, length change, and mass change of L4 concrete prisms are given in Figure 5.5, Figure 5.6, and Figure 5.7, respectively. Each data point represents an average of two prisms, each measurement taken during the last two hours of the drying cycle. Length and mass change were negligible for concrete prisms regardless of solution or coarse aggregate type.

Relative modulus values increased and then remained constant, reflecting continuing hydration of cement. Relative modulus values did varied for L4 prisms in NaCl, but this was reflective of inconsistent readings from one specimen rather than damage. Aside from L4 prisms in NaCl, for each aggregate type relative modulus values for were within 4% of each other throughout the test.

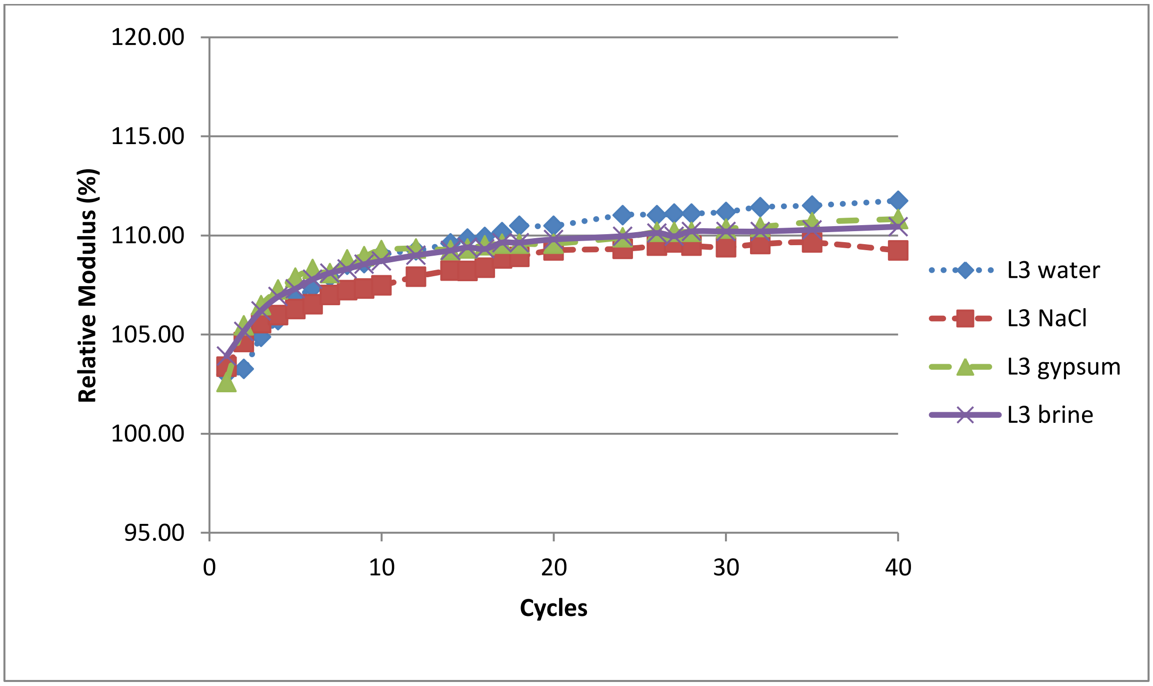

Figure 5.2: Average Relative Modulus of L3 Concrete Prisms

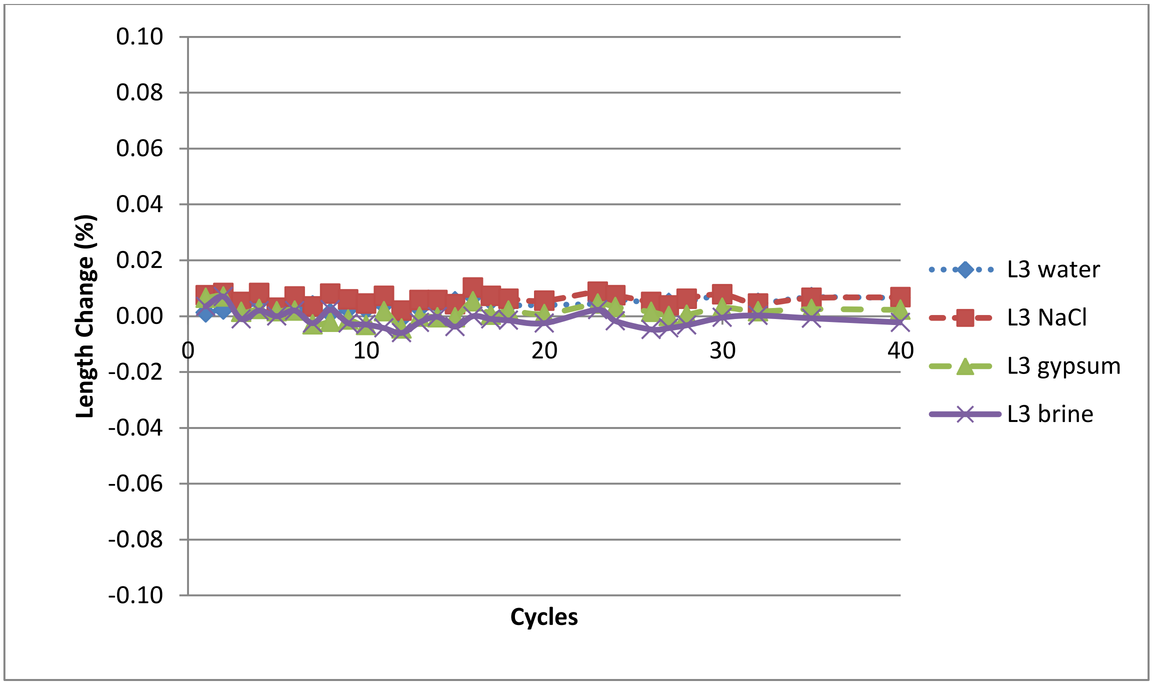

Figure 5.3: Average Length Change of L3 Concrete Prisms

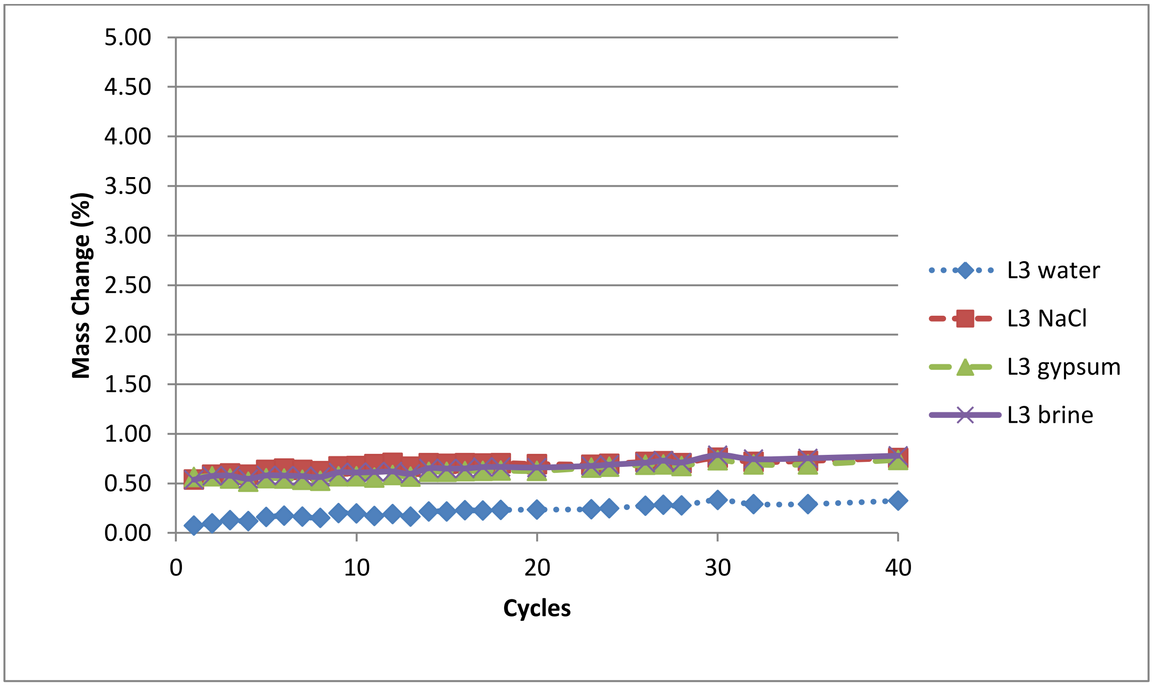

Figure 5.4: Average Mass Change of L3 Concrete Prisms

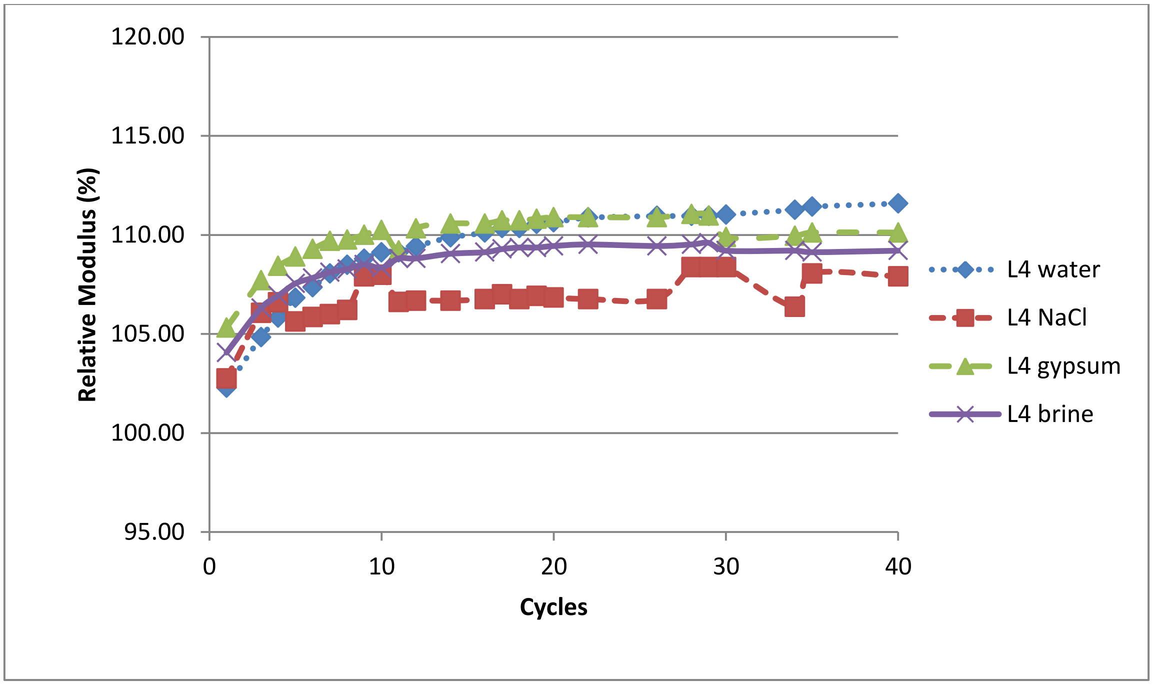

Figure 5.5: Average Relative Modulus of L4 Concrete Prisms

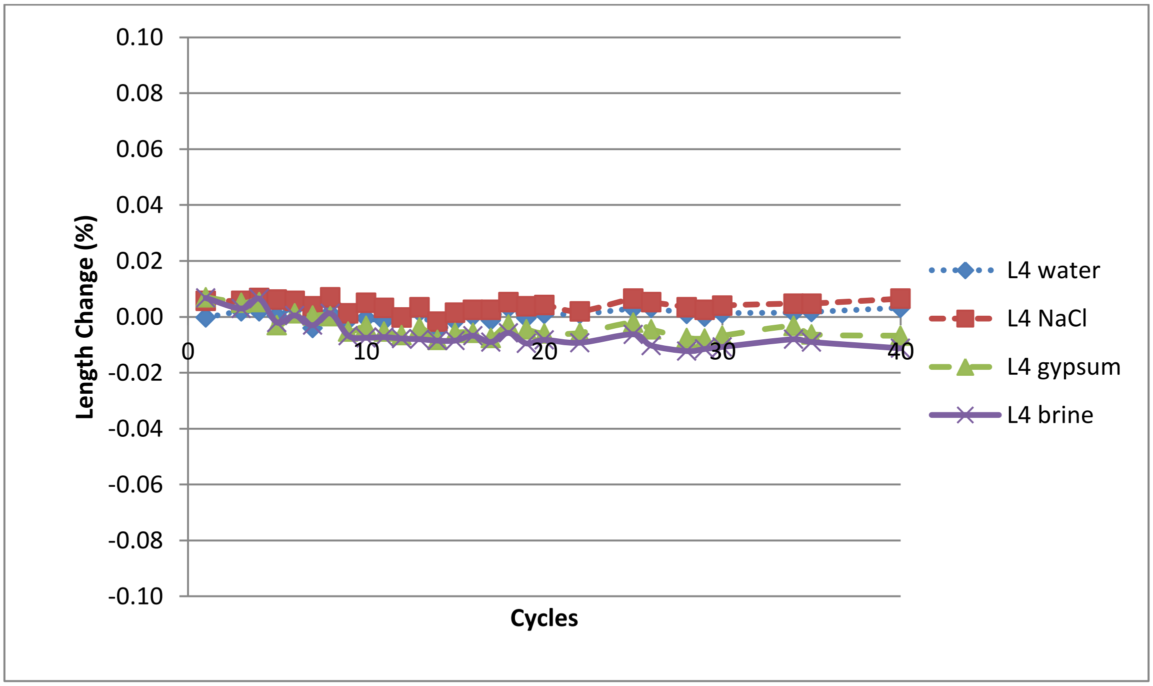

Figure 5.6: Average Length Change of L4 Concrete Prisms

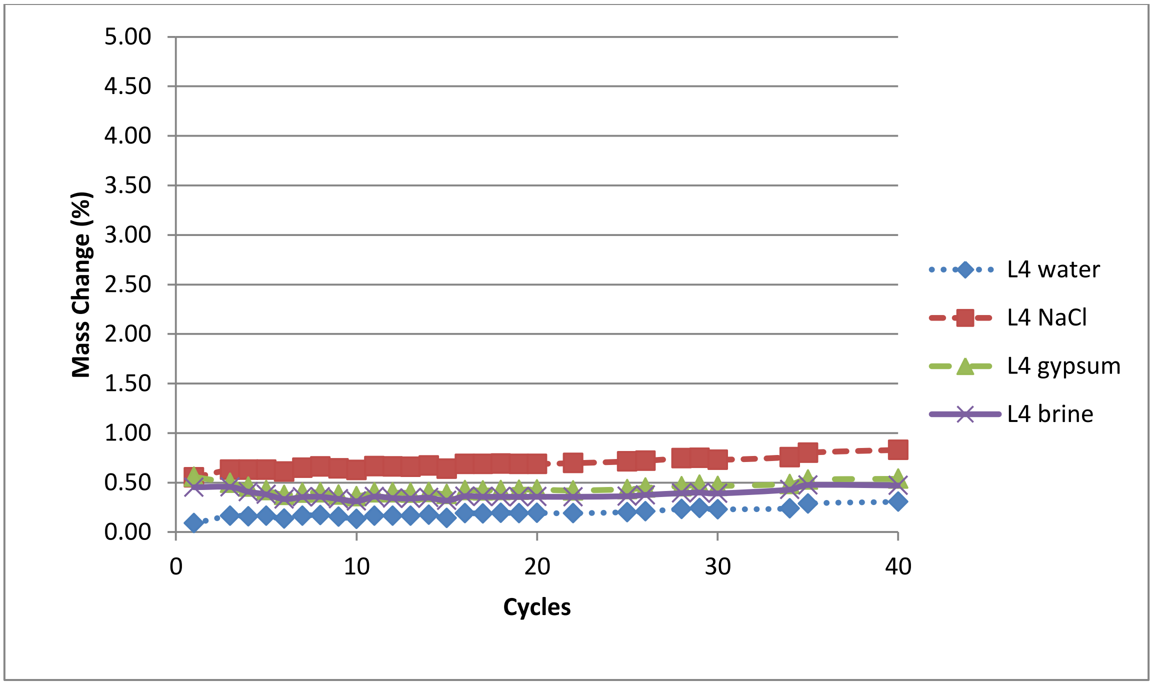

Figure 5.7: Average Mass Change of L4 Concrete Prisms

Limestone Prism Wet-Dry Test

Average length change for limestone prisms is given in Figure 5.8 through Figure 5.11 and average mass change is given in Figure 5.12 through Figure 5.15. Each data point represents the average of three prisms with four exceptions. Two exceptions are length change data for L1 and L2 prisms in water, which average of two prisms since one L1 prism broke during the oven-drying process and one L2 prism was too fractured to drill holes for gauge pins. The other two exceptions are length and mass change for L3 prisms in NaCl from cycles 46 to 50 because one prism was dropped and broke at the start of the 46th cycle. Photographs of the prisms before and after testing are given in Appendix A.

Length change data only starts from cycle 11 because the method of length measurement was changed at that point. Initially, prisms were measured by placing the sample in the comparator and taking a reading without rotating the sample, relying on consistent prism placement for accuracy. Beginning in cycle 11, samples were placed in the comparator, rotated 360 degrees, and the lowest comparator reading was taken as the measurement. For both measurement methods, the comparator was set to zero using an invar rod that was rotated 360 degrees, and the lowest comparator reading set as the zero measurement.

Variation in average length change is minimal with variations possibly due to the method of measuring expansion rather than damage from salt weathering. Gauge pins used to measure expansion were set in holes with epoxy and the holes were drilled into the limestone so the pins were not perfectly aligned, causing alignment of the longitudinal axis of the limestone prism to vary as the prism was rotated in the comparator. This factor alone is likely insufficient to explain the variation, but the comparator used was adjustable to accommodate prisms of different lengths, and the comparator was adjusted during wet-dry testing to measure both concrete and limestone prisms which were different lengths. Because of adjusting the comparator, exact alignment of the limestone prism could change depending on adjustment of the comparator, possibly affecting the measurement. Prism flaws and comparator adjustment would be sufficient to cause the observed length change, particularly as values were entirely within ±0.02%. Also, length change measurements for all four limestone prism types show peaks at roughly cycles 27 and 38, suggesting variation from the measurement procedure rather than damage from salt solution.

One L1 prism in brine contracted 0.07% at cycle 24, causing noticeable contraction in average length change for L1 prisms in brine at cycle 24, as shown in Figure 5.8. Subsequent measurements of this prism remained within ±0.02% of this amount, suggesting change came from mishandling of the specimen (though it is unclear what may have caused the change) rather than salt weathering. Contraction of this specimen accounts for the apparent contraction of L1 prisms in brine, as seen in Figure 5.8.

Mass change data shows slight loss in mass, particularly after cycle 25 when cycle duration was increased. The noticeable drop in mass change after the 25th cycle is due to increased cycle length which allowed the samples to lose more water during drying. The drop in mass change for L1 prisms in brine at cycle 31 is due to the loss of a fragment from one of the three samples during handling. The sharp drop at cycle 46 for L3 prisms in NaCl is due to breaking of one of the samples, as mentioned previously.

Overall scaling was observed only the salt solutions. During wet-dry testing two large fragments detached from two L1 prisms: one during the first immersion cycle from a sample in NaCl and another prism lost a fragment during cycle 31. The outline of the second fragment in question appeared during the first few cycles, as indicated by crack formation even though the fragment did not break off entirely at that point. Loss of these fragments appeared to be caused by swelling of a clay seam within the limestone prism.

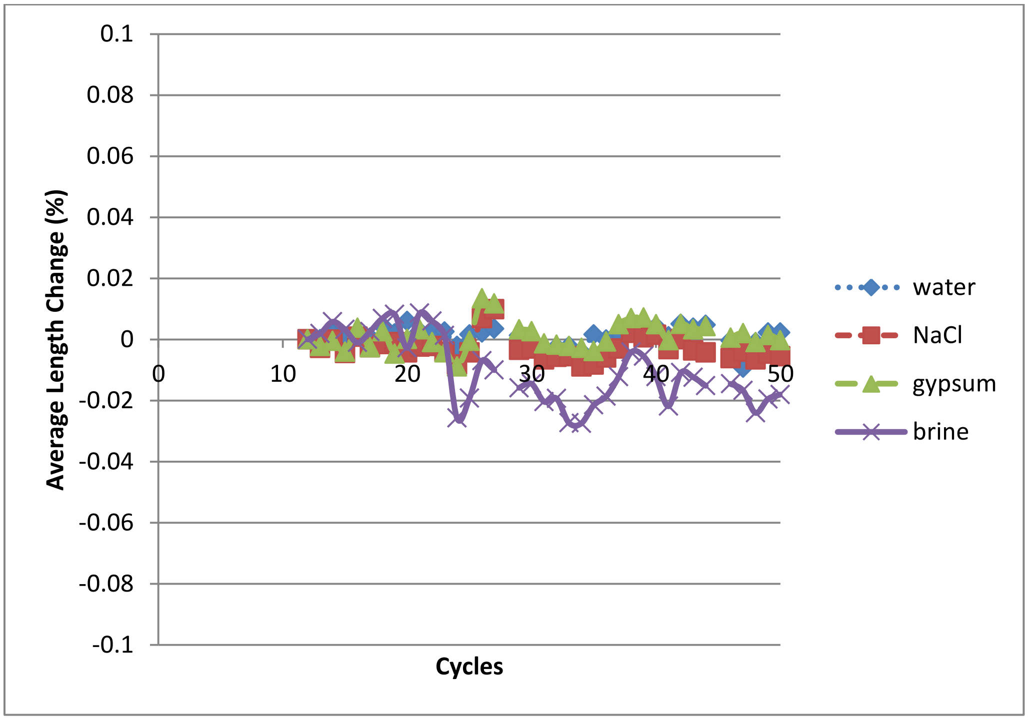

Figure 5.8: L1 Average Length Change

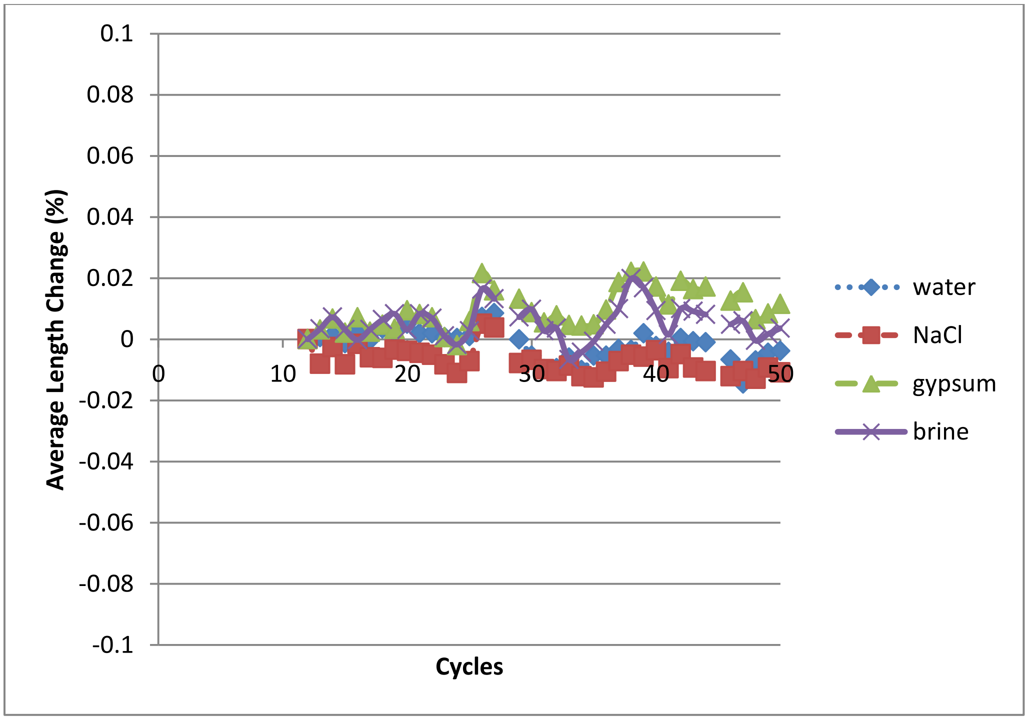

Figure 5.9: L2 Average Length Change

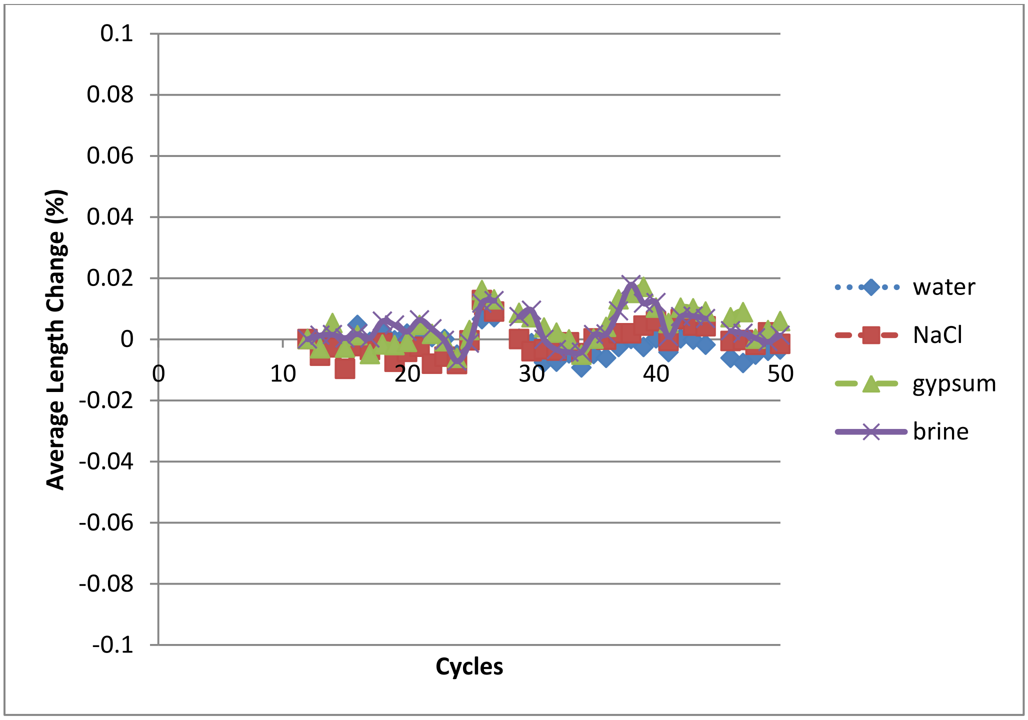

Figure 5.10: L3 Average Length Change

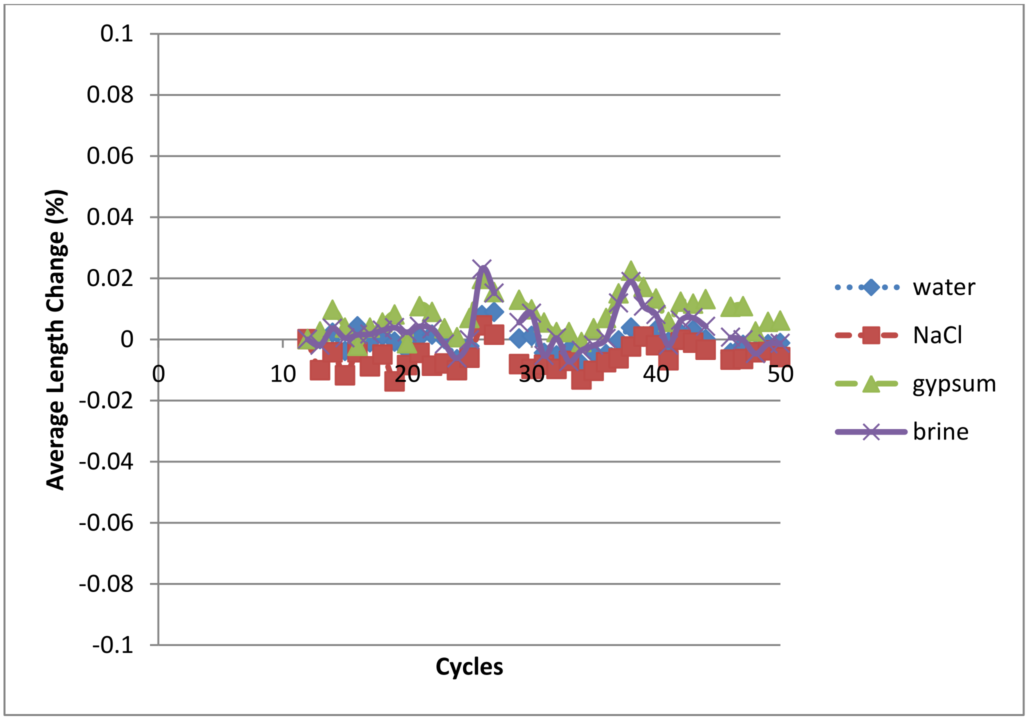

Figure 5.11: L4 Average Length Change

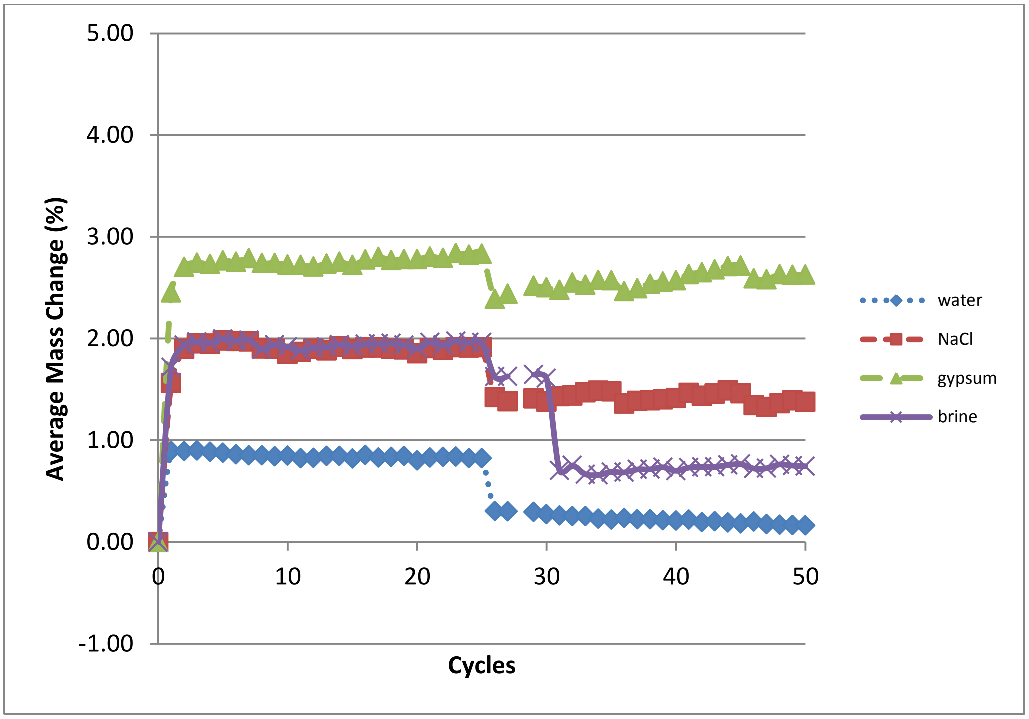

Figure 5.12: L1 Average Mass Change

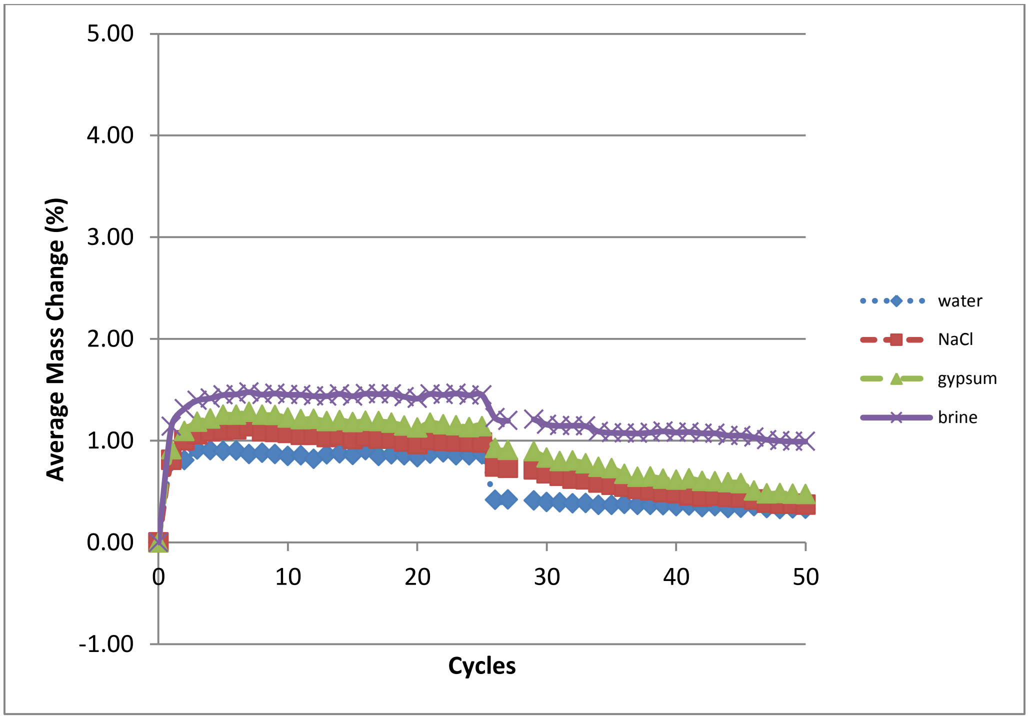

Figure 5.13: L2 Average Mass Change

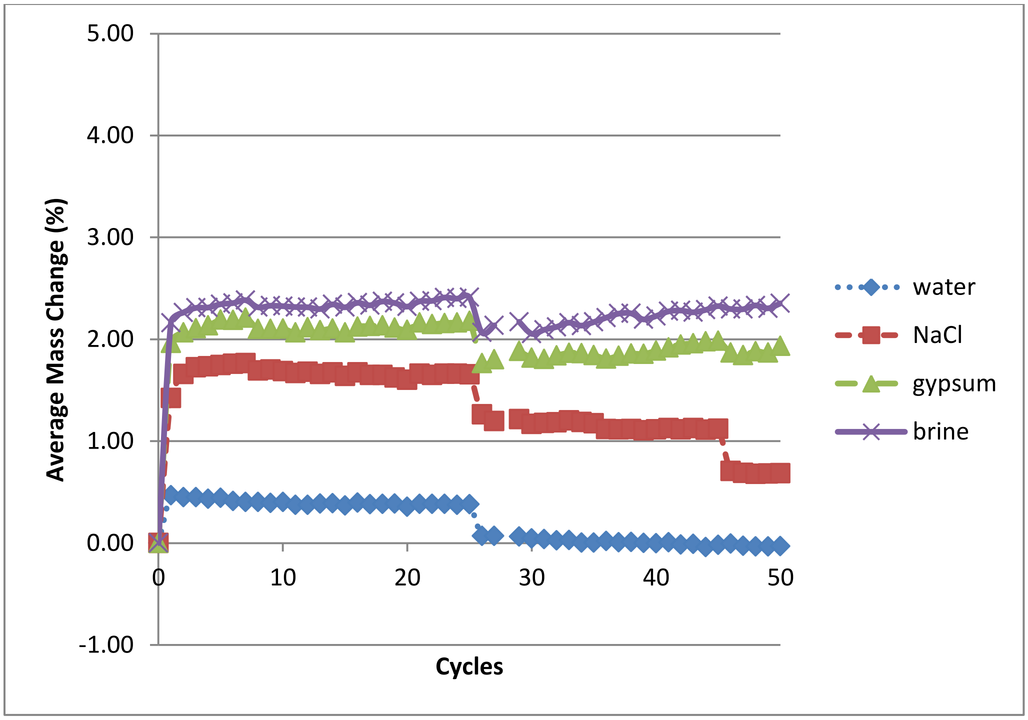

Figure 5.14: L3 Average Mass Change

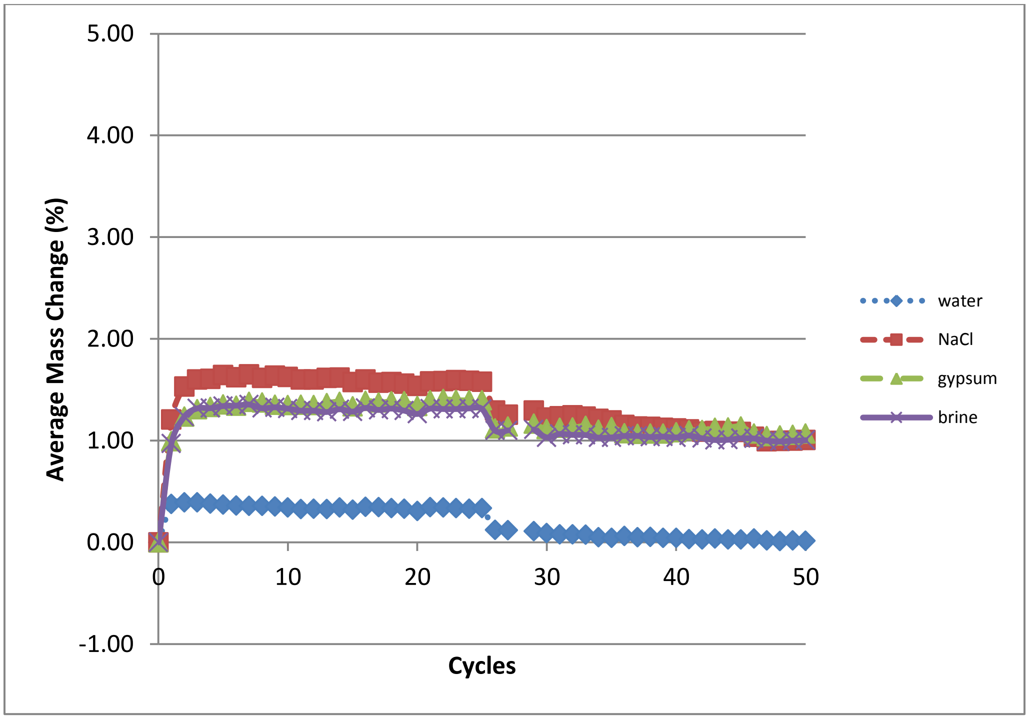

Figure 5.15: L4 Average Mass Change

Limestone Prism Critical Degree of Saturation Test

Visually, no apparent damage in the form of scaling or pop-outs was evident. Figure 5.16 shows results of this test procedure for L4 limestone prisms, using the relative modulus as calculated according to Equation 1. The wide gap in relative modulus for samples of the same limestone and the same degree of saturation indicate that prisms vary too much for the test to yield meaningful results. However, three prisms were cut from one block and showed a trend of decreasing relative modulus with increasing saturation level, as shown in Figure 5.16. Since the other prisms were cut from different blocks and their results do not match, a quality difference based on the block a prism is cut from is indicated. All the prisms from one limestone source would not be expected to respond the same under the same freeze-thaw conditions so a uniform critical degree of saturation for this particular limestone source could not be determined with this test.

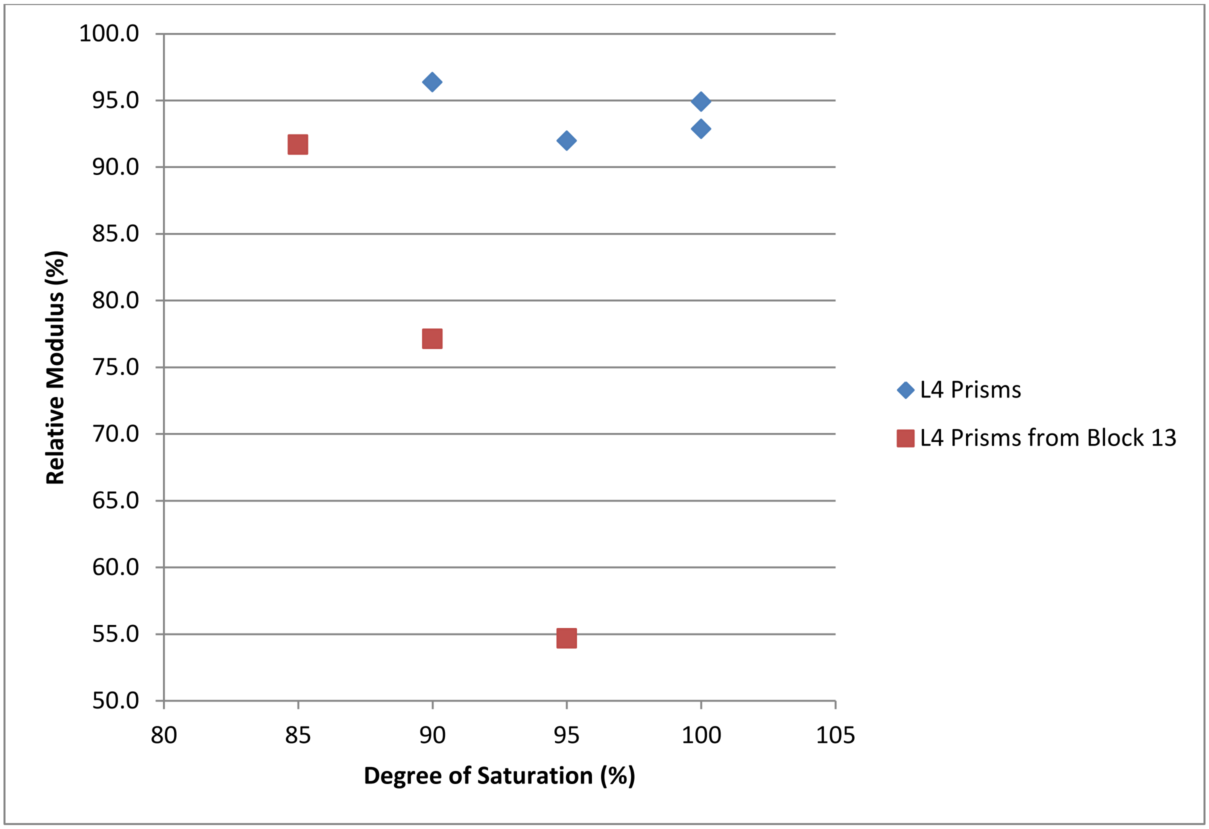

Figure 5.16: L4 Limestone Prism Critical Degree of Saturation Results

Limestone Prism Freeze-Thaw Test in Salt Solution Results

This test produced inconsistent results due to variations in limestone prisms. Ten prisms showed widely varying results, ranging from negligible damage to complete disintegration, even though the source was the same. Cracks in the prisms were exploited by frost action as well as laminations in the limestone. The wide range of results indicates that prisms were too variable for this test to give meaningful results. Figure 5.17 through Figure 5.23 show L4 prisms after test exposure. In the photographs containing eight faces, the four on the left are from before the test and the four faces on the right are corresponding sides after freezing and thawing. Only seven of the ten prisms are shown as the other three completely disintegrated. Figure 5.17 shows one prism that lost its surface during the test and could not be positively identified as three other prisms disintegrated. Therefore, process of elimination could not be used.

Figure 5.17: Unidentifiable Prism After Salt-Frost Exposure

Figure 5.18 shows L4 sample 146 before and after freeze-thaw cycling. Significant material was lost, although in a non-uniform manner. This particular prism was cut so that the exterior of the source rock was very near the sample corner on the right side. Fragmentation that occurred at this location during freezing and thawing may indicate lower stone quality at the stone's surface.

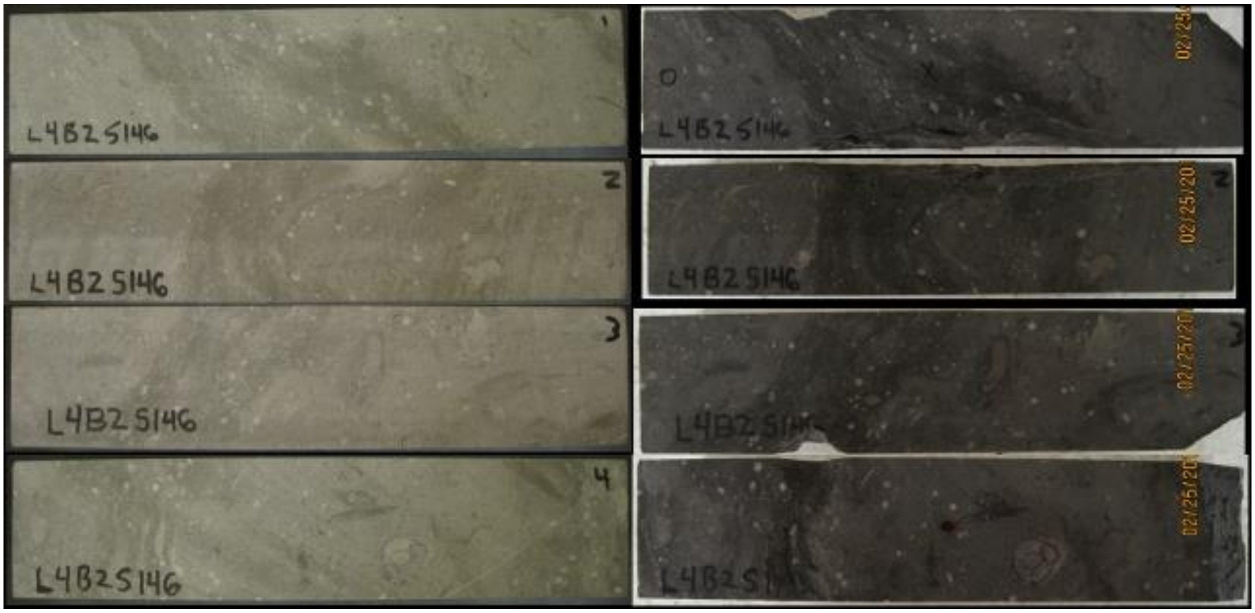

Figure 5.18: L4 Sample 146 After Salt-Frost Exposure

Figure 5.19 shows L4 sample 153 before and after freeze-thaw cycling. Scaling and loss of material is observable, with varying performance over different areas of the prism.

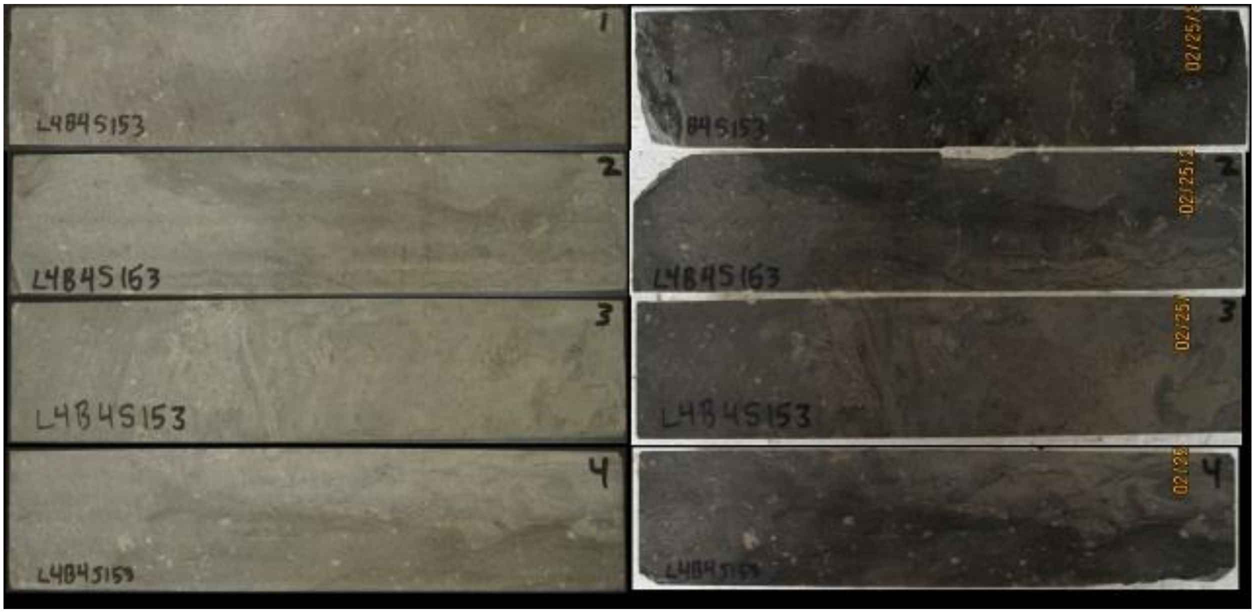

Figure 5.19: L4 Sample 153 After Salt-Frost Exposure

Figure 5.20 shows L4 sample 187 before and after freeze-thaw cycling, showing that some of the sample was susceptible to frost damage.

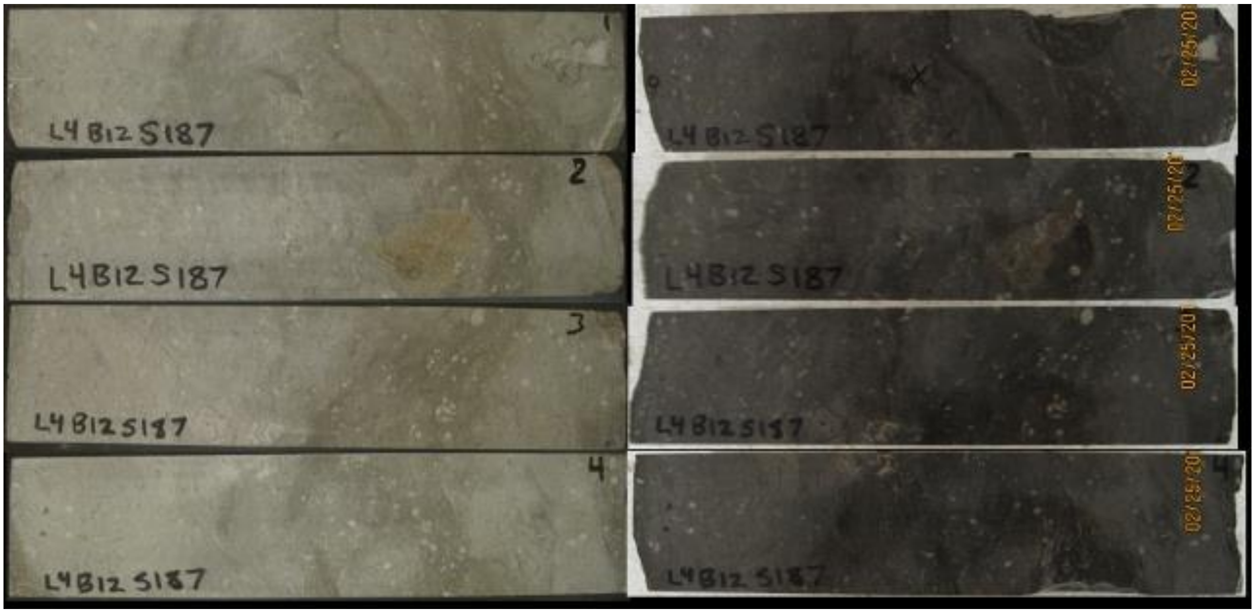

Figure 5.20: L4 Sample 187 After Salt-Frost Exposure

Figure 5.21 shows L4 sample 189. The sample was cut from a rock that was not quite long enough for a perfect 2x2x9 in. prism. The stone split at a visible lamination in the prism.

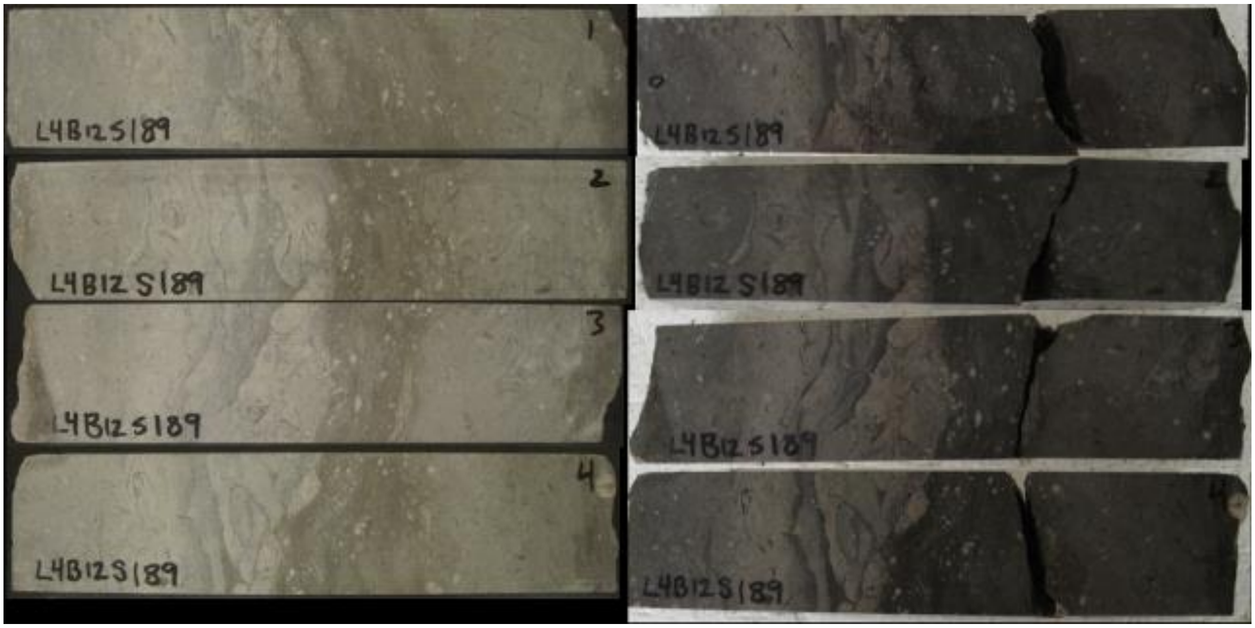

Figure 5.21: L4 Sample 189 After Salt-Frost Exposure

Figure 5.22 shows L4 sample 199, the only prism that showed no visual damage from the test.

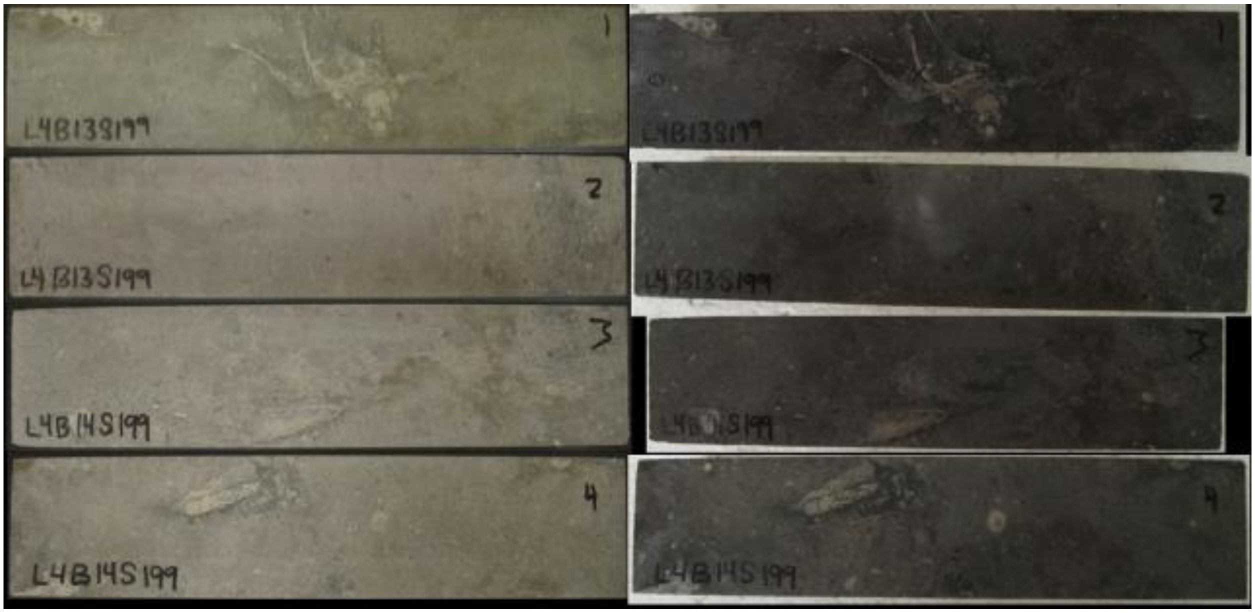

Figure 5.22: L4 Sample 199 After Salt-Frost Exposure

Figure 5.23 shows L4 sample 212, which split along a crack mid-height on the stone. Scaling and fragmentation also occurred in this sample.

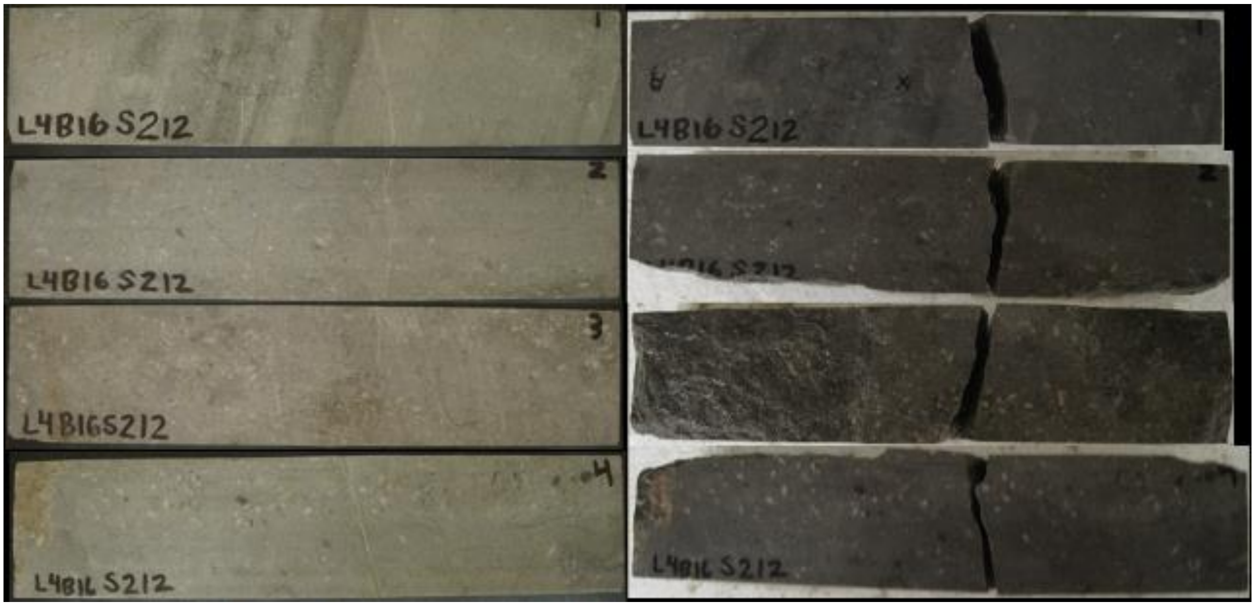

Figure 5.23: L4 Sample 212 After Salt-Frost Exposure

Salt-Treated Aggregate Results

Six coarse aggregate types, L2, L3, L4, L5, L6 and L7, as described in Table 3-1, were treated in salt solution before casting concrete prisms subjected to freeze-thaw testing. Results of the salt-treated aggregate method are shown in Figure 5.24 through Figure 5.27 and contain an average of three prisms per aggregate type. However, length change data for L7-STA prisms averages two prisms, as a gauge pin of one prism fell out during casting. Designations and batch designs for concrete prisms correspond to those given in Table 3-4.

The drop in relative modulus was negligible. Length change values showed some variation, but in light of consistent relative modulus values do not indicate damage to prisms from freeze-thaw action. Mass change, based on comparison to sample mass right before freeze-thaw cycling, was negligible. Durability factors are only given for L2, L3 and L4-STA prisms as L5, L6 and L7-STA prisms were only subjected to 284 freeze-thaw cycles and the durability factor would be misleadingly low.

This test procedure failed to cause significant damage to any concrete prisms, indicating that all coarse aggregates were durable or that the test method failed to degrade frost-susceptible aggregate. The latter is more plausible since at least L2 aggregates were considered frost-susceptible.

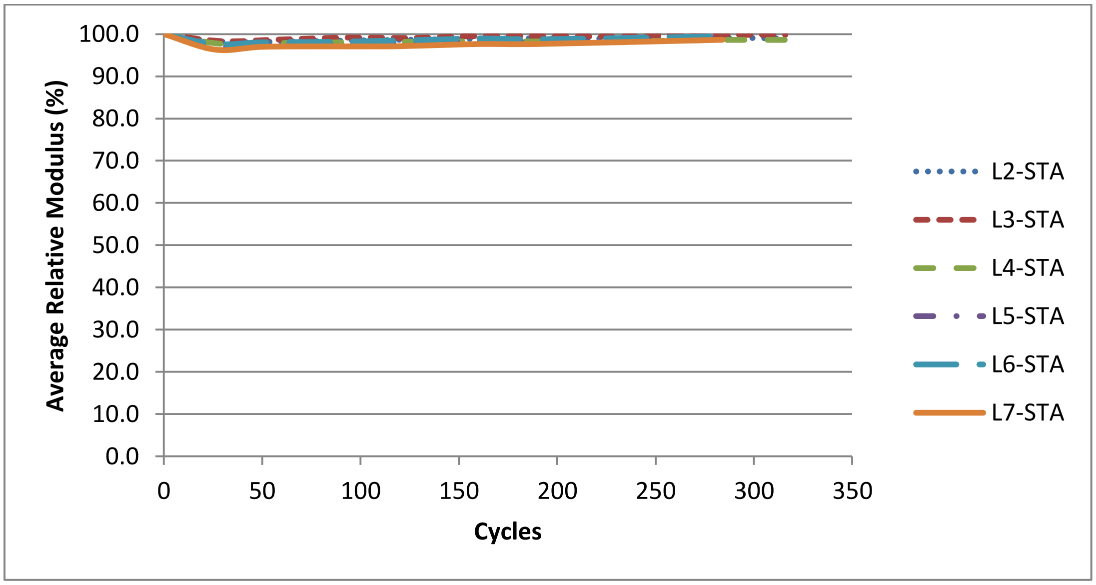

Figure 5.24: Relative Modulus of Salt-Treated Aggregate Samples

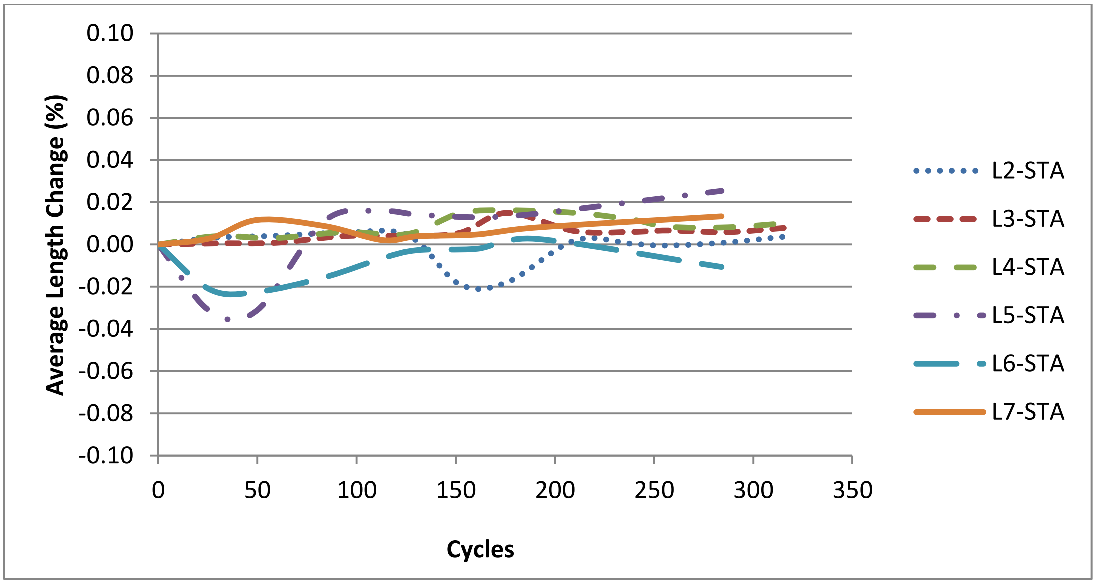

Figure 5.25: Length Change of Salt-Treated Aggregate Samples

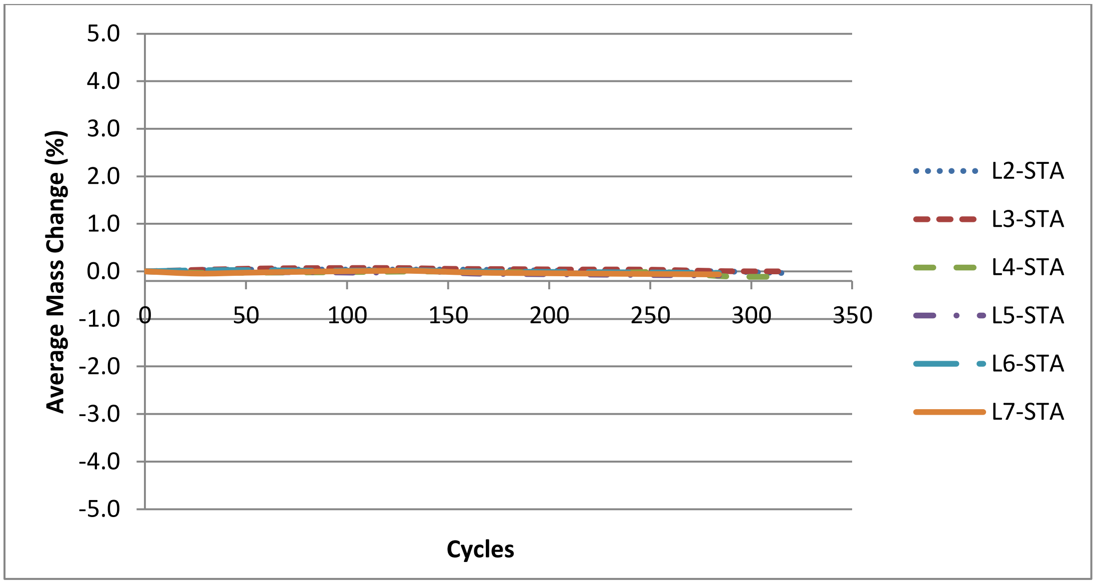

Figure 5.26: Average Mass Change of Salt-Treated Aggregate Samples

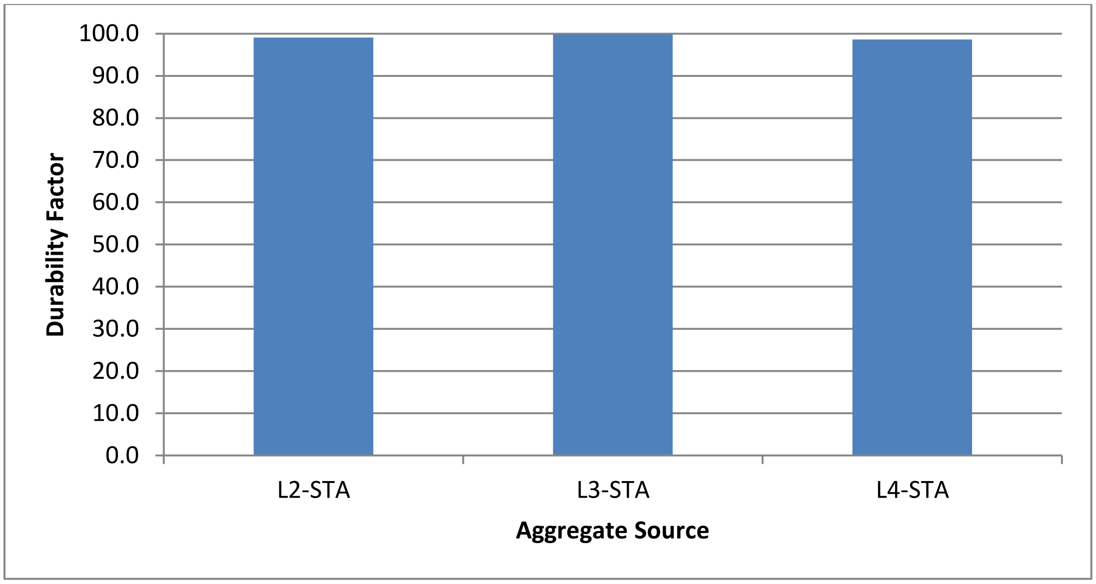

Figure 5.27: Durability Factors of Salt-Treated Aggregate Samples

Half-Immersed Results

The same six coarse aggregate types used in the salt-treatment method were also used in concrete subjected to freeze-thaw testing half-immersed in salt solution. L2, L3, L4, L5, L6 and L7 coarse aggregates, as described in Table 3-1, were used. Designations and batch designs for concrete prisms correspond to those given in Table 3-5. Coarse aggregates were not salt-treated before casting concrete. Results of the half-immersion method are shown in Figure 5.28 through Figure 5.31 and are the average of two prisms per aggregate type.

Relative modulus values for half-immersed samples are slightly lower than those of the salt-treated aggregate samples but still show negligible quantifiable differences between the aggregates tested. Significant scaling occurred on immersed portions of the prisms. Several exposed aggregates showed visible deterioration, from salt scaling or frost damage when directly exposed to salt solution. Scaling influenced the mass change data, shown by decline for all samples even though the aggregate type does not appear to have a significant influence on mass change.

Expansion results show considerable variation but relative modulus values did not significantly decline. The expansion variation could be an effect of the half-immersion. Scaling occurred around the gauge pins, which could have influenced results. Though the pins were wiped before insertion in the comparator, it is possible scaled material could have become lodged in the comparator and altered measurements.

The test failed to quantifiably differentiate between aggregates. Qualitatively the exposed aggregate did deteriorate, although measured results were not influenced. For example, L2 concrete prisms contained numerous aggregates that showed signs of scaling or caused pop-outs. In one L2 prism an aggregate disintegrated, as shown in Figure 5.32, which shows a L2 prism after completion of the freeze-thaw test and three days drying. L4 concrete prisms also contained numerous aggregates that either scaled or caused pop-outs. L3 concrete prisms also showed aggregates that caused pop-outs or scaled, but to a lesser extent compared to L4 and particularly L2 concrete prisms. A prism made with L3 aggregate is shown in Figure 5.33 after the test and a drying period of three days. Severe scaling and aggregate damage, including surface flaking, are apparent. These effects indicate that some aggregate tested was not frost durable.

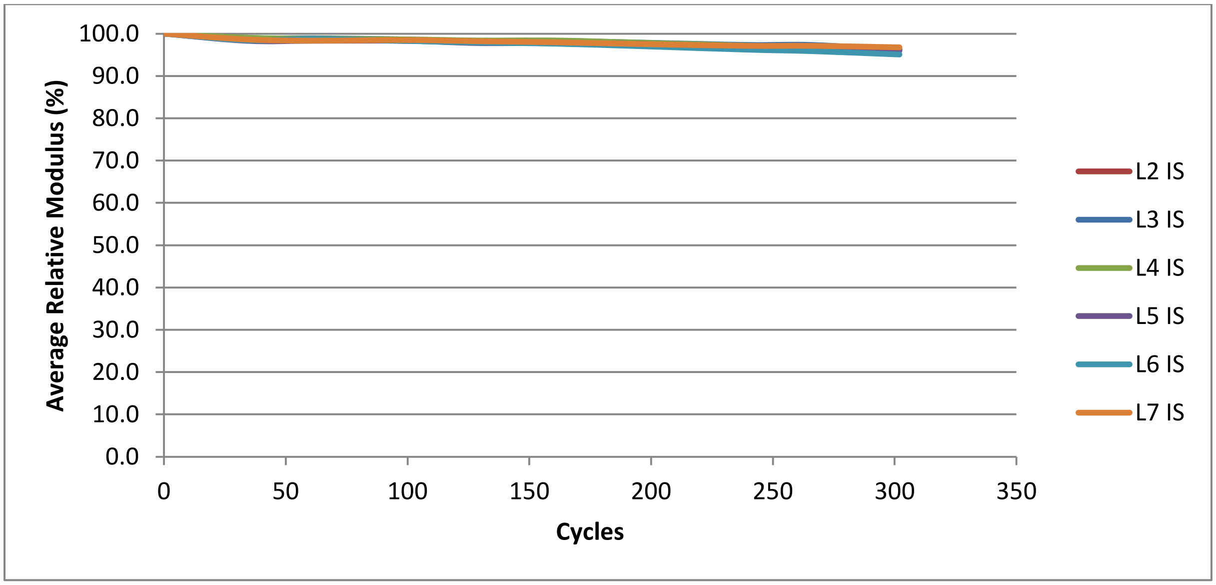

Figure 5.28: Average Relative Modulus of Salt-Immersed Samples

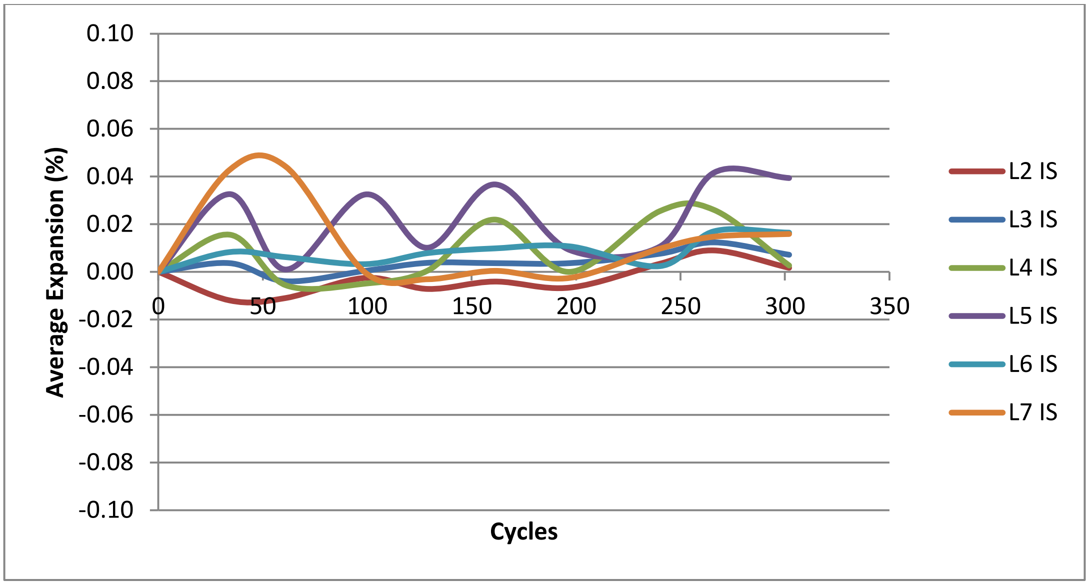

Figure 5.29: Average Length Change of Salt-Immersed Samples

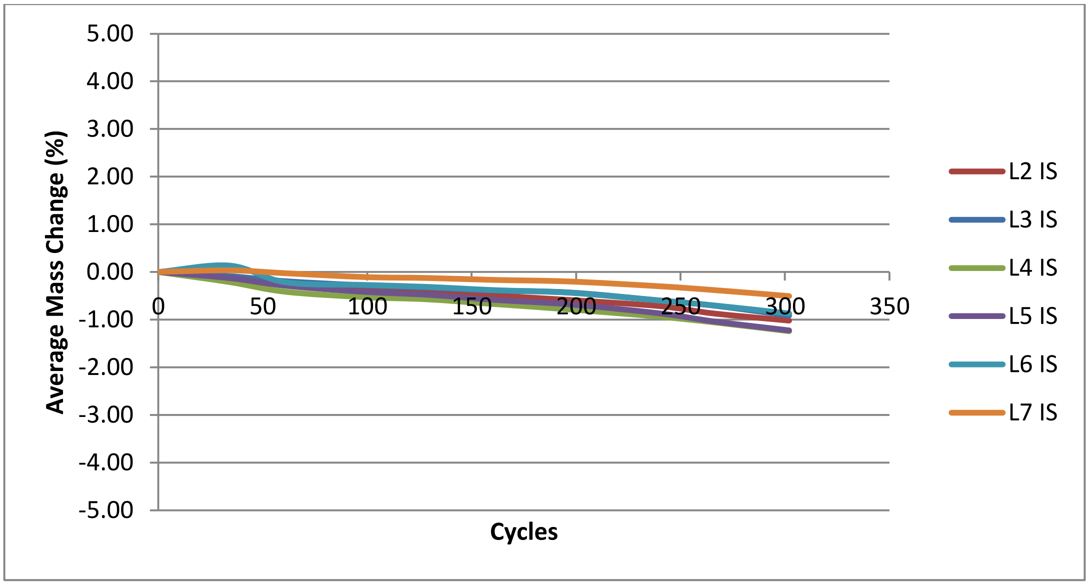

Figure 5.30: Average Mass Change of Salt-Immersed Samples

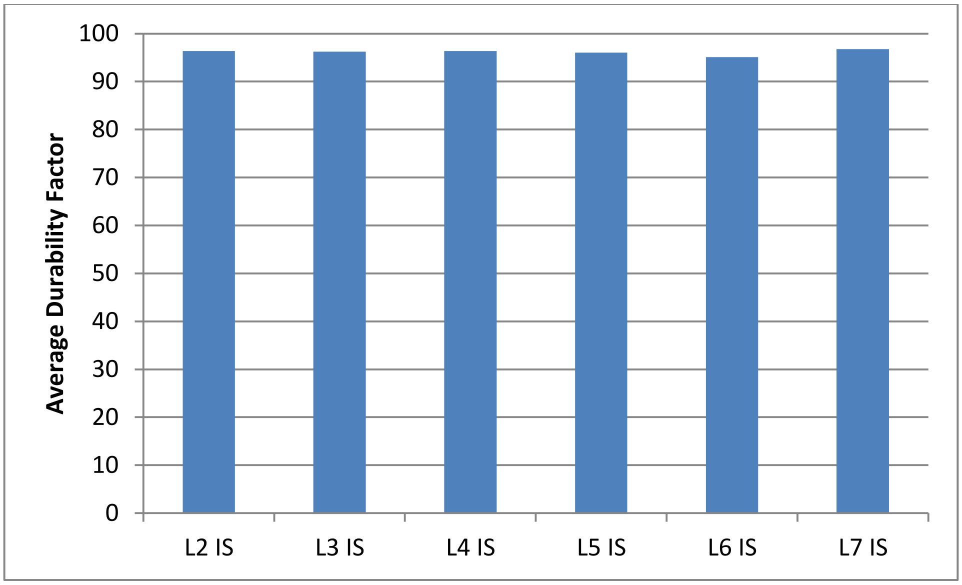

Figure 5.31: Durability Factors of Salt-Immersed Samples

Figure 5.32: L2 Half-Immersed Concrete Prism

Figure 5.33: L3 Half-Immersed Concrete Prism

Chapter 6 - Discussion

Rock Salt Analysis

Chemical analysis shows trace compounds present in the salt. X-ray diffraction (XRD) analysis generally identified only Ca_2SO_4 as a trace compound in the sample. This finding does not rule out the presence of other compounds, but may indicate that insufficient amounts of trace compound phases were present for detection by XRD without Rietveld analysis. In particular ICP analysis showed that magnesium was also present though magnesium-bearing phases were not positively identified in XRD patterns, suggesting that Ca_2SO_4 is the most common sulfur-bearing phase in rock salt and could possibly govern the chemical interaction between sulfur in rock salt and hydrated cement paste in concrete pavement. The presence of other sulfur compounds is not ruled out by this analysis and their presence could also have an influence on concrete durability.

A back-of-the-envelope calculation, the results of which are given in Table 5-2, based on the ICP results shows that there is enough sulfate content in the rock salt to generate a moderate or even severe sulfate exposure condition depending on the rock salt concentration. The ICP analysis was conducted on rock salt solution, so the sulfur content was water soluble even if it was not all present as sulfate ions. The appreciable sulfate content shows that examining the effect of rock salt on concrete durability by using NaCl with low sulfate content, such as USP grade NaCl, may underestimate the severity of exposure to rock salt solution.

Impurities in the rock salt may be relatively insoluble and therefore not completely dissolved during the brine production process. Insolubility of rock salt impurities is demonstrated by the difference between the XRD pattern of rock salt brine residue and the XRD pattern of the other rock salt samples. The brine residue pattern had a more prominent Ca_2SO_4 peak (at roughly $25.5° \, 2\theta$) and peaks not present in other sample patterns. This would indicate the rock salt brine residue sample contained more material other than NaCl relative to the other samples, which could mean brine may have a higher NaCl content than rock salt thereby reducing the influence of rock salt impurities on concrete durability. However, if dry rock salt is applied to roads, then whatever impurities present would have an influence on concrete pavement performance.

Concrete Wet-Dry Test

Scaling was the principal damaging effect for this test. Lack of internal damage, indicated by lack of excessive length change or decline in relative modulus, proves the test was insufficiently severe. This may be due to the drying period, which was conducted at 73°F and 50% RH. Darwin et al. (2007) noticed some decline in relative modulus to concrete prisms in NaCl solution. Their drying conditions were at a higher temperature and therefore more severe. That they saw a decline in relative modulus in NaCl solution and this testing did not indicates that to further study the interaction of the impure salts on concrete requires more severe drying conditions for a wet-dry test. Alkali-aggregate reaction may also be a factor in this type of testing as salt solutions contained sodium, but negligible expansion indicates that the reaction did not occur to a deleterious degree.

A freeze-thaw test in varying salt solution and concentrations would show more clearly the influence of impure salts on concrete frost durability.

Limestone Wet-Dry Test

Each prism tested was unique to the extent that a comparison of limestone performance in the wet-dry test based on salt solution is inconclusive. Damage principally occurred from scaling, and each prism showed a non-uniform response to exposure conditions. The extent of scaling varied even on the same prism face. Therefore, individual characteristics of a limestone prism influenced the test more than the salt solution to which the prism was exposed.

Damage to prisms occurred principally through scaling. Negligible length change and lack of cracking indicate this test did not produce conditions similar to those which would cause D-cracking in a coarse aggregate, particularly as some of the samples contained cracks before the test which could have been exploited to cause internal sample damage. Expansive clay in L1 prisms caused fragmentation in the limestone, but crushed aggregate from this source was not tested. Without testing crushed aggregate the importance of this effect in concrete aggregate performance cannot be determined from the limestone prism test results alone.

Limestone samples generally did not crack during wet-dry exposure but they did crack when subjected to freeze-thaw cycles in salt solution. This result indicates that a more severe test method would be to subject limestone to freeze-thaw cycles in varying salt solutions. The same solutions used in the wet-dry test would be suitable, although varying the concentration as well would be useful in determining the interaction of impure salts with limestone. Given the inconsistent nature of limestone prisms, crushed aggregate samples are more suitable for consistent results.

Limestone Prism Freeze-Thaw Tests

For both limestone prism freeze-thaw tests prism performance varied considerably even though only one limestone type was used. Results indicate neither of these test methods is suitable for determining aggregate performance, particularly given the wide range of performance in the freeze-thaw test in salt solution. However, non-durable characteristics of prisms may be identified in this test. The presence of cracks prior to testing was detrimental, as shown in Figure 5.23. The portion of a stone near the exterior may be of lower quality, as shown in Figure 5.18. The lamellar nature of limestone may also provide a weak plane susceptible to damage as shown in Figure 5.21 and possibly Figure 5.18.

Samples were saw-cut limestone prisms rather than crushed aggregate. The difference between the two may be enough that saw-cut prisms are not suitable for determination of aggregate durability.

ASTM C666 with Salt-Treated Aggregates

Damage in this test was negligible which did not agree with predicted aggregate performance. In particular, L2 prisms were expected to deteriorate but did not and performed approximately the same as prisms containing other aggregate. The salt-treatment removed material from coarse aggregates because scaled aggregate particles were left in salt containers following the salt-treatment.

Insufficient salt may have been present in the aggregate to cause damage during freeze-thaw testing. Marks and Dubberke (1985) used saturated NaCl solution, so perhaps the 23% rock salt brine was too dilute. The rock salt brine was also adjusted to 23±1% by weight by the addition of distilled water after each removal of aggregates from salt solution. Another factor reducing test severity may be the rinsing procedure could have removed too much salt from the aggregate and reduced its effect in freeze-thaw testing. Since Marks and Dubberke used more saturated solutions, this may not have influenced their results.

Another factor reducing severity could be the curing procedure. Concrete samples were dried for 21 days during the curing period. Verbeck and Landgren (1960) observed that a drying period before samples were placed in the freeze-thaw chamber reduced the saturation level of concrete samples and delay frost damage. The drying period may be a factor as Marks and Dubberke (1985) do not explicitly mention a drying period during the curing of their samples. Another factor reducing severity could be salt leaching during moist curing, although Marks and Dubberke moist-cured their samples for 90 days and still observed a significant increase in damage during freeze-thaw cycling (1985). However, since they used more concentrated salt solution, the leaching effect could have been less of a factor in their testing.

ASTM C666 with Half-Immersed Samples

Measured data shows negligible differences between various aggregates, which does not agree with predicted aggregate durability. For example, L2 samples were expected to degrade in the test but had a durability factor approximately the same as L3 samples, which were expected to show little damage. Based on expected aggregate performance, this test is unsuitable for differentiating aggregate performance. Significant scaling did occur but is not necessarily a satisfactory indicator of aggregate performance since internal concrete deterioration is the symptom most related to D-cracking susceptibility of an aggregate. Since the relative modulus of these samples did not appreciably decline during the test, internal damage to the specimens was negligible.

Qualitatively, aggregate performance differed in the deterioration of exposed aggregate by sample scaling as well as formation of pop-outs. One exposed aggregate particle from an L2 prism disintegrated, so frost susceptible aggregate was present in the concrete. The less durable aggregate, particularly L2 and L4 aggregate samples, tended to have more pop-outs as well as aggregate deterioration. Whether aggregate deterioration resulted from scaling, internal frost damage of the individual aggregate particle, or a combination of scaling and internal frost damage is debatable.

Results of this test method indicate little internal deterioration in the concrete, as the relative modulus did not appreciably decline. Similar to the salt-treated aggregate test method, samples for the half-immersion method were dried for 21 days during the curing period, which could have reduced test severity. Additionally, ice was occasionally observed on samples when removed for measurement, typically at the solution level. Therefore, the salt solution froze, although it may not have completely thawed, possibly explaining the lack of deterioration.

Insufficient thawing may be indicated by sample temperature which tended to reach 37-38°F, the low end of the acceptable sample temperature at the end of the thaw period. The un-immersed half of all specimens appeared dry when measured. Incomplete thawing could have prevented capillary action from bringing salt solution to the top of the specimen. In that case, the top half of the specimen would dry and not contain sufficient solution for freeze-thaw damage. Solution evaporated from the samples, which could also have reduced test severity.

Chapter 7 - Conclusions

Concrete and saw-cut limestone prisms were subjected to both wet-dry and freeze-thaw testing. The testing provided little quantitative difference in limestone or concrete performance in NaCl solutions containing varying amounts of impurities. Concrete freeze-thaw testing also failed to differentiate quantitatively limestone aggregate quality.

Chemical analysis shows that impurities are present in rock salt and impurities are less soluble than NaCl. However, impurities such as sulfur are still present in rock salt brine and may contain enough sulfate that its effects would need to be considered in concrete performance.

Limestone prism wet-dry testing in varying salt solutions did not indicate a quantitative difference in performance based on the amount of impurities in the solution. However, significant damage occurred in limestone prisms subjected to freeze-thaw cycling in salt solution. Freeze-thaw testing in varying salt solutions and concentrations would more accurately show the influence of rock salt impurities. The inconsistency between limestone prisms from the same source indicates that crushed coarse aggregate would be more consistent material to test.

Concrete prism wet-dry testing also did not indicate a quantitative performance difference based on salt solution. Increasing severity of the drying period or conducting freeze-thaw testing in salt solution would likely be more indicative of a difference based on salt composition.

Neither salt-treated aggregate nor half-immersion freeze-thaw test procedures discriminated between limestone aggregate performance, indicating both test methods are insufficiently severe rather than all aggregates were durable. Eliminating the drying period during sample curing would increase test severity in both test methods. Increasing salt concentration and reducing aggregate rinsing would likely increase test severity in the salt-treated aggregate method. Sealing samples in plastic to eliminate drying would likely increase severity in the half-immersion test method. Full immersion in salt solution may also increase severity. Conducting the standard ASTM C666 method A test may be useful as a control to gauge test severity.

It cannot be stated whether or not trace compounds in rock salt influence limestone aggregate durability based on test data shown. Testing procedures did not quantifiably produce a difference in sample performance based on salt composition, and more severe testing would be required to show if there is such a difference.

Recommendations

Test results so far are inconclusive. To study the influence of deicing salt impurities on limestone itself a soundness test on bare crushed aggregate in salt solutions used in the wet-dry test, similar to that conducted by Hassan et al. (2002), may be advisable. Hassan et al. (2002) also investigated the effect of salt concentration, another factor for consideration in addition to sulfate content. Using saw-cut limestone prisms is not recommended as crushing limestone may change its properties, prisms from the same source have variable quality, and prisms are labor-intensive to make.

For further concrete wet-dry testing, low temperature exposure like that of Sutter et al. (2008) or high temperature drying period like that of Darwin et al. (2007) may increase the test severity and better indicate of the role of impurities in deicing salt.

In further concrete freeze-thaw testing eliminating the drying period during curing would increase test severity for either the salt-treated aggregate or half-immersion methods. If further use of the salt-treated aggregate test is done, using saturated salt solution rather than 23% by weight would increase severity. Adjusting salt solution concentration during salt-treatment would not be necessary if using saturated salt solution.

In the half-immersion method, sealing samples with plastic while in the freeze-thaw chamber is essential to prevent evaporation of salt solution, thereby reducing the amount of salt released into the freeze-thaw chamber or samples from drying. Lengthening the thawing period to ensure that complete thawing occurs is also essential. If sample containers are used to house the half-immersed samples, then it is imperative to wipe these containers dry before placing them in the chamber to prevent any spilled salt solution from entering the freeze-thaw chamber.

References

Angeli, M., Hebert, R., Menendez, B., David, C. and Bigas, J.P. (2010). “Influence of temperature and salt concentration on the salt weathering of a sedimentary stone with sodium sulphate.” *Engineering Geology*, 115(3-4), 193-199

American Concrete Institute (ACI) (2008). “Exposure Categories and Classes,” *ACI 318-08: Building Code Requirements for Structural Concrete and Commentary*, Farmington Hills, MI, 56

ASTM International (ASTM) (2008a). “ASTM C192: Standard Test Method for Making and Curing Concrete Test Specimens in the Laboratory.” *Annual Book of ASTM Standards: Volume 4.02: Concrete and Aggregates*, West Conshohocken, PA

ASTM (2008b). “ASTM C666: Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing.” *Annual Book of ASTM Standards: Volume 4.02: Concrete and Aggregates*, West Conshohocken, PA

Benavente, D., Garcia del Cura, M.A., Garcia-Guinea, J., Sanchez-Moral, S. and Ordonez, S. (2004). “Role of pore structure in salt crystallisation in unsaturated porous stone.” *Journal of Crystal Growth*, 260(3-4), 532-544

Buj, O., Gisbert, J., McKinley, M. and Smith, B. (2011). “Spatial characterization of salt accumulation in early stage limestone weathering using probe permeametry.” *Earth Surface Processes and Landforms*, 36(3), 383-394

Cardell, C., Benavente, D. and Rodriguez-Gordillo, J. (2008). “Weathering of limestone building material by mixed sulfate solutions. Characterization of stone microstructure, reaction products and decay forms.” *Materials Characterization*, 59(10), 1371-1385

Chen, T.C., Yeung, M.R., and Mori, N. (2004). “Effect of water saturation on deterioration of welded tuff due to freeze-thaw action.” *Cold Regions Science and Technology*, 38(2-3), 127-136

Collins, R.J. (1988). “Microstructural studies of Jurassic limestone aggregates with reference to durability in concrete.” *Magazine of Concrete Research*, 40(142), 35-42

Crumpton, C., Smith, B. and Jayaprakash, G.P. (1989). “Salt Weathering of Limestone Aggregate and Concrete Without Freeze-Thaw.” *Transportation Research Record*, No. 1250, 8-16

Darwin, D., Browning, J., Gong, L., and Hughes, S.R. (2007). *Effects of Deicers on Concrete Deterioration*. The University of Kansas Center for Research, Inc., Lawrence, KS

Darwin, D., Browning, J., Gong, L., and Hughes, S.R. (2008). “Effects of Deicers on Concrete Deterioration.” *ACI Materials Journal*, 105(6), 622-627

Detwiler, R.J. and Powers-Couche, L.J. (1999). "Effect of Sulfates in Concrete on Their Resistance to Freezing and Thawing." *American Concrete Institute (ACI) Special Publication 177: Ettringite-The Sometimes Host of Destruction*, B. Erlin ed, Farmington Hills, MI, 219-248

Dubberke, W. and Marks, V. (1985). "The Effect of Deicing Salt on Aggregate Durability." *Transportation Research Record,* No. 1031, 27-34

Dunn, J.R. and Hudec, P.P. (1966). "Water, clay and rock soundness." *The Ohio Journal of Science,* 66(2), 153-168

Gillott, J.E. (1978). "Effect of deicing agents and sulphate solutions on concrete aggregate." *The Quarterly Journal of Engineering Geology*, 11(2), 177-192

Gillott, J.E. (1980). "Effect of Microstructure and Composition of Limestone, Marble, Basalt, and Quartzite Aggregate on Concrete Durability in Presence of Solutions of Calcium Chloride and Magnesium Sulfate." *ASTM Special Technical Publication 691: Durability of Building Materials and Components,* P.J. Sereda and G.G. Litvan, eds., West Conshohocken, PA, 605-615

Goncalves, T.D., Pel, L. and Rodrigues, J.D. (2007). "Drying of salt-contaminated masonry: MRI laboratory monitoring." *Environmental Geology,* 52(2), 293-302

Goudie, A.S. (1999). "Experimental salt weathering of limestones in relation to rock properties." *Earth Surface Processes and Landforms,* 24(8),715-724

Hassan, Y., Abd El Halim, A.O., Razaqpur, A.G., Bekheet, W. and Farha, M.H. (2002). "Effects of Runway Deicers on Pavement Materials and Mixes: Comparison with Road Salt." *Journal of Transportation Engineering*, 128(4), 385-391

Haynes, H., O'Neill, R., Neff, M. and Mehta, P. K. (2010). "Salt Weathering of Concrete by Sodium Carbonate and Sodium Chloride." *ACI Materials Journal*, 107 (3), 258-266

Haynes, H., O'Neill, R., Neff, M. and Mehta, P. K. (2008). "Salt Weathering Distress on Concrete Exposed to Sodium Sulfate Environment." *ACI Materials Journal*, 105 (1), 35-43

Hudec, P.P. (1980). "Effect of Deicing Salts on Deterioration and Dimensional Changes of Carbonate Rocks." *ASTM Special Technical Publication 691: Durability of Building Materials and Components*, P.J. Sereda and G.G. Litvan, eds., West Conshohocken, PA, 629-640

Hudec, P. (1987). "Deterioration of aggregates – the underlying causes." *Concrete Durability*, 2, 1325-1342

Ingham, J.P. (2005). "Predicting the frost resistance of building stone." *Quarterly Journal of Engineering Geology and Hydrogeology*, 38(4), 387-399

Kansas Department of Transportation (KDOT) (2009). “Chapter Seven: Snow and Ice Control and Other Motorist Services.” *KDOT Highway Maintenance Manual*, Topeka, KS, 7-1 to 7-35

KDOT (2006). “KTMR-22: Resistance of Concrete to Rapid Freezing and Thawing.” *KDOT Standard Specifications for State Road and Bridge Construction*, Topeka, KS

KDOT (2007). “KT-6: Specific Gravity and Absorption of Aggregate.” *KDOT Construction Manual: Part IV*, Topeka, KS

Koubaa, A. and Snyder, M. (1996). “Evaluation of Frost Resistance Tests for Carbonate Aggregates.” *Transportation Research Record*, No. 1547, 35-45

Koubaa, A., Snyder, M.B. and Janssen, D.J. (2002). “Development and Evaluation of D-Cracking Mitigation Techniques.” *PRO 25: International RILEM Workshop on Frost Damage in Concrete*, J. Janssen, M.J. Setzer, and M.B. Snyder eds, RILEM, Bagneux, France, 265-288

Koubaa, A., Snyder, M.B., and Peterson, K.R. (1997). *Mitigating Concrete Aggregate Problems in Minnesota*. Minnesota Department of Transportation, St. Paul, Minnesota

Li, W., Pour-Ghaz, M., Castro, J., and Weiss, J. (2012). “Water Absorption and Critical Degree of Saturation Relating to Freeze-Thaw Damage in Concrete Pavement Joints.” *Journal of Materials in Civil Engineering*, 24(3), 299-307

Litvan, G.G. (1976). “Frost action in cement in the presence of de-icers.” *Cement and Concrete Research*, 6(3), 351-356

McCabe, S., McKinley, J.M., Gomez-Heras, M., and Smith, B.J. (2011). “Dynamical instability in surface permeability characteristics of building sandstones in response to salt accumulation over time.” *Geomorphology*, 130(1-2), 65-75

McGreevy, J.P. (1982). “‘Frost and salt’ weathering: further experimental results.” *Earth Surface Processes and Landforms*, 7(5), 475-488

McLeod, H.A. (2012). *D-Cracking Field Performance of Portland Cement Concrete Pavements Containing Limestone in Kansas: Phase 1 Report*. Kansas Department of Transportation, Topeka, KS

Newlon, H.H. (1978). *Modification of ASTM C666 for testing resistance of concrete to freezing and thawing in sodium chloride solution*. Virginia Highway & Transportation Research Council, Charlottesville, VA

Pétursson, P and Schouenborg, B (2004). *NORDTEST PROJECT No. 1624-03: Frost Resistance Test on Aggregates With and Without Salt (FRAS)*. Icelandic Road Administration, Reykjavik, Iceland

Pigeon, M. and Pleau, R. (1995). *Durability of Concrete in Cold Climates*, Taylor & Francis, London, England

Pitt, J.M., Schluter, M.C., Lee, D.Y. and Dubberke, W. (1987). *Effects of Deicing Salt Trace Compounds on Deterioration of Portland Cement Concrete*. Iowa State University Department of Civil Engineering, IA

Rodriguez-Navarro, C. and Doehne, E. (1999). "Salt weathering: influence of evaporation rate, supersaturation and crystallization pressure." *Earth Surface Processes and Landforms*, 24(3), 191-209

Ruedrich, J., Kirchner, D. and Siegesmund, S. (2011). "Physical weathering of building stones induced by freeze-thaw action: a laboratory long-term study." *Environmental Earth Sciences*, 63(7-8), 1573-1586

Ruedrich, J. and Siegesmund, S. (2006). "Fabric dependence of length change behaviour induced by ice crystallisation in the pore space of natural building stones." *Heritage, Weathering, and Conservation: Proceedings of the International Heritage, Weathering, and Conservation Conference (HWC-2006)*, Fort, R., de Buergo, M.A., Gomez-Heras, M., and Vazquez-Calvo, C. eds, Taylor & Francis, London, UK, 497-505

Ruiz-Agudo, E., Mees, F., Jacobs, P. and Rodriguez-Navarro, C. (2007). "The role of saline solution properties on porous limestone salt weathering by magnesium and sodium sulfates." *Environmental Geology*, 52(2), 269-281

Scherer, G. W. (2004). "Stress from crystallization of salt." *Cement and Concrete Research*, 34(9), 1613-1624

Scherer, G.W. and Valenza II, J.J. (2005). "Mechanisms of Frost Damage." *Materials Science of Concrete VII*, J. Skalny and F. Young, eds., American Ceramic Society, Westerville, OH, 209-246

Shi, X., Fay, L., Peterson, M.M. and Yang, Z. (2010). "Freeze-thaw damage and chemical change of a portland cement concrete in the presence of diluted deicers." *Materials and Structures*, 43(7), 933-946

Spragg, R.P., Castro, J., Li, W., Pour-Ghaz, M., Huang, P.T. and Weiss, J. (2011). "Wetting and drying of concrete using aqueous solutions containing deicing salts." *Cement and Concrete Composites*, 33(5), 535-542

Sun, Z. (2010). "Mechanism of Frost Damage to Concrete." Doctoral dissertation, Princeton University, Princeton, NJ

Sutter, L., Peterson, K., Julio-Betancourt, G., Hooton, D., Van Dam, T. and Smith, K. (2008). *SD2002-01-F: The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete*, South Dakota Department of Transportation, Pierre, SD

Verbeck, G. and Landgren, R. (1960). “Influence of Physical Characteristics of Aggregates on Frost Resistance of Concrete.” *Proceedings of the American Society for Testing Materials*, 60, 1063-1079

Vogler, R.H. and Grove, G.H. (1989). “Freeze-Thaw Testing of Coarse Aggregate in Concrete: Procedures Used by Michigan Department of Transportation and Other Agencies.” *Cement, Concrete and Aggregates*, 11(1), 57-66

Wang, K., Nelsen, D.E. and Nixon, W.A. “Damaging effects of deicing chemicals on concrete materials.” *Cement and Concrete Composites*, 28 (2), 173-188

Warke, P.A. and Smith, B.J. (2007). “Complex weathering effects on durability characteristics of building stone.” *Geological Society, London, Special Publications: Building Stone Decay: From Diagnosis to Conservation*, 271, 211-224

Wessman, L.M. (1996). “Deterioration of natural stone by freezing and thawing in salt solutions.” *Proc., the 1996 7th International Conference on Durability of Building Materials and Components*, Sjostrom, C. ed, E & FN Spon, London, UK, 342-351

W.R. Grace & Co. (2009). “Daravair® 1000 Air-entraining admixture.” *Grace Construction Products*, <http://www.na.graceconstruction.com/concrete/download/AIR-7G.pdf> (6/24/2013)

Appendix A - Limestone Prism Wet-Dry Samples

Limestone prisms were photographed before and after completion of the wet-dry test. The after pictures of the prisms in water were taken after the end of the last wet-dry cycle. The prisms were first rinsed in distilled water and wiped with a paper towel to remove excess surface water. Next prisms were immersed in distilled water for two days, dried for two days, and then photographed. Each figure is a compilation of photos taken of the four longitudinal faces of a prism before and after the test. The left column shows prism faces before the test and the right column the corresponding prism faces after the test and the rinsing procedure.

There was no scaling on the samples in water. Qualitatively the amount of scaling was greatest in NaCl followed by gypsum then brine. Some samples subjected to brine when rinsed seemed to have no scaling over a large portion of the prism surface area.

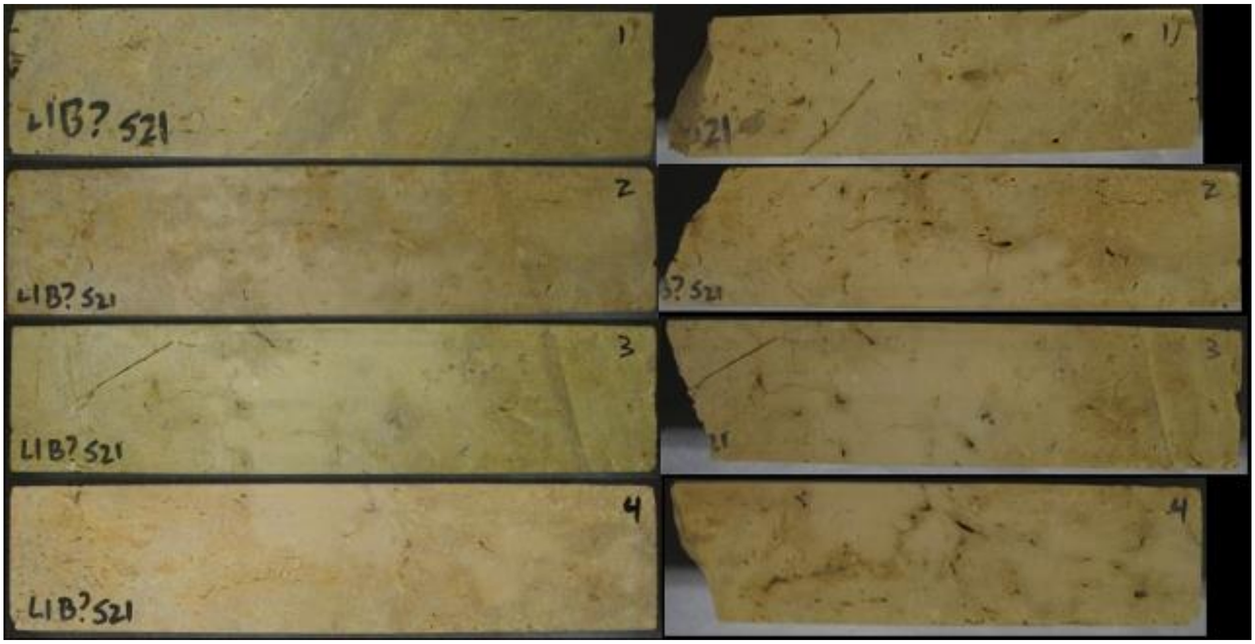

Figure A.1: L1 Sample 21 in Water

L1 sample 21 split during the oven-drying stage. Otherwise, damage was negligible.

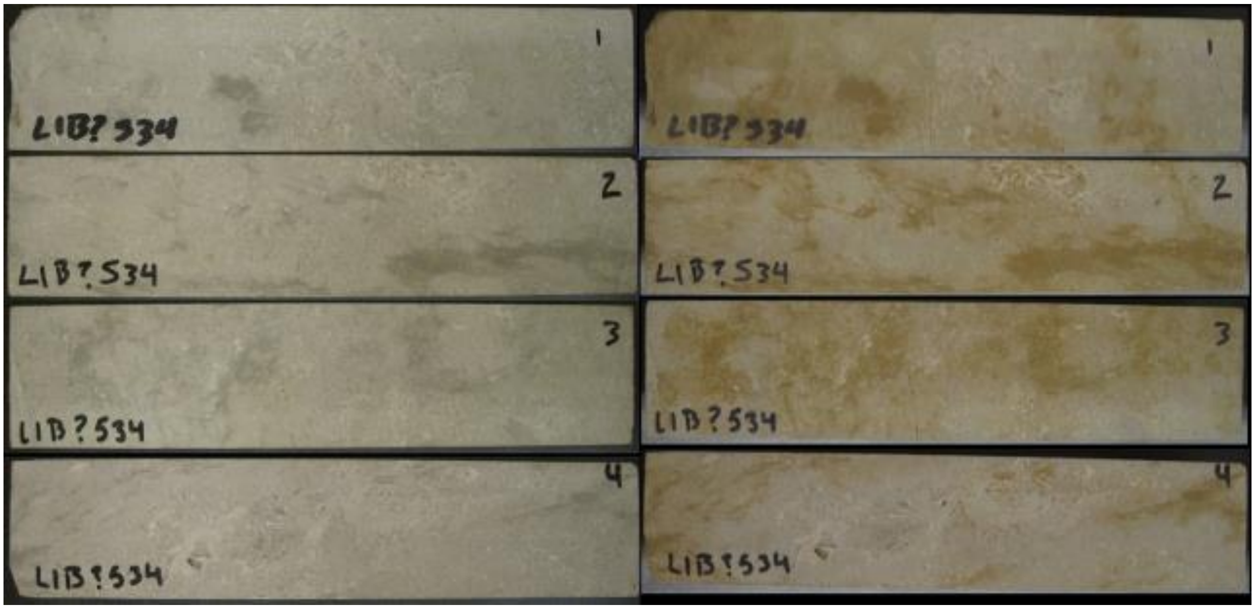

Figure A.2: L1 Sample 34 in Water

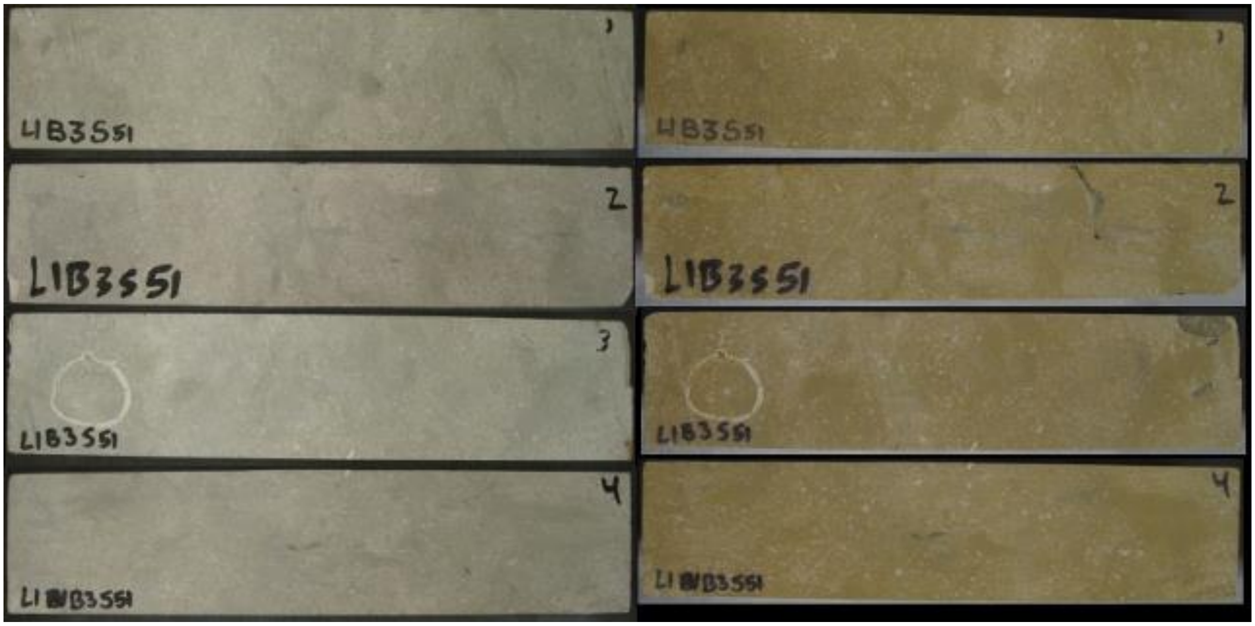

Figure A.3: L1 Sample 51 in Water

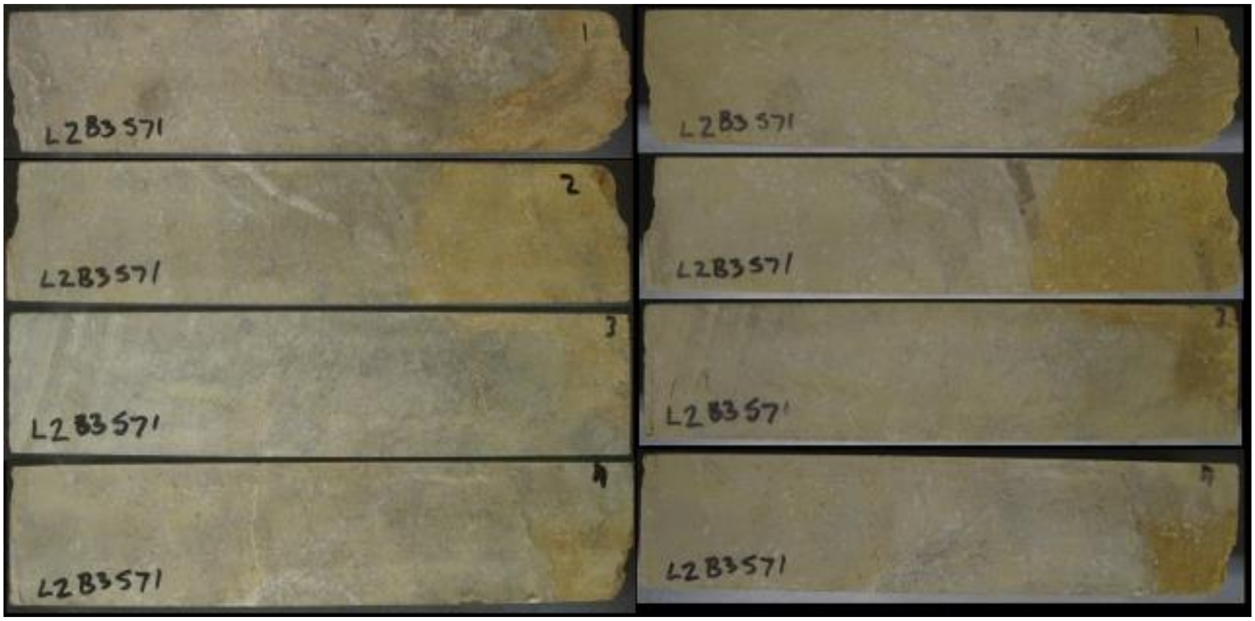

Figure A.4: L2 Sample 71 in Water

Figure A.5: L2 Sample 73 in Water

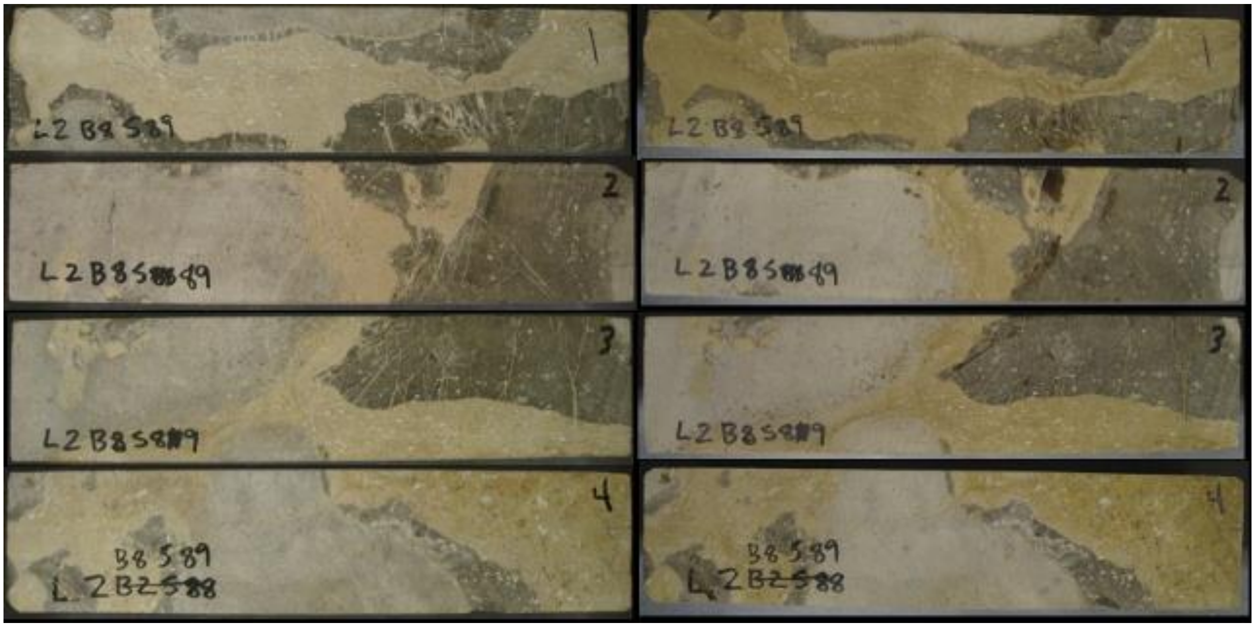

Figure A.6: L2 Sample 89 in Water

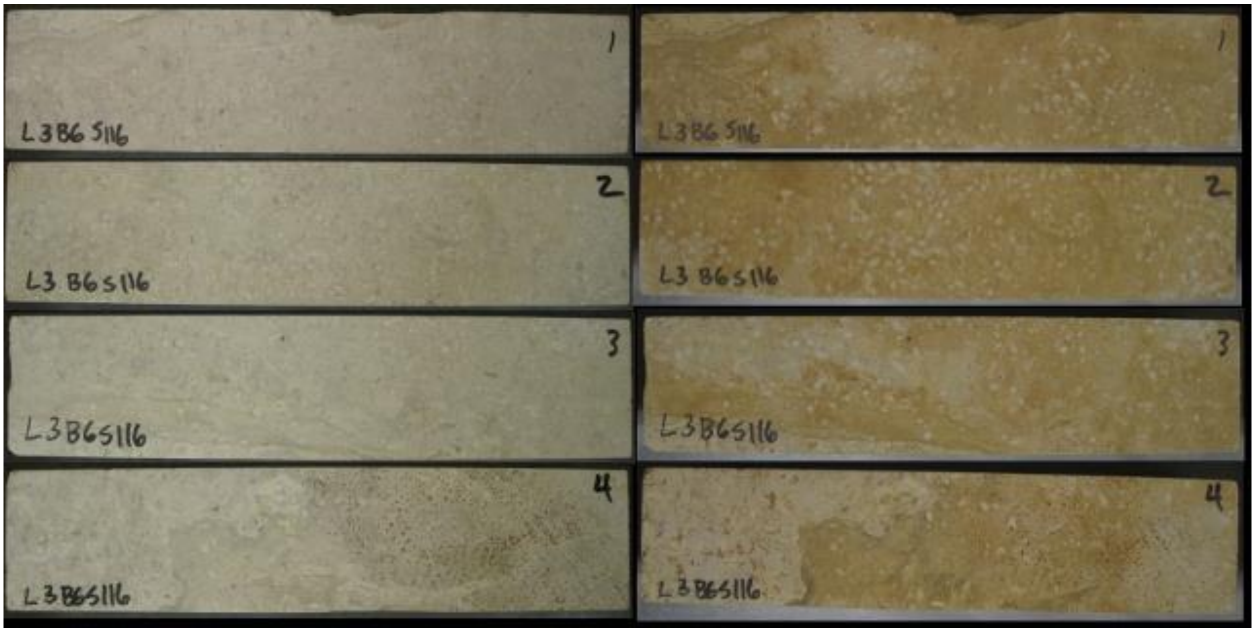

Figure A.7: L3 Sample 116 in Water

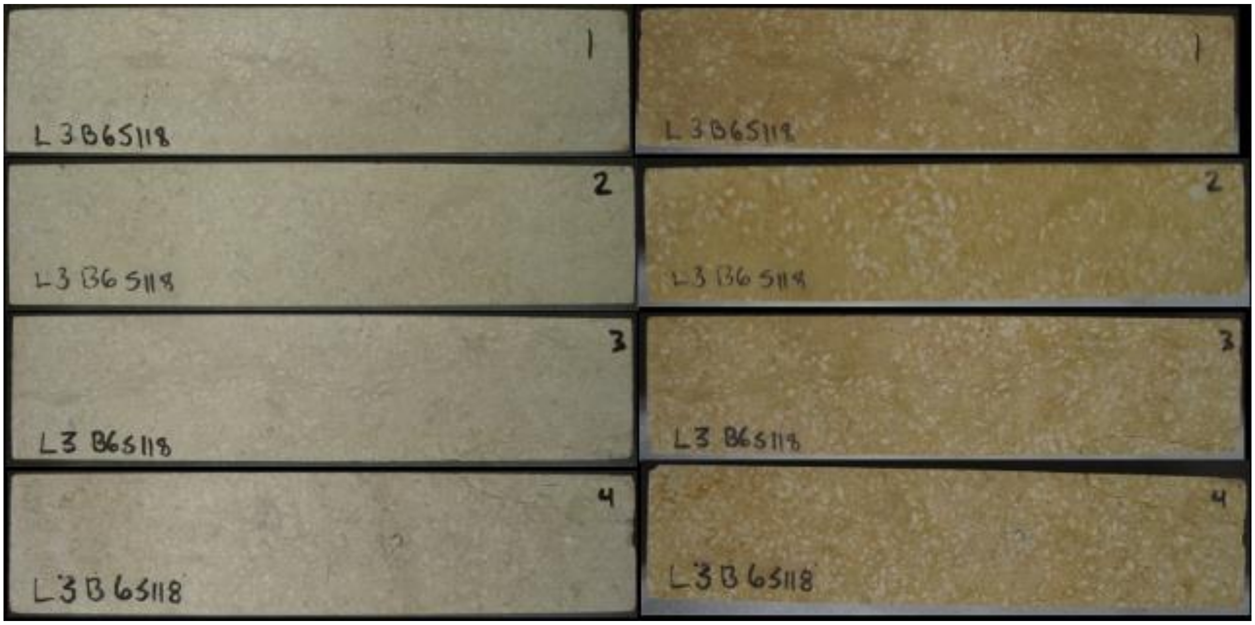

Figure A.8: L3 Sample 118 in Water

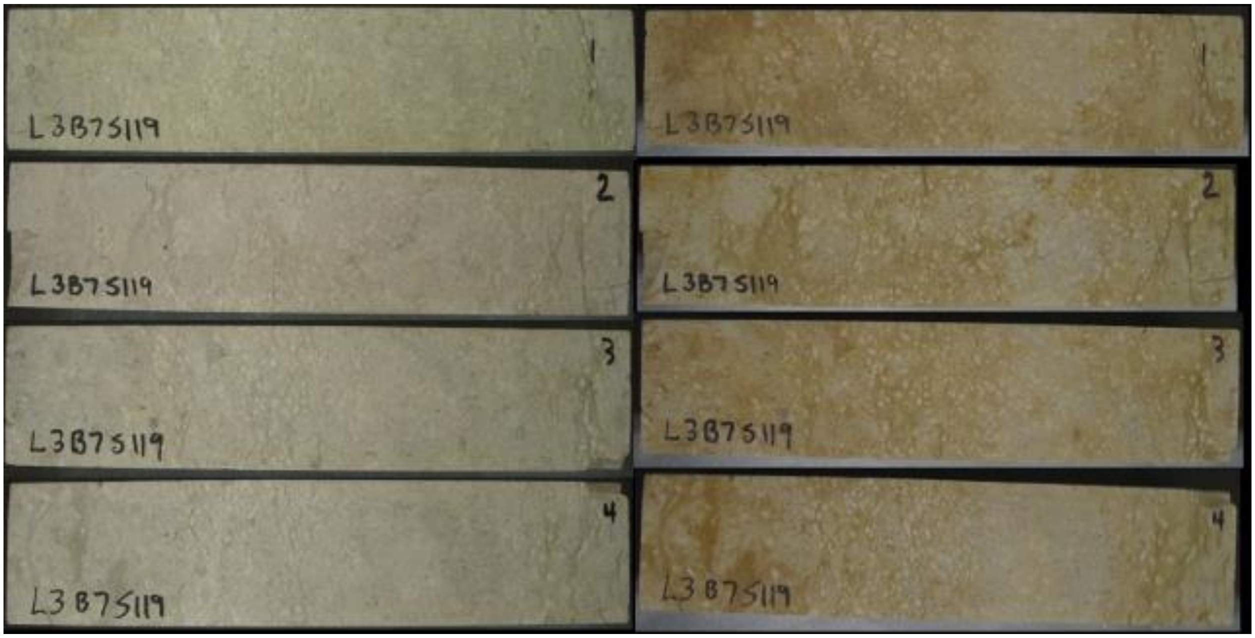

Figure A.9: L3 Sample 119 in Water

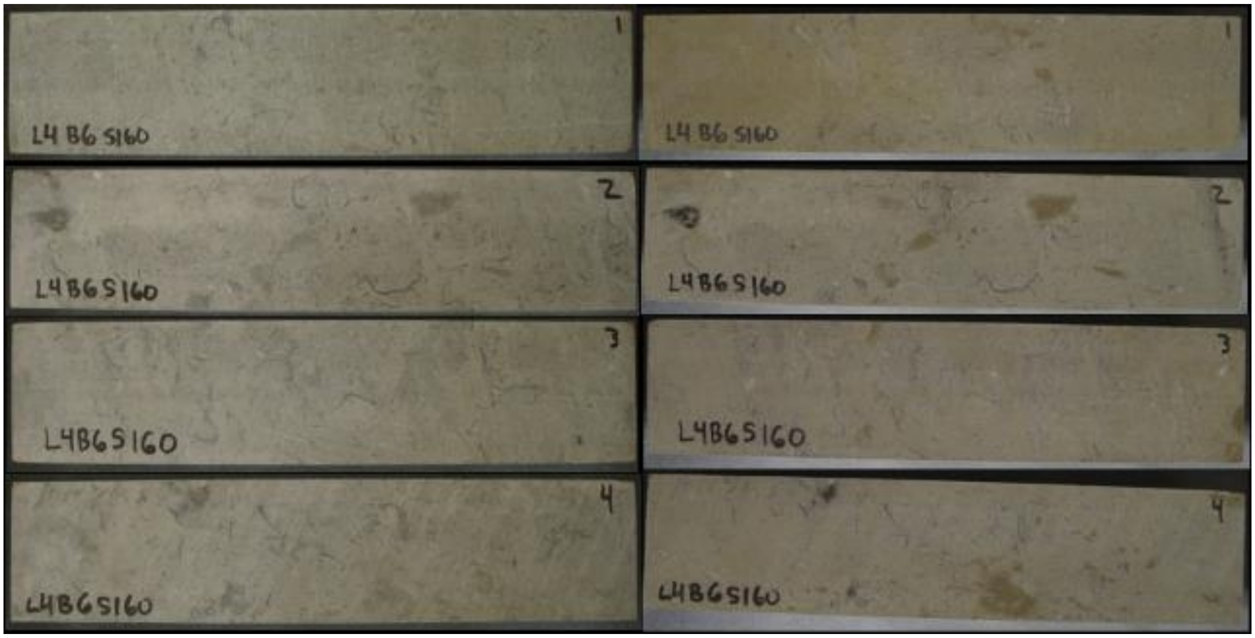

Figure A.10: L4 Sample 160 in Water

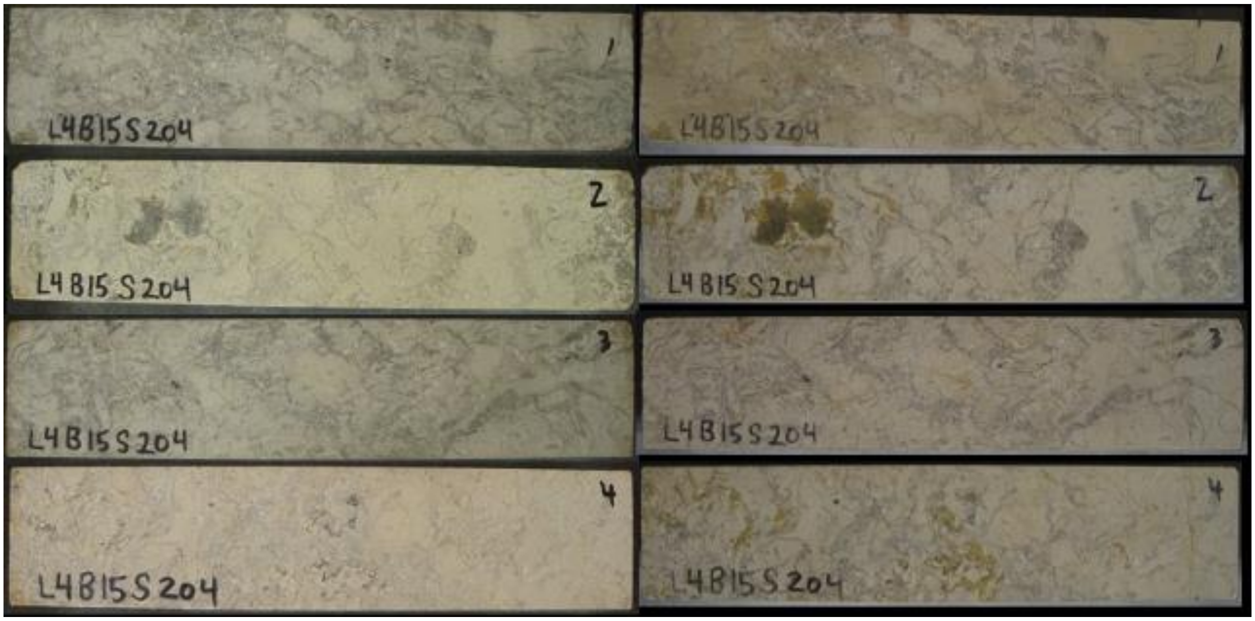

Figure A.11: L4 Sample 204 in Water

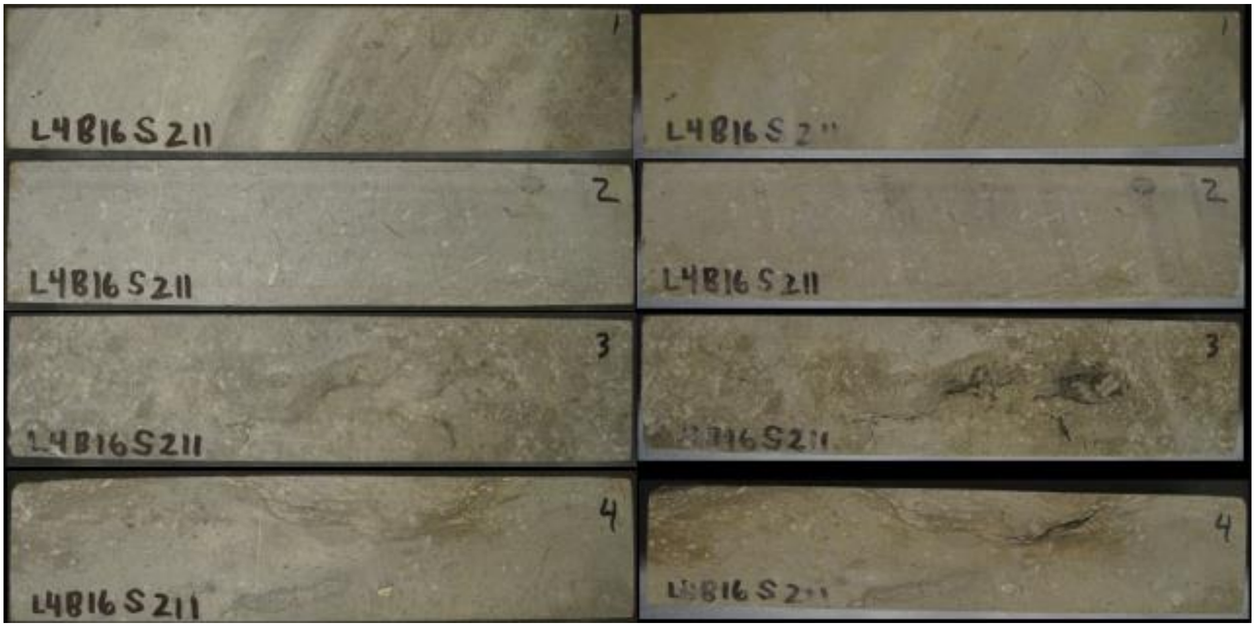

Figure A.12: L4 Sample 211 in Water

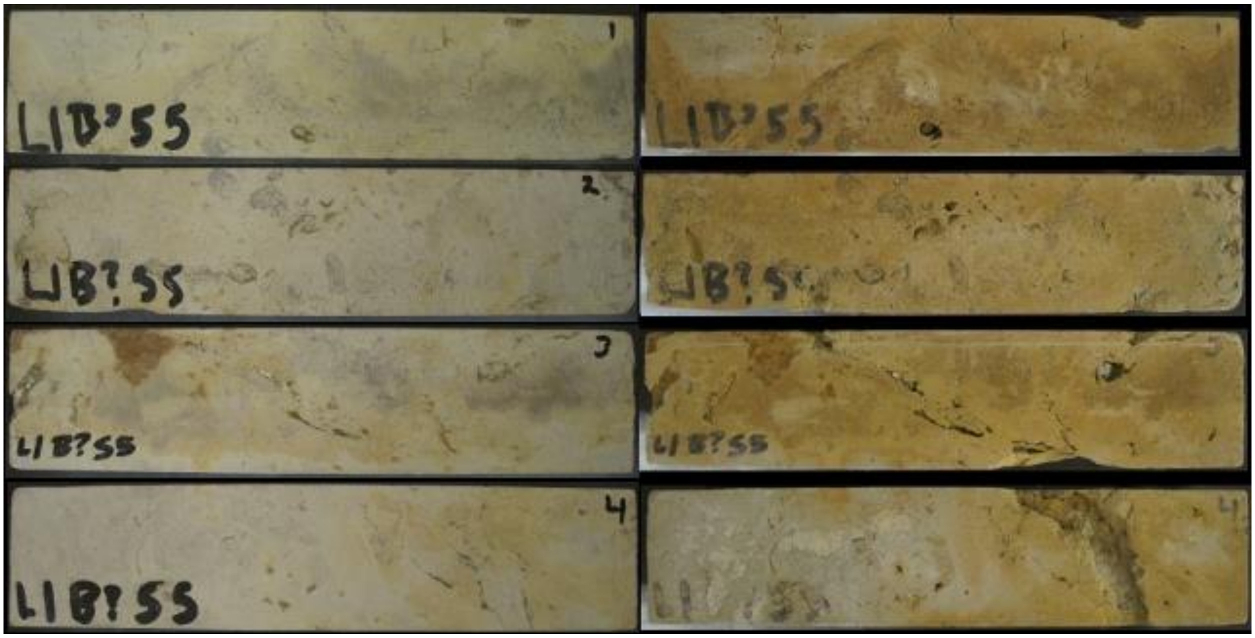

Figure A.13: L1 Sample 5 in NaCl

L1 sample 5 lost a fragment during the first wetting cycle. When the prism was removed from NaCl solution the first time, the section loss apparent on the face labeled "4" was noticed. Clay swelling underneath a weak layer of limestone during immersion appeared to be the cause.

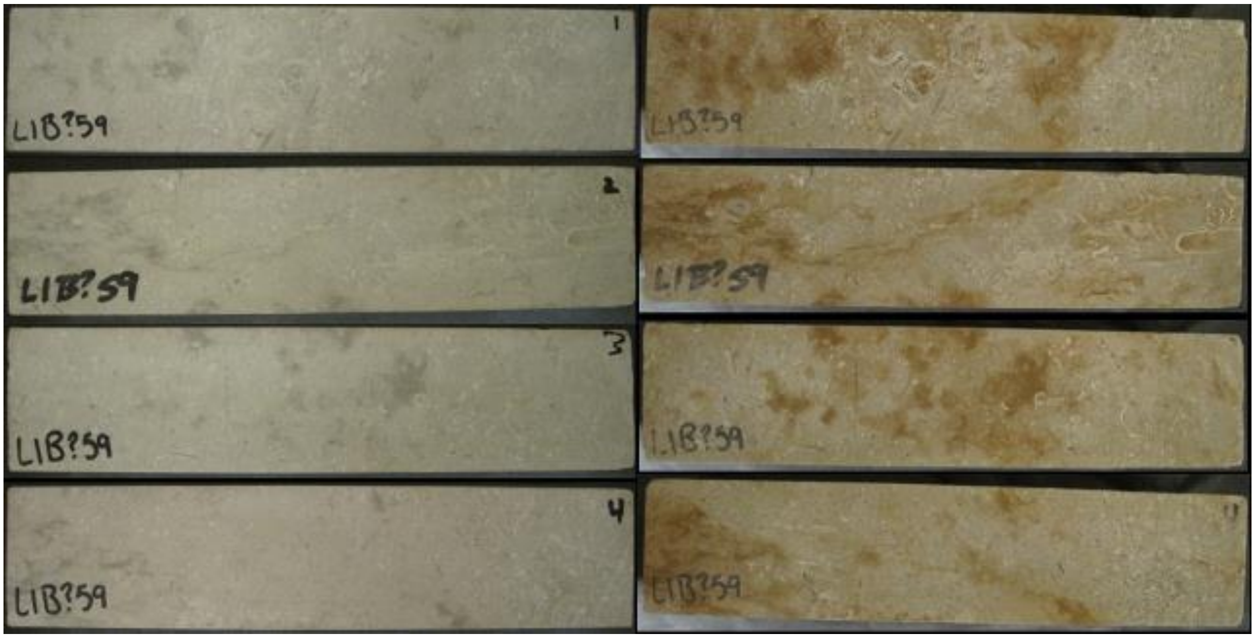

Figure A.14: L1 Sample 9 in NaCl

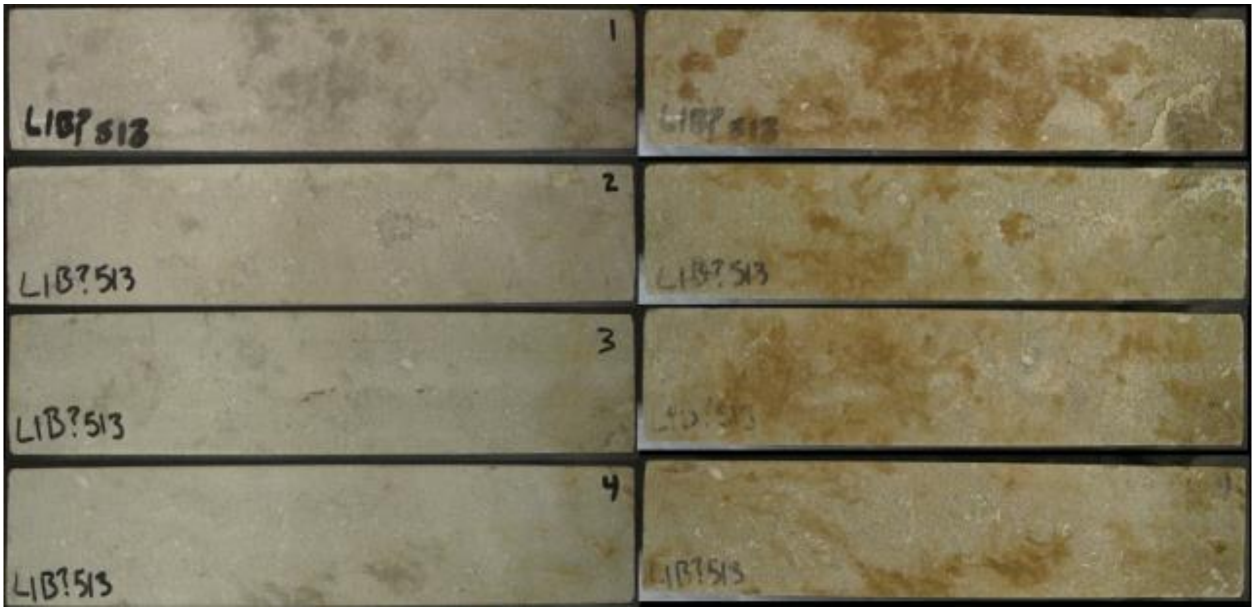

Figure A.15: L1 Sample 13 in NaCl

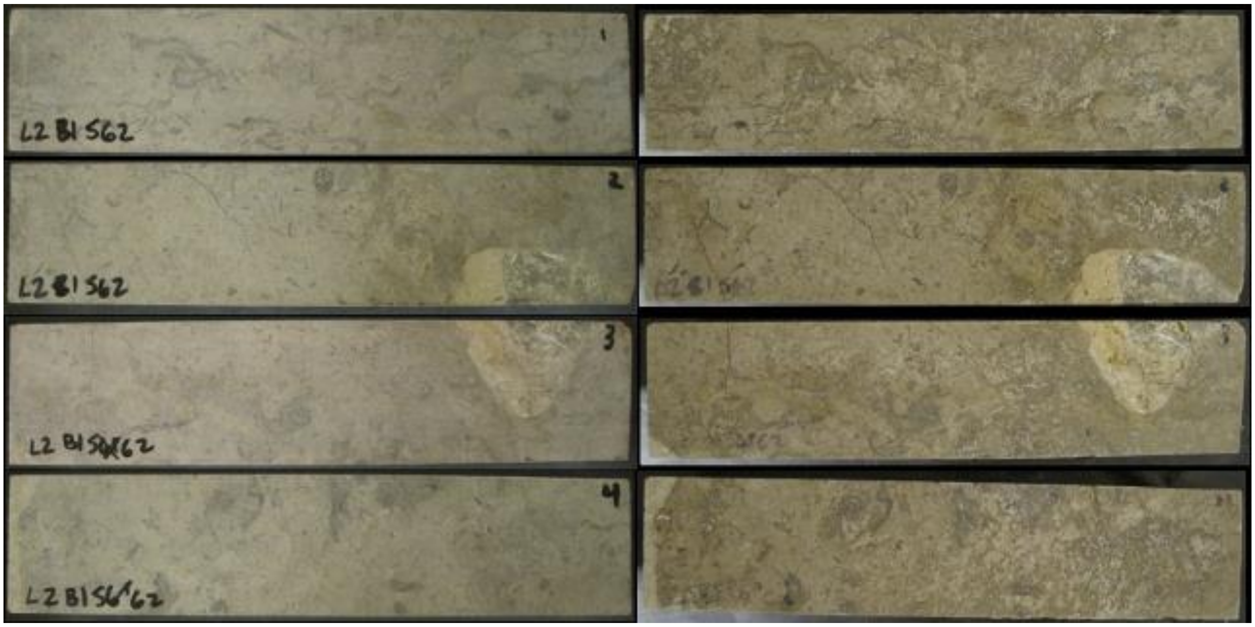

Figure A.16: L2 Sample 62 in NaCl

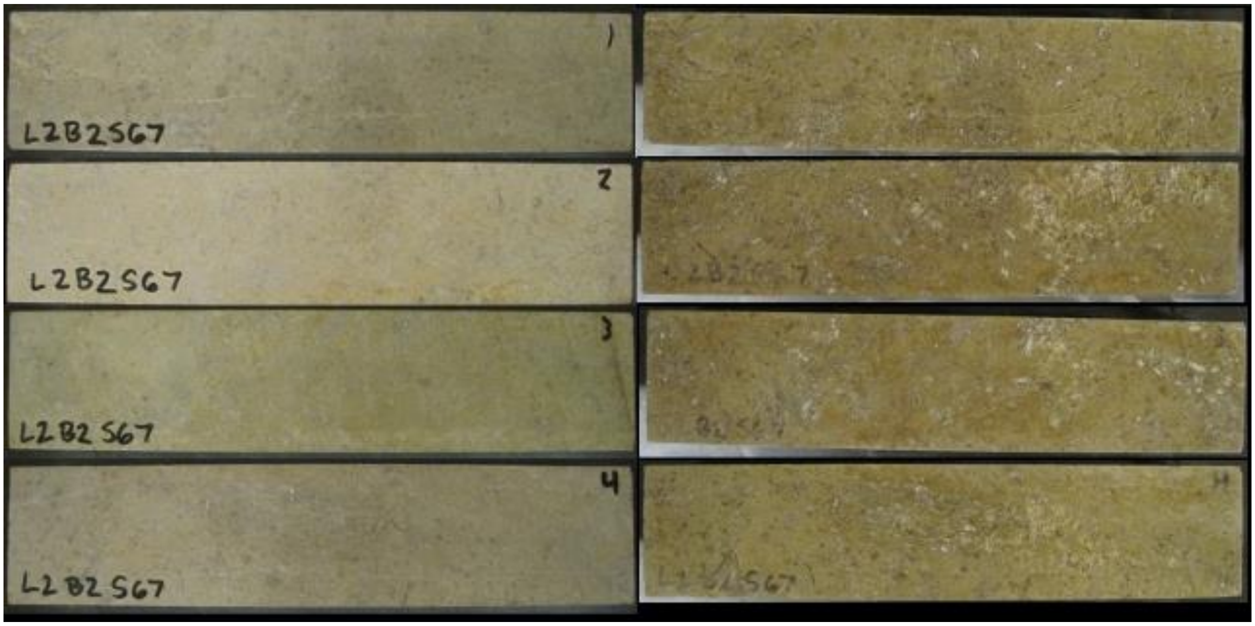

Figure A.17: L2 Sample 67 in NaCl

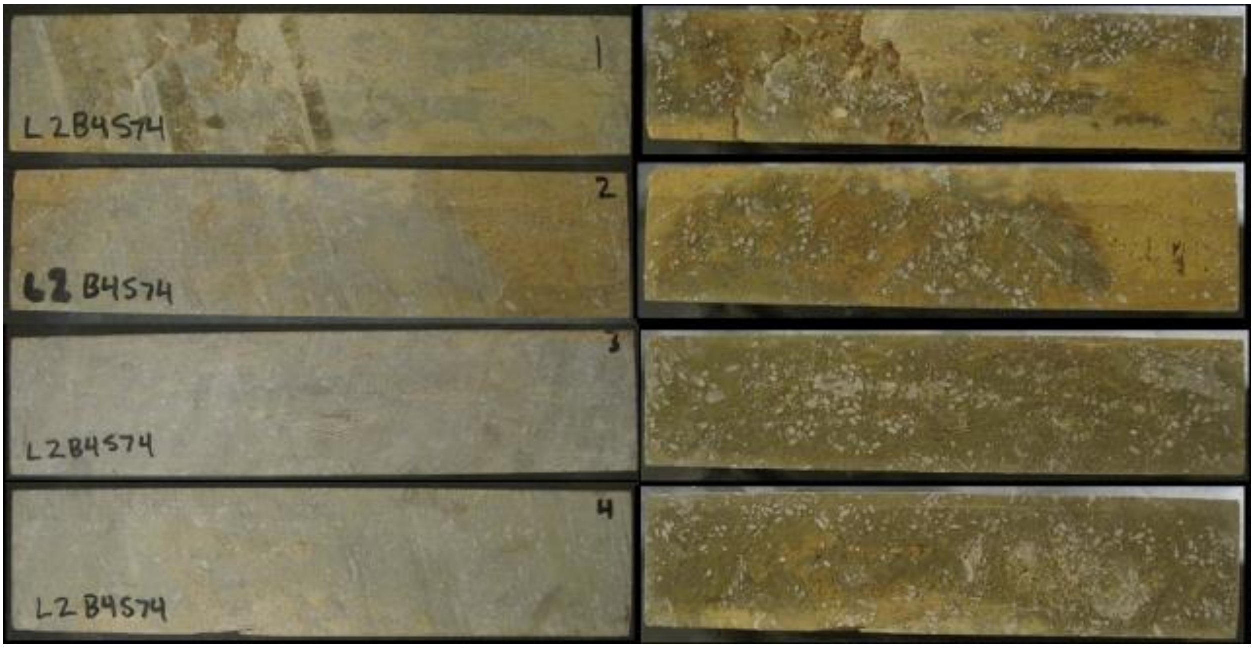

Figure A.18: L2 Sample 74 in NaCl

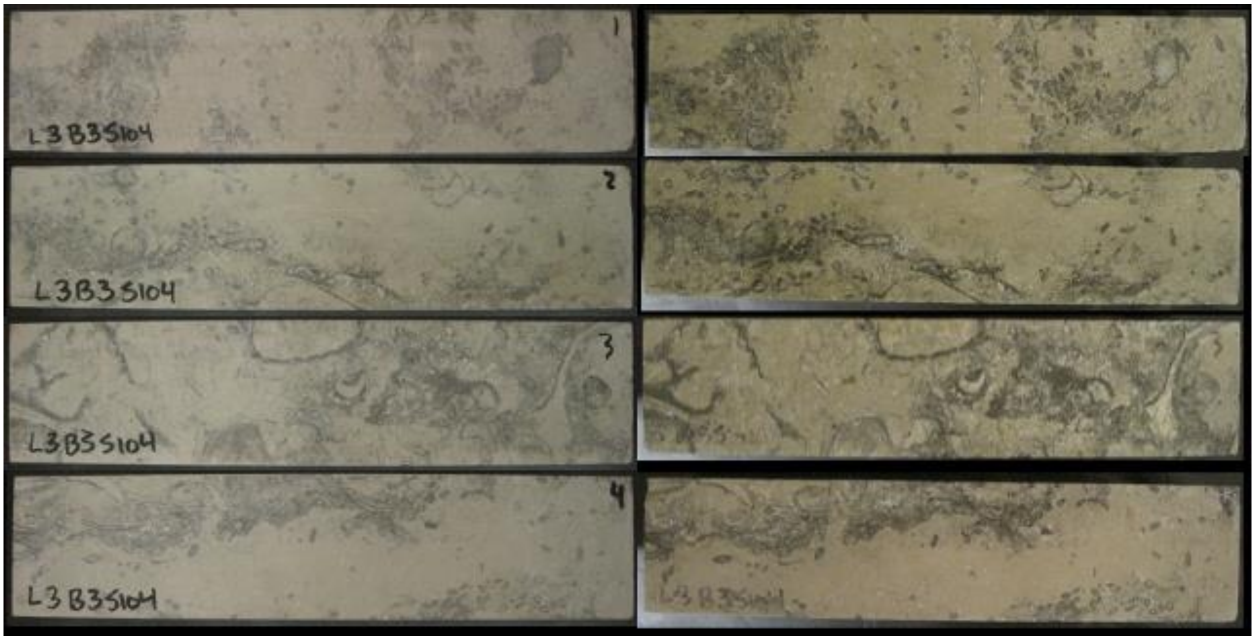

Figure A.19: L3 Sample 104 in NaCl

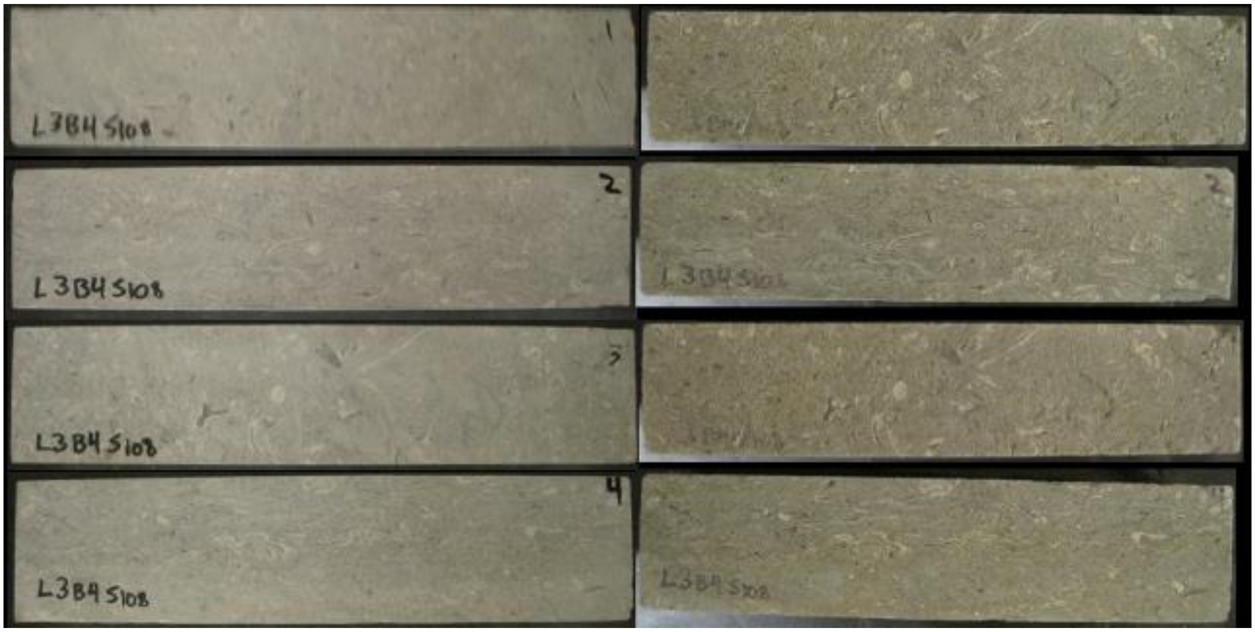

Figure A.20: L3 Sample 108 in NaCl

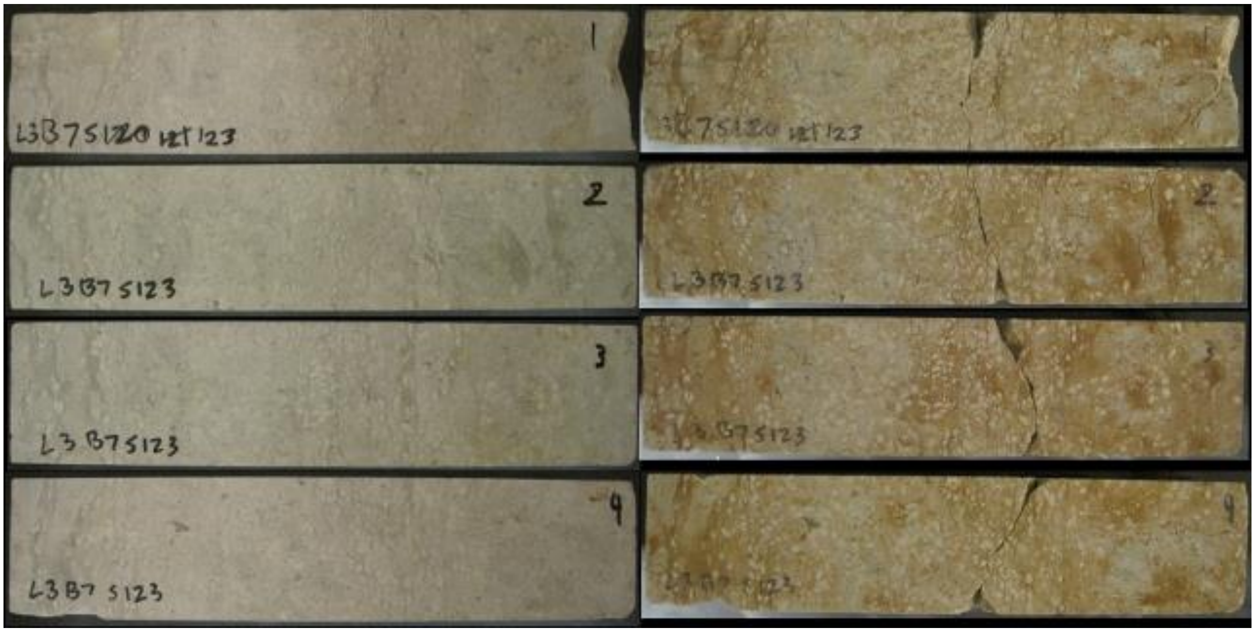

Figure A.21: L3 Sample 123 in NaCl

L3 sample 123 was dropped just before placement in solution for the start of the 46th wet-dry cycle, which is where the crack originated. Prior to that the sample showed minor scaling and behaved similarly to other L3 prisms. This particular sample was not measured for mass or length after being dropped but was continued in the test to see if any visual changes occurred.

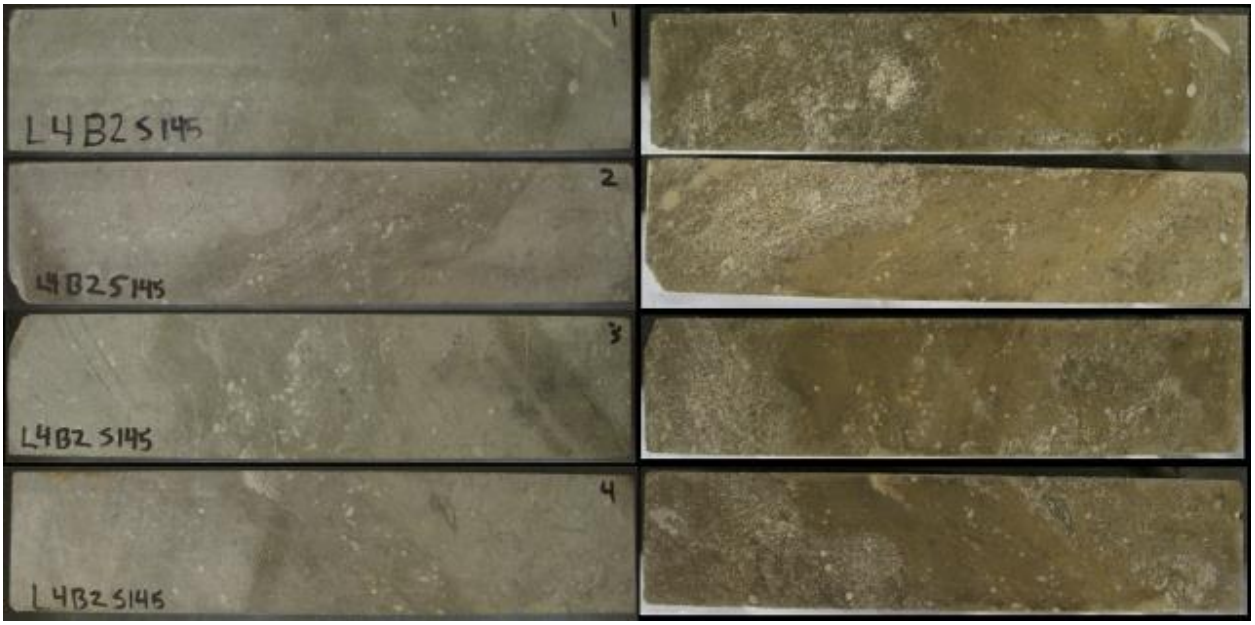

Figure A.22: L4 Sample 145 in NaCl

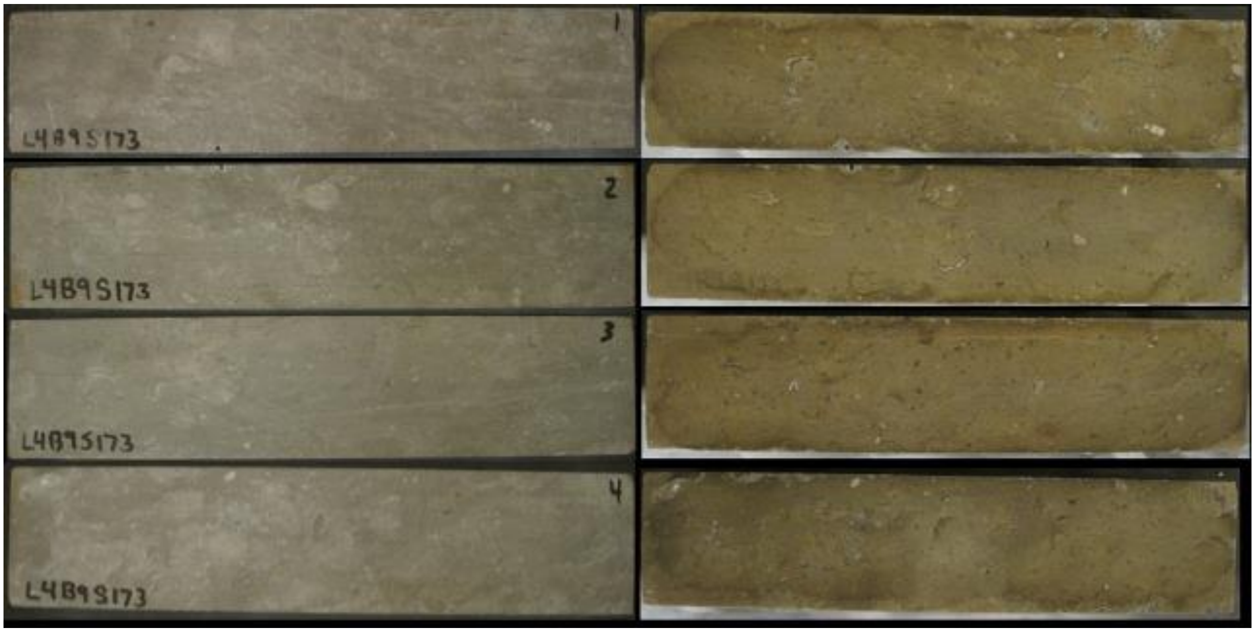

Figure A.23: L4 Sample 173 in NaCl

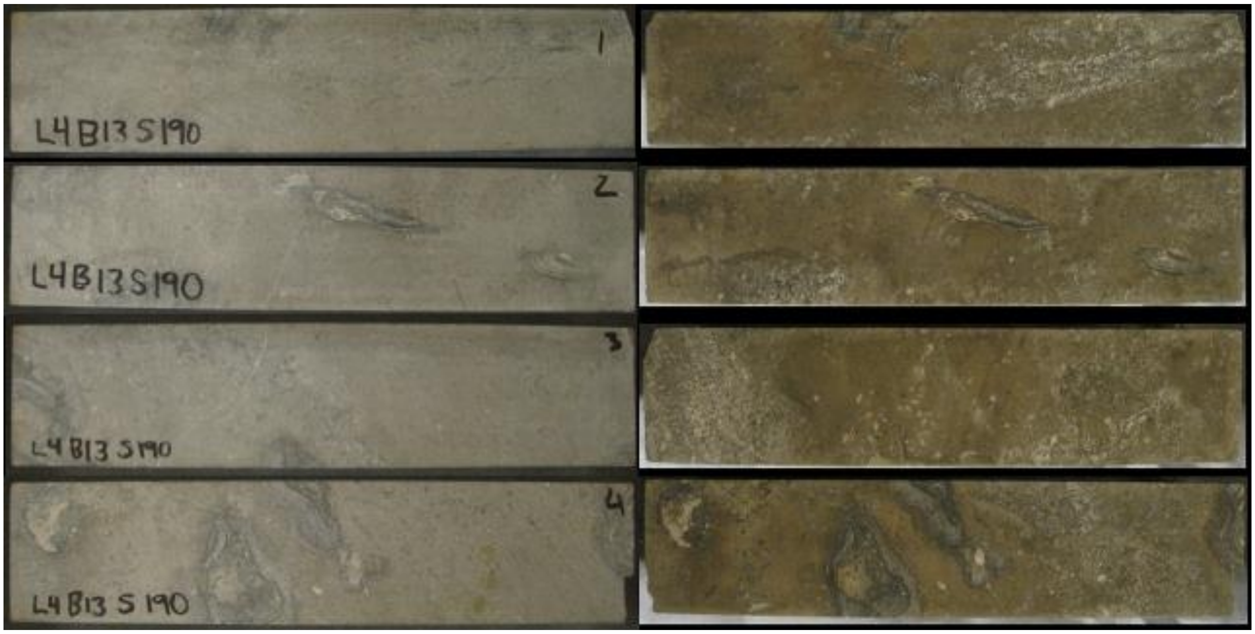

Figure A.24: L4 Sample 190 in NaCl

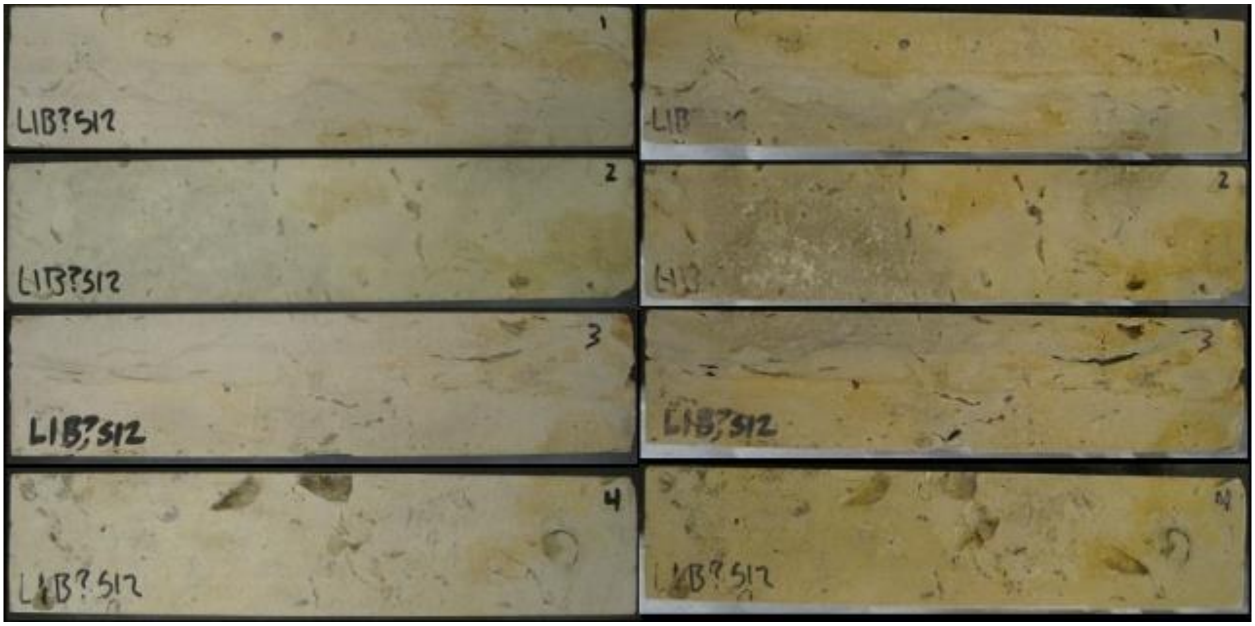

Figure A.25: L1 Sample 12 in Gypsum

Figure A.26: L1 Sample 43 in Gypsum

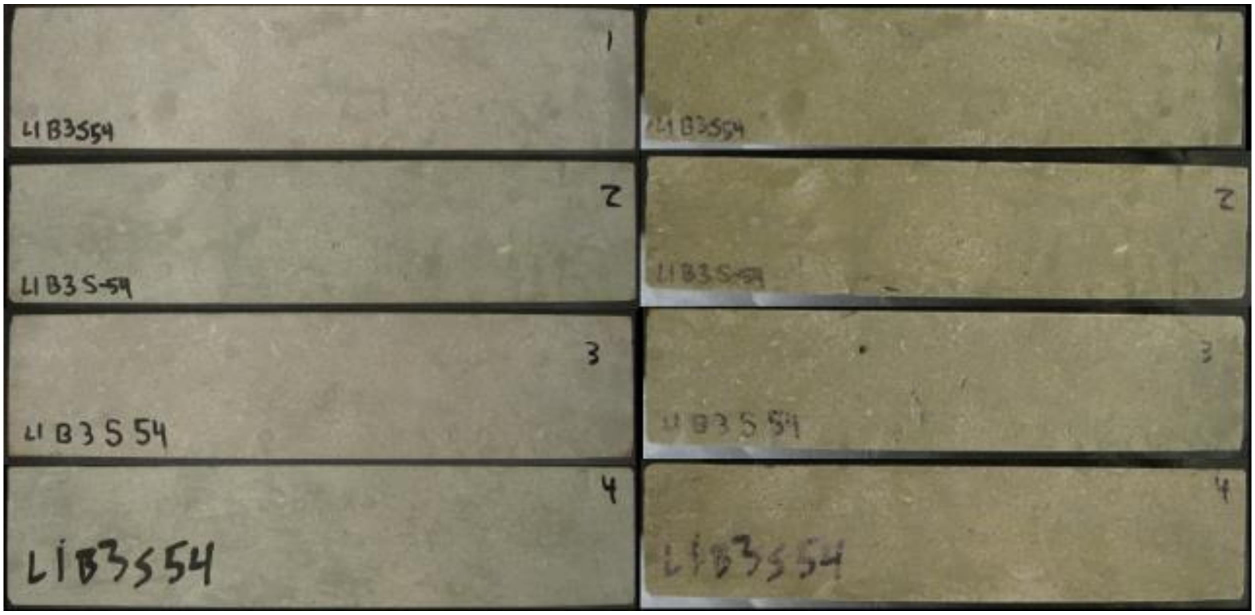

Figure A.27: L1 Sample 54 in Gypsum

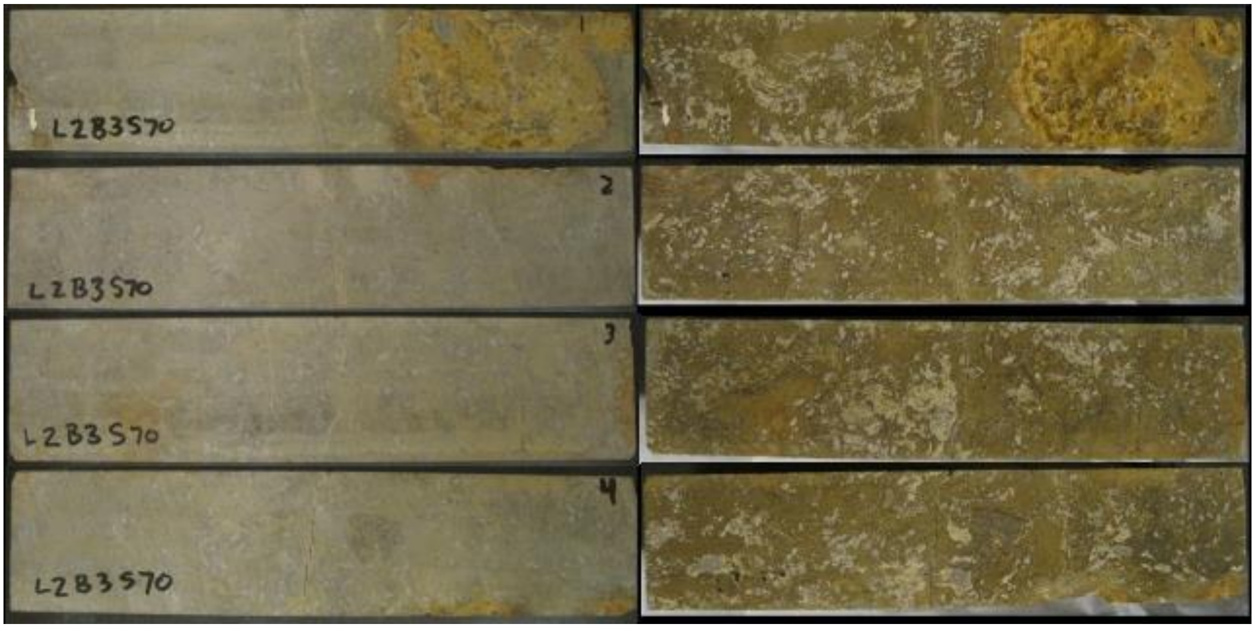

Figure A.28: L2 Sample 70 in Gypsum

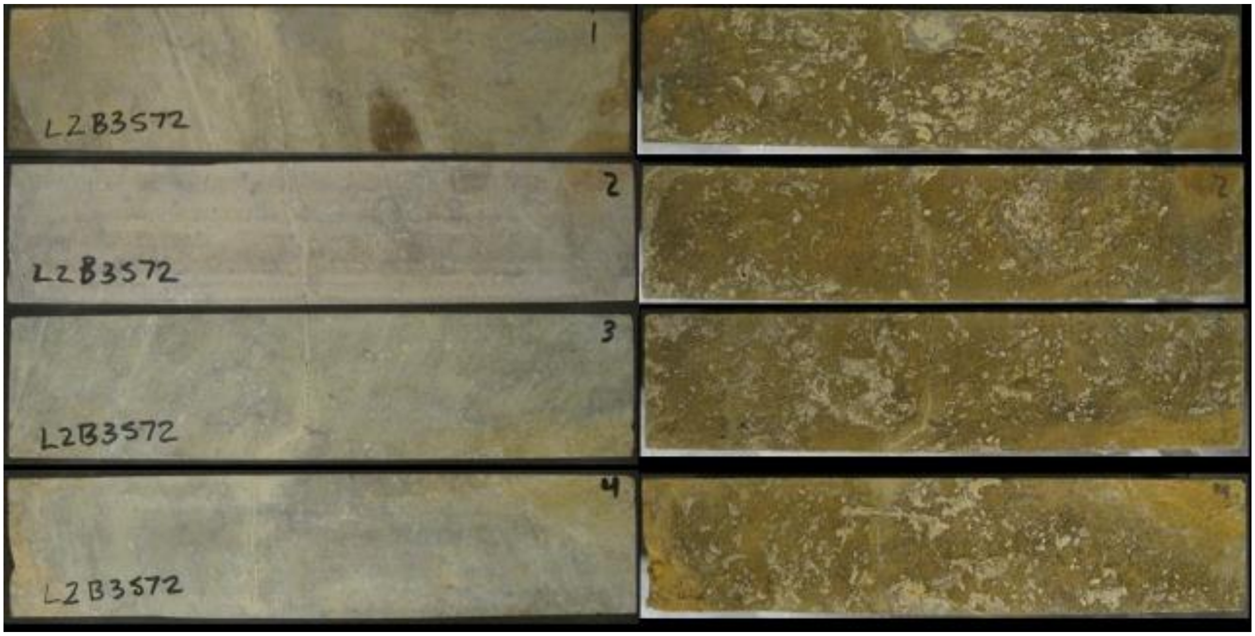

Figure A.29: L2 Sample 72 in Gypsum

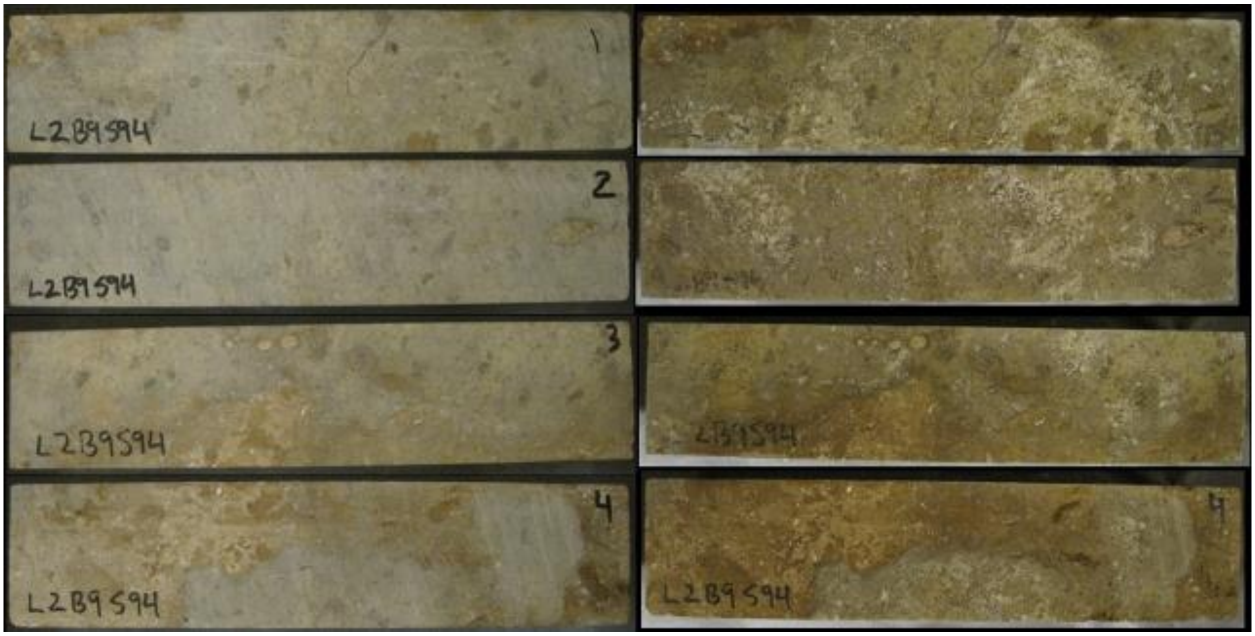

Figure A.30: L2 Sample 94 in gypsum

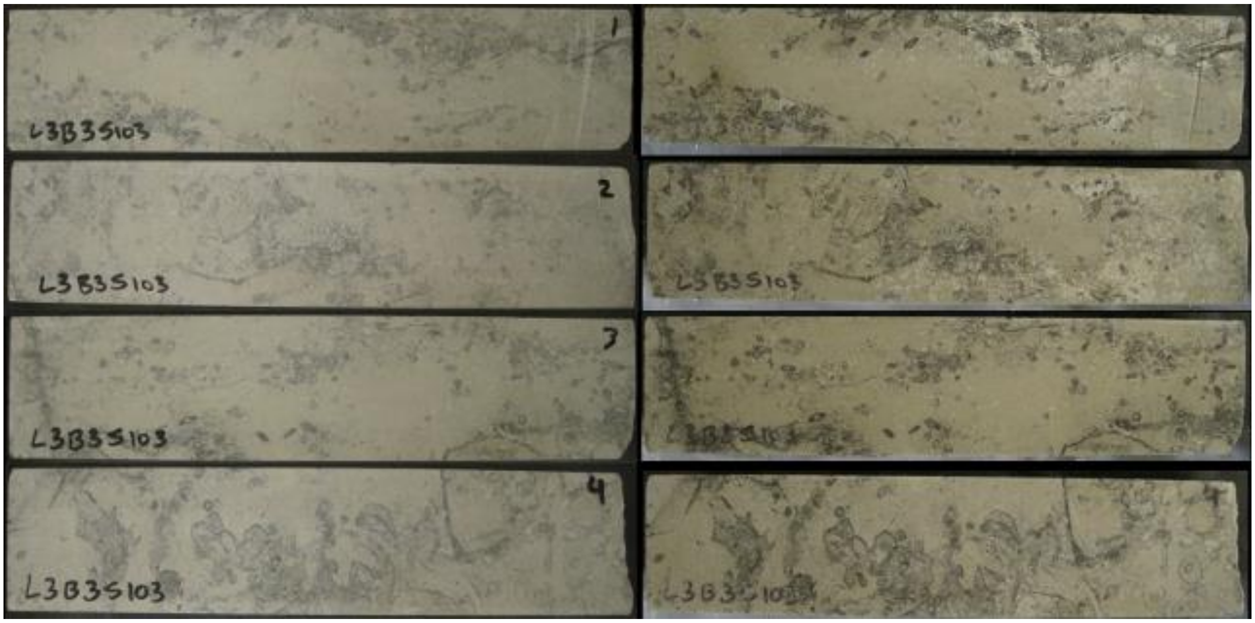

Figure A.31: L3 Sample 103 in Gypsum

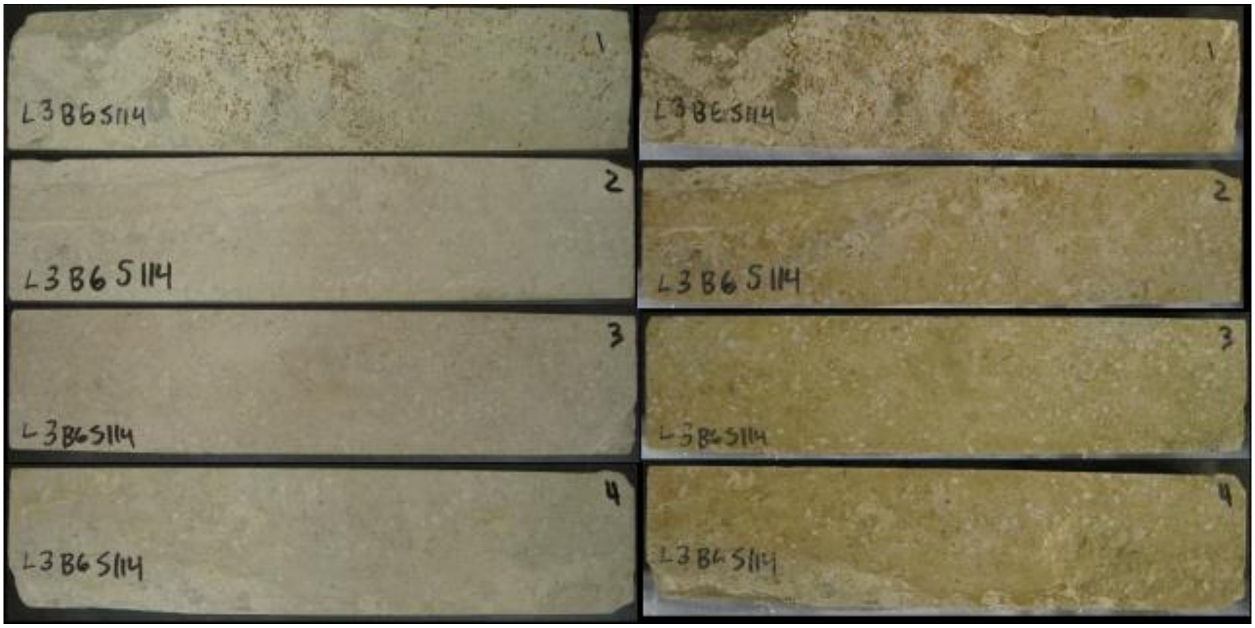

Figure A.32: L3 Sample 114 in Gypsum

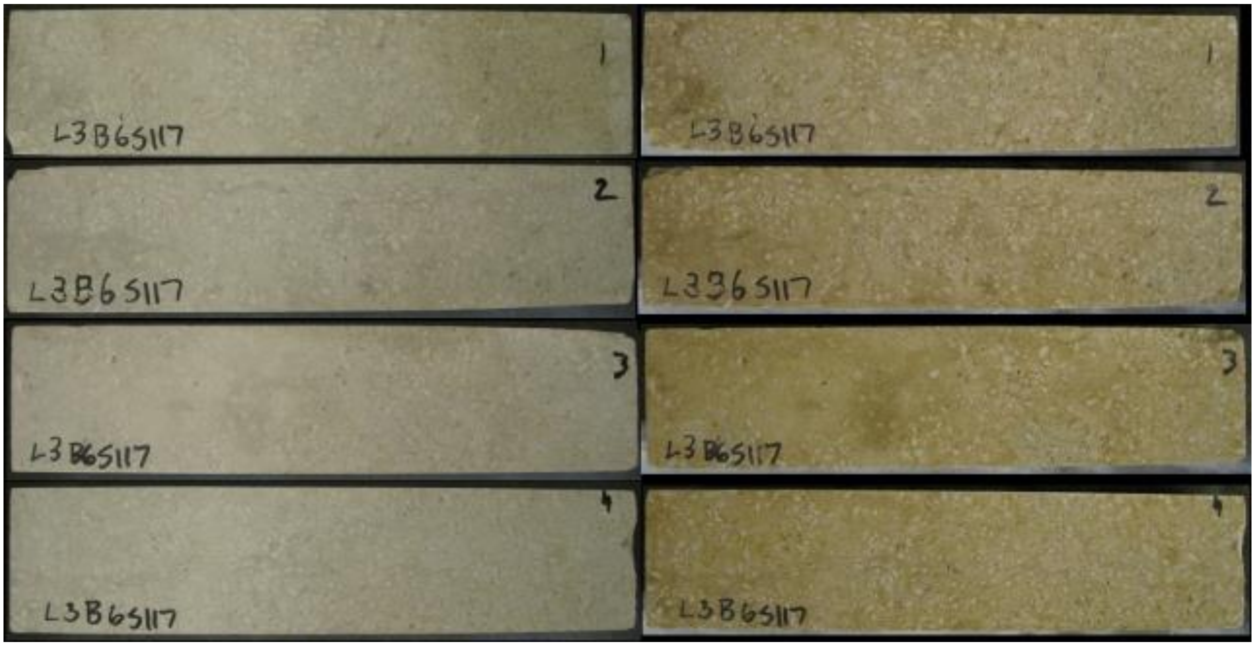

Figure A.33: L3 Sample 117 in Gypsum

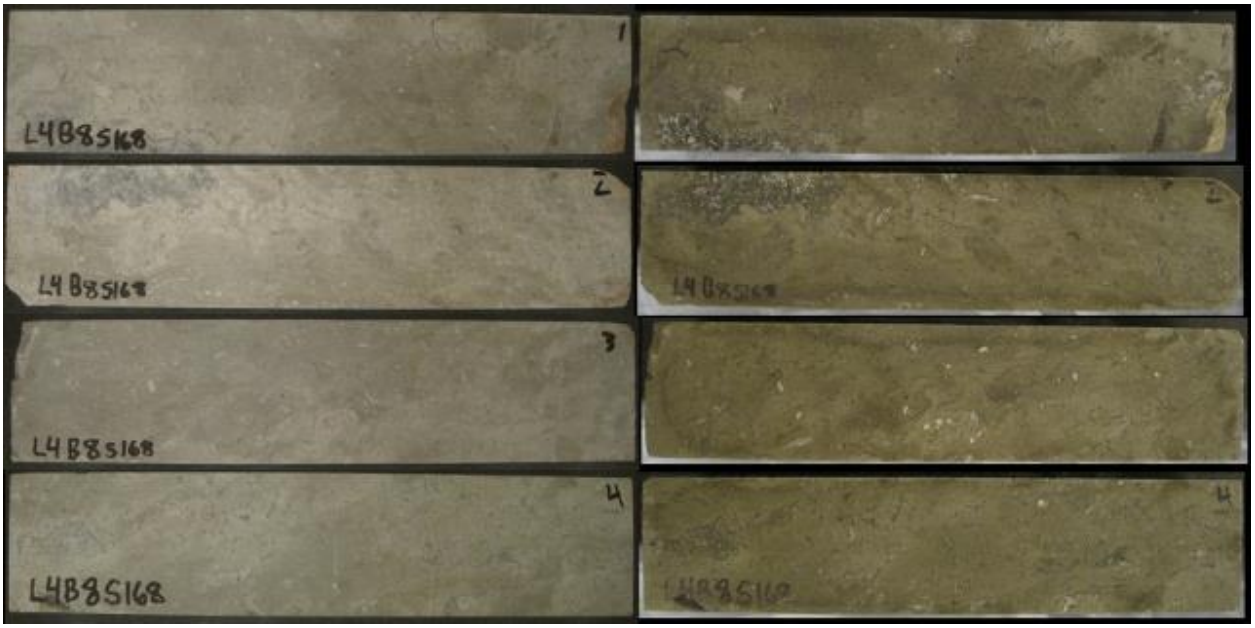

Figure A.34: L4 Sample 168 in Gypsum

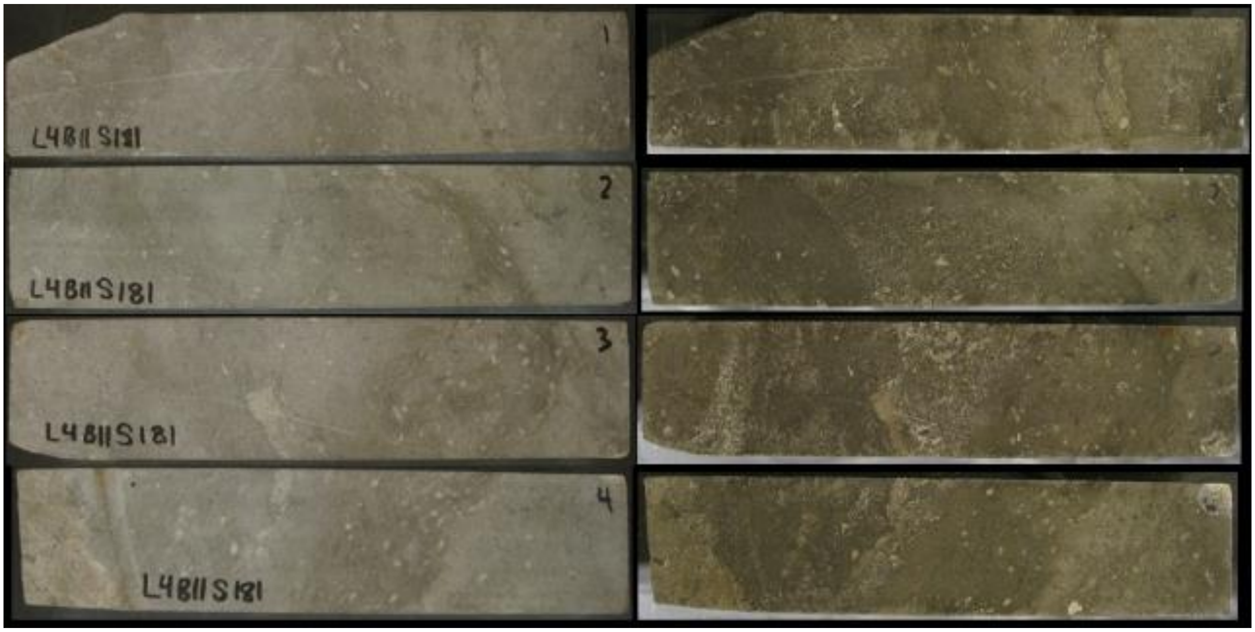

Figure A.35: L4 Sample 181 in Gypsum

Figure A.36: L4 Sample 210 in gypsum

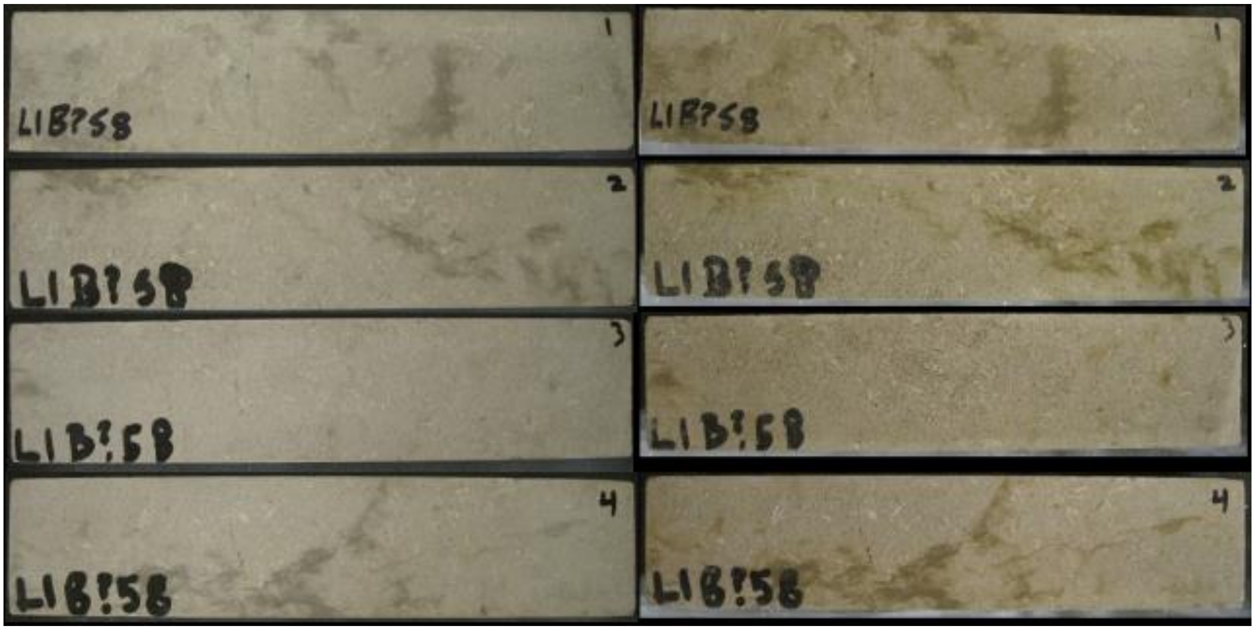

Figure A.37: L1 Sample 8 in Rock Salt Brine

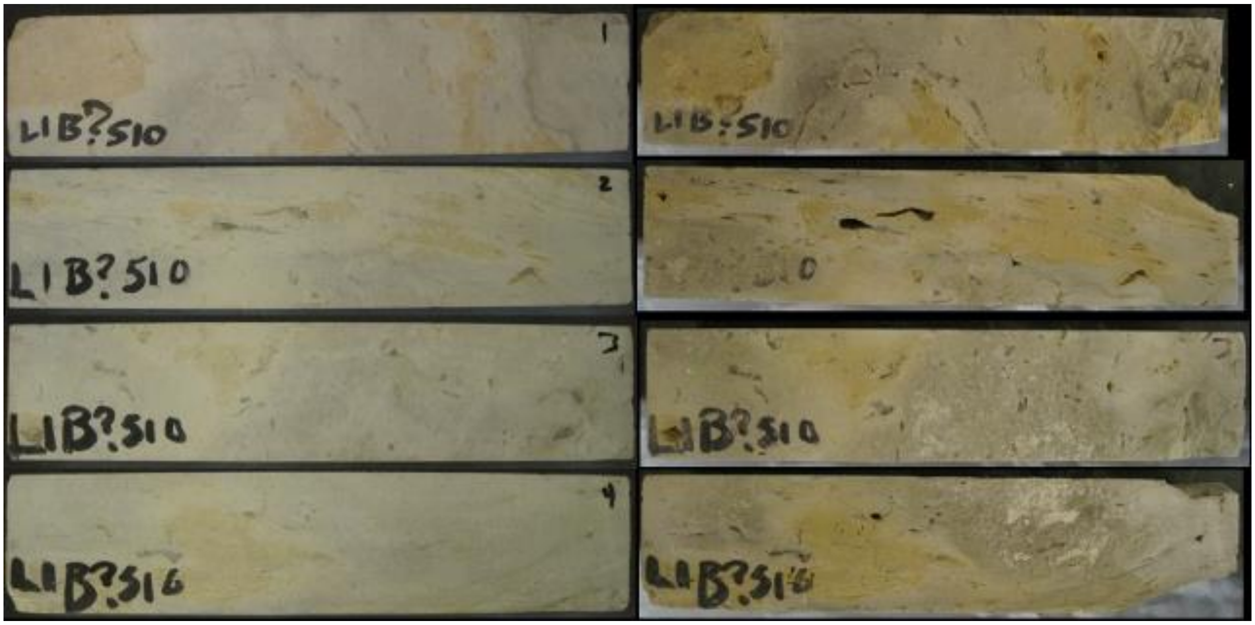

Figure A.38: L1 Sample 10 in Rock Salt Brine

L1 sample 10 contained, similarly to L1 sample 5, clay pockets causing section loss when clay swelled in the presence of brine. The corner that fragmented off visibly cracked early on in the testing, though the corner did not fall off until about the 30th wet-dry cycle.

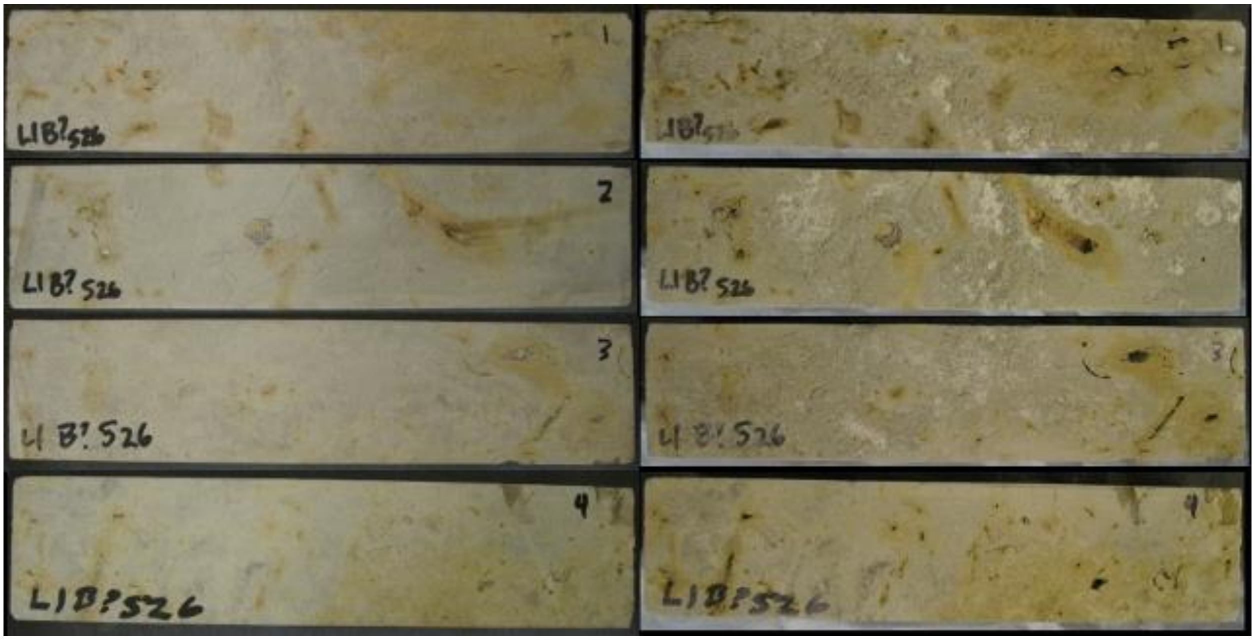

Figure A.39: L1 Sample 26 in Rock Salt Brine

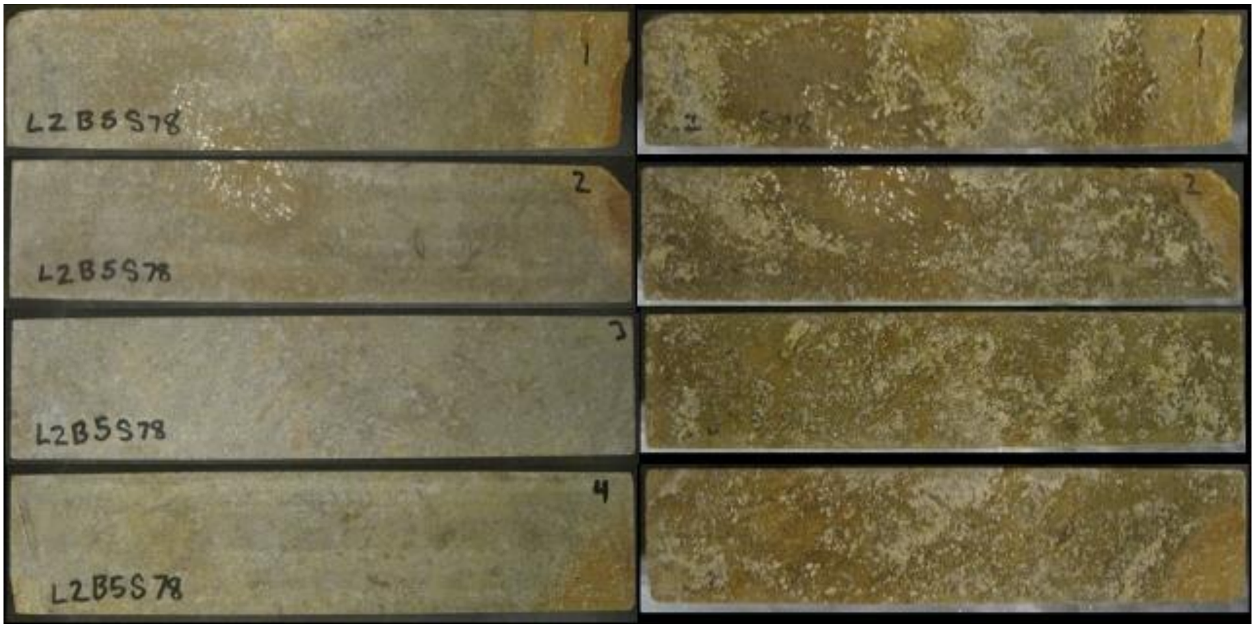

Figure A.40: L2 Sample 78 in Rock Salt Brine

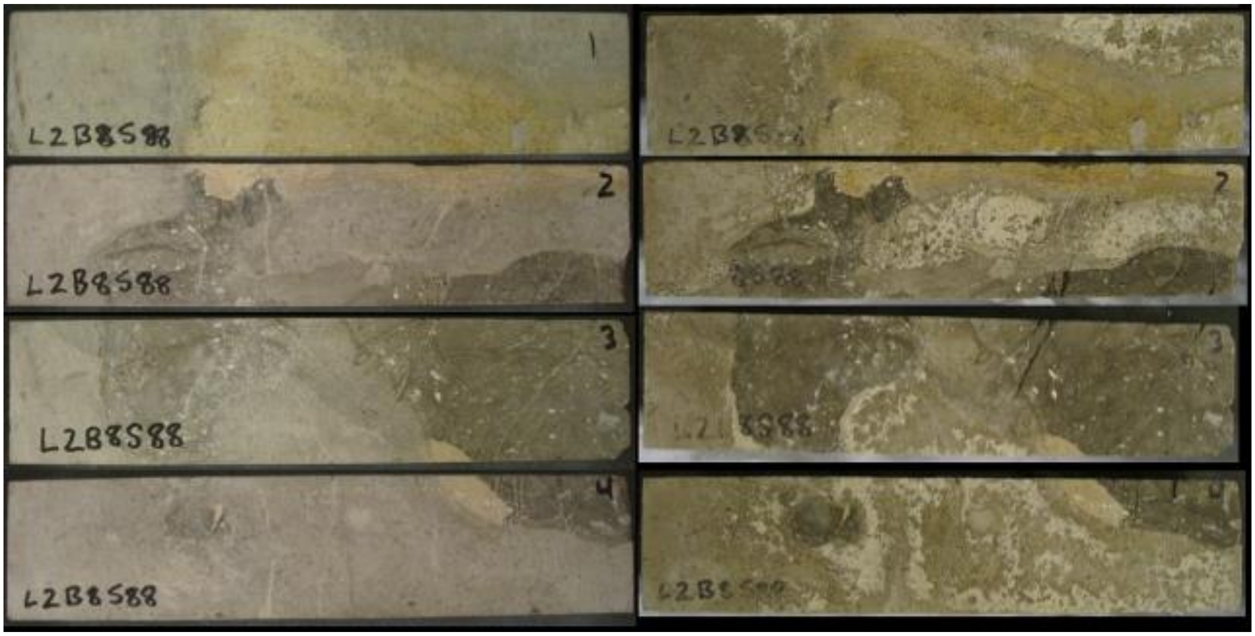

Figure A.41: L2 Sample 88 in Rock Salt Brine

Figure A.42: L2 Sample 97 in Rock Salt Brine

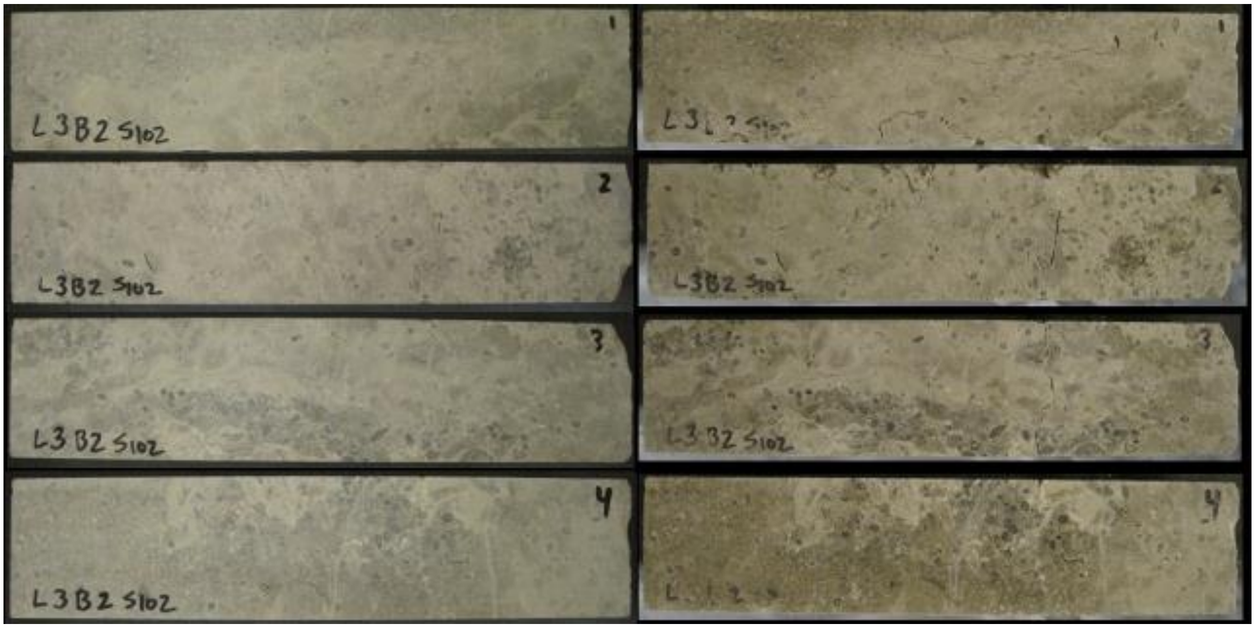

Figure A.43: L3 Sample 102 in Rock Salt Brine

Figure A.44: L3 Sample 112 in Rock Salt Brine

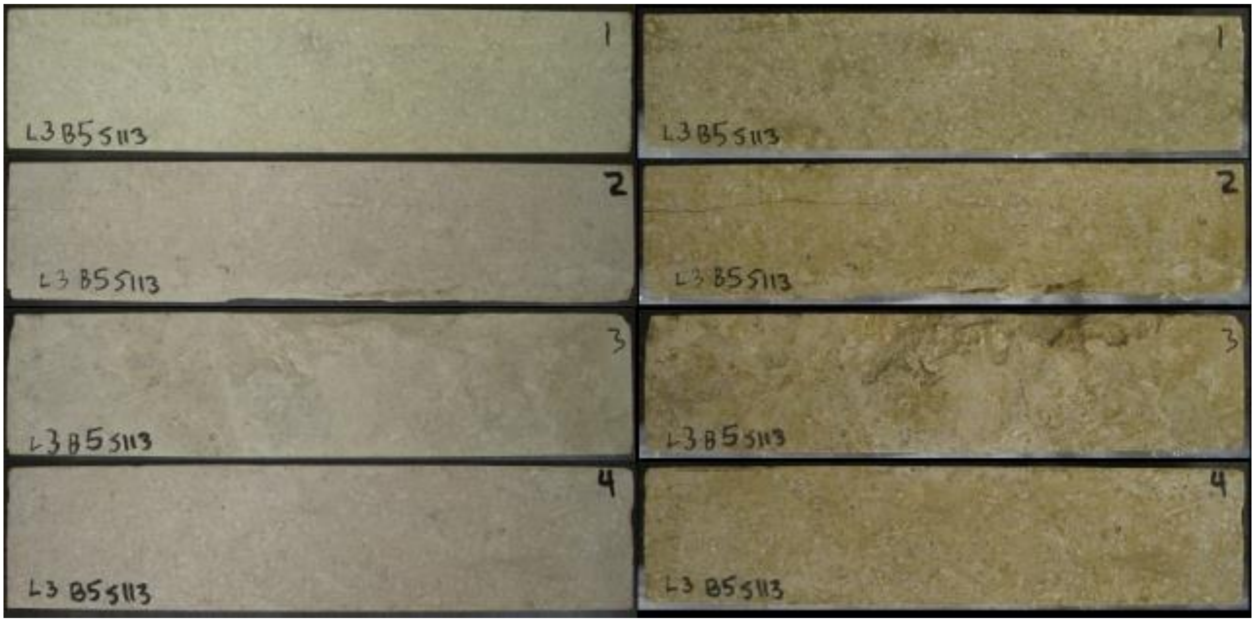

Figure A.45: L3 Sample 113 in Rock Salt Brine

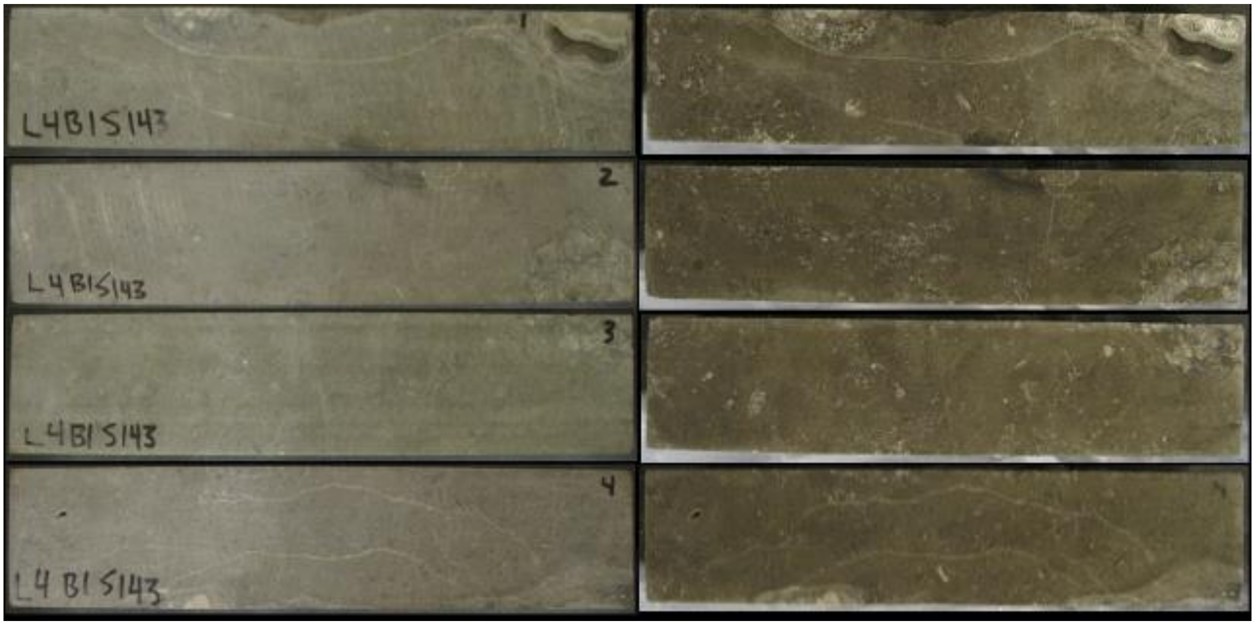

Figure A.46: L4 Sample 143 in Rock Salt Brine

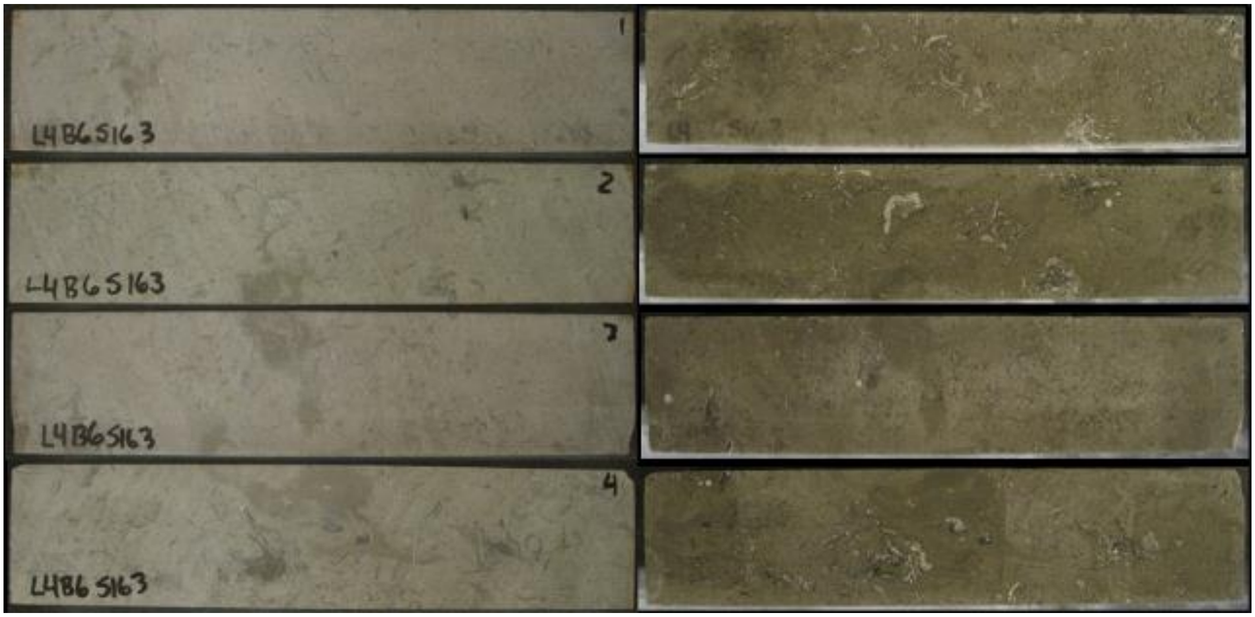

Figure A.47: L4 Sample 163 in Rock Salt Brine

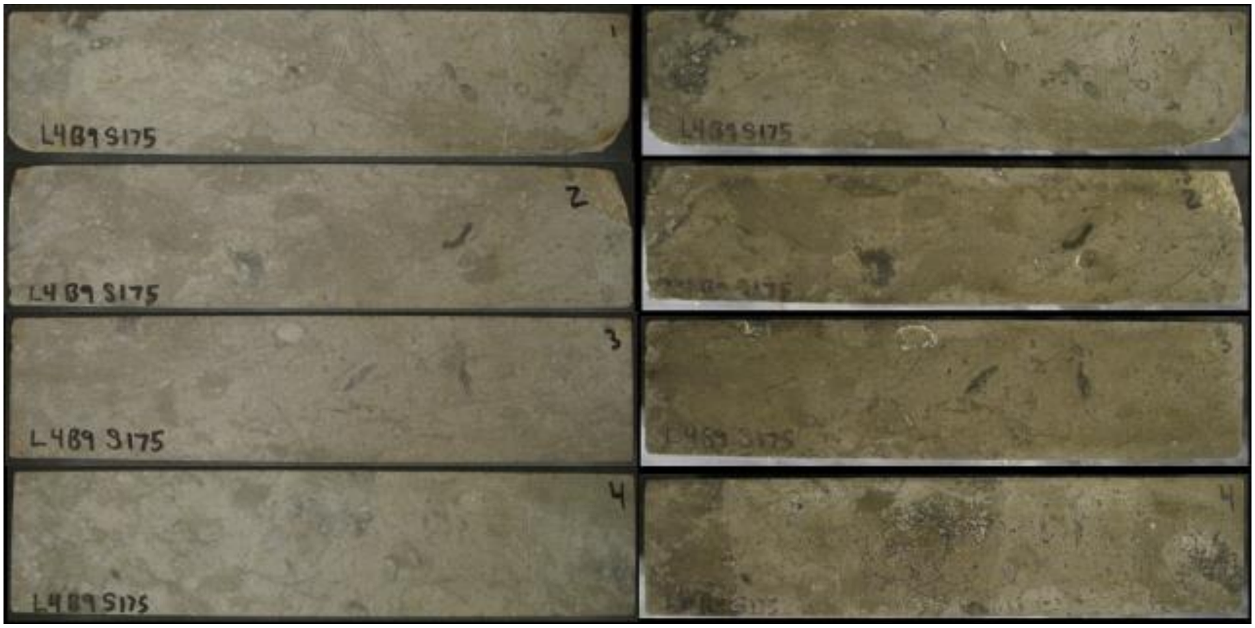

Figure A.48: L4 Sample 175 in Rock Salt Brine

Appendix B - Concrete Prism Wet-Dry Samples

The following figures show concrete prisms before and after completion of 40 wet-dry cycles in various solutions. Each figure shows on the left four prism faces before the start of wet-dry cycling. The right side of each figure shows the corresponding prism faces after completion of wet-dry cycling. Samples were photographed at the end of the last drying stage with no steps taken to rinse salt from the sample surfaces.

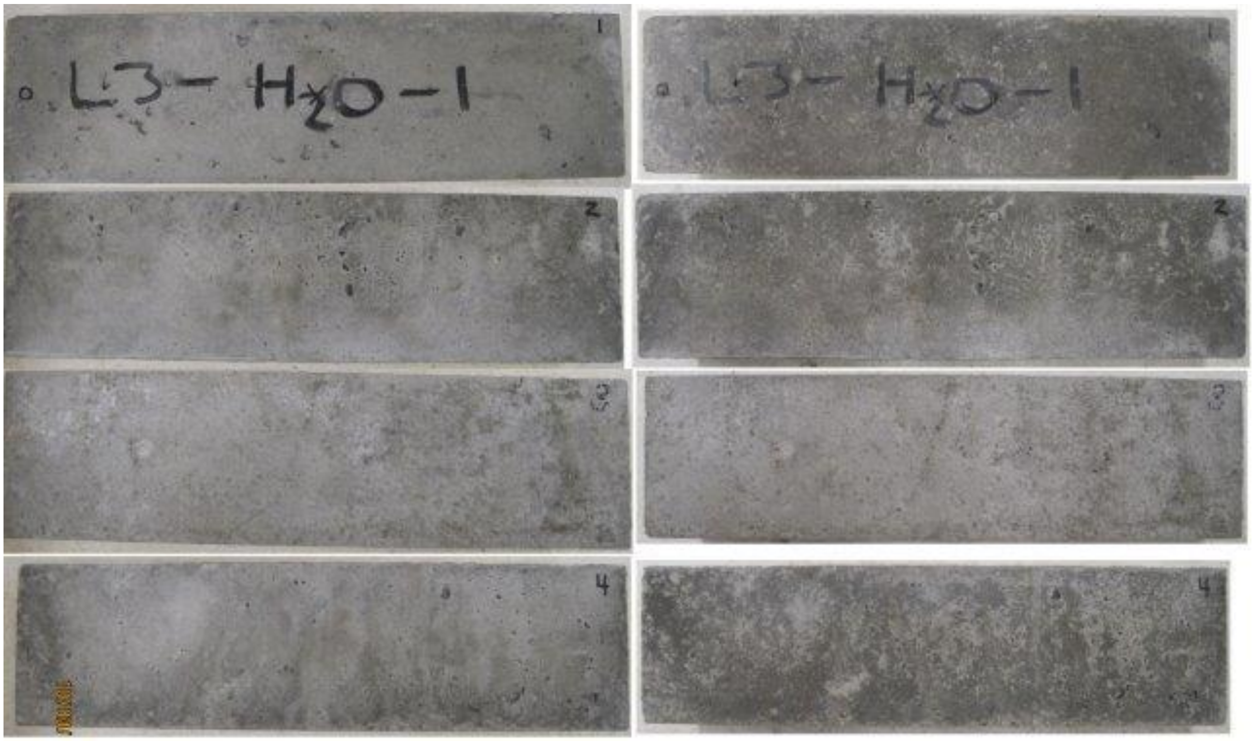

Figure B.1: First L3 Prism in Water

Figure B.2: Second L3 Prism in Water

Figure B.3: First L4 Prism in Water

Figure B.4: Second L4 Prism in Water

Figure B.5: First L3 Prism in NaCl

Figure B.6: Second L3 Prism in NaCl

Figure B.7: First L4 Prism in NaCl

Figure B.8: Second L4 Prism in NaCl

Figure B.9: First L3 Prism in Gypsum

Figure B.10: Second L3 Prism in Gypsum

Figure B.11: First L4 Prism in Gypsum

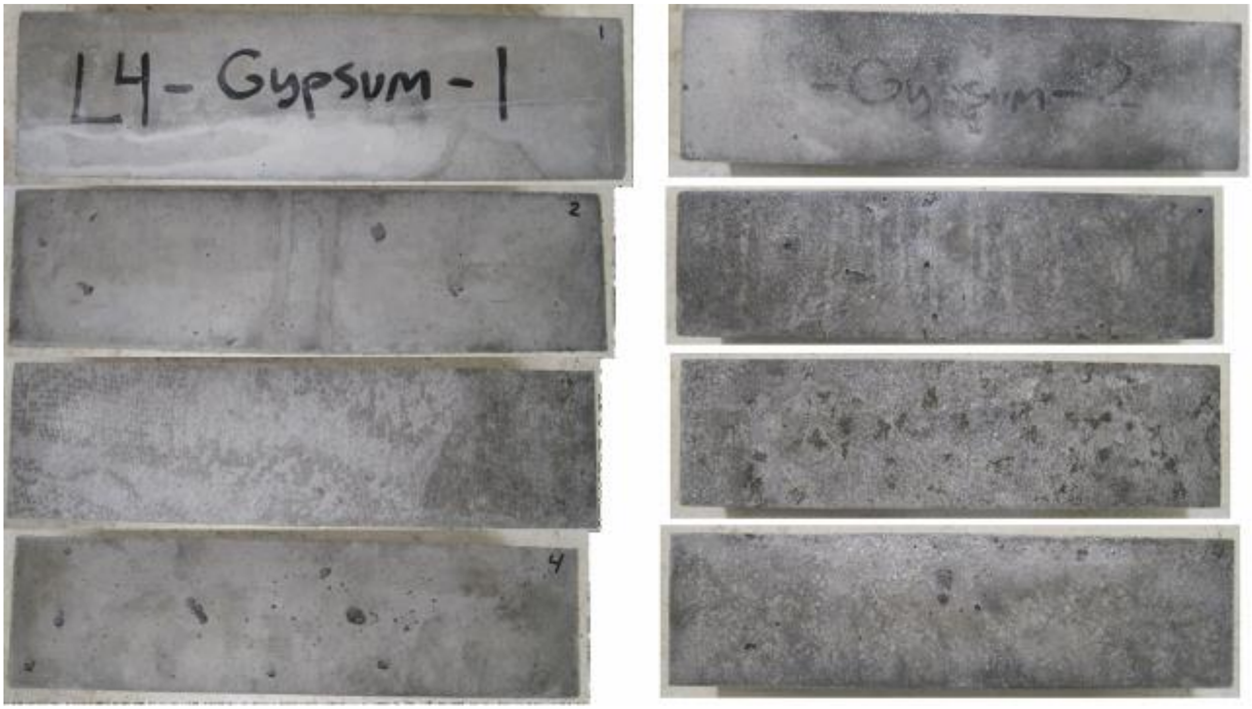

Figure B.12: Second L4 Prism in Gypsum

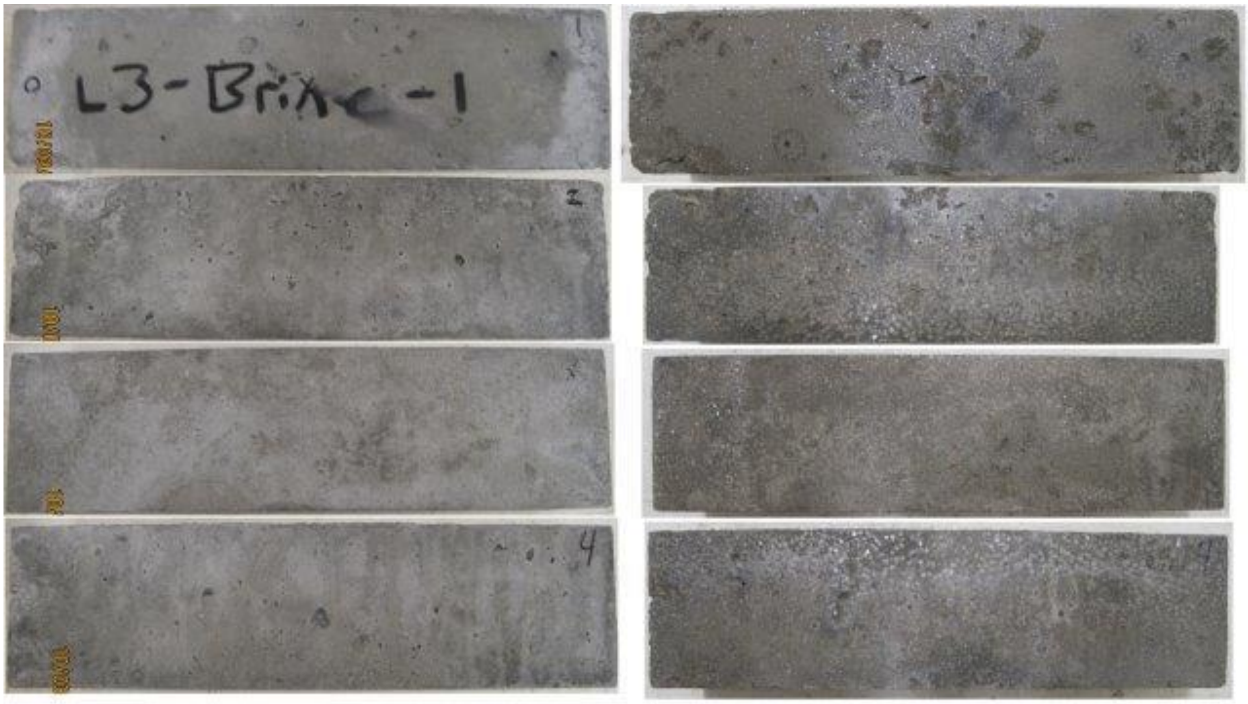

Figure B.13: First L3 Prism in Brine

Figure B.14: Second L3 Prism in Brine

Figure B.15: First L4 Prism in Rock Salt Brine

Figure B.16: Second L4 Prism in Rock Salt Brine

Appendix C - Permissions

The following is the copyright permission to reuse a figure from Spragg et al. (2011):

ELSEVIER LICENSE
TERMS AND CONDITIONS

Aug 07, 2013

This is a License Agreement between Jonathan Varner ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier Elsevier Limited
The Boulevard,Langford Lane
Kidlington,Oxford,OX5 1GB,UK
Registered Company Number
1982084
Customer name Jonathan Varner
Customer address 3278 31st St.
GRANTVILLE, KS 66429
License number 3203641372412
License date Aug 07, 2013
Licensed content publisher Elsevier
Licensed content publication Cement and Concrete Composites
Licensed content title Wetting and drying of concrete using aqueous solutions containing deicing salts
Licensed content author Robert P. Spragg,Javier Castro,Wenting Li,Mohammad Pour-Ghaz,Pao-Tsung Huang,Jason Weiss
Licensed content date May 2011
Licensed content volume number
33
Licensed content issue number
5
Number of pages 8
Start Page 535
End Page 542
Type of Use reuse in a thesis/dissertation
Portion figures/tables/illustrations
Number of figures/tables /illustrations
1
Format both print and electronic
Are you the author of this Elsevier article?
No
Will you be translating? No
Order reference number

Rightslink Printable License https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID...
1 of 5 8/7/2013 8:18 AM

Title of your thesis/dissertation
Influence of Rock Salt Impurities on Limestone Aggregate Durability
Expected completion date Aug 2013

Estimated size (number of pages)
130
Elsevier VAT number GB 494 6272 12
Permissions price 0.00 USD
VAT/Local Sales Tax 0.0 USD / 0.0 GBP
Total 0.00 USD
Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this

licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily

granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

Rightslink Printable License https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID...
3 of 5 8/7/2013 8:18 AM

The following terms and conditions apply only to specific license types:

15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Website**: The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the web site is to be

password-protected and made available only to bona fide students registered on a relevant course if:
This license was made in connection with a course,
This permission is granted for 1 year only. You may obtain a license for future website posting,
All content posted to the web site must maintain the copyright information line on the bottom of each image,
A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com , and
Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
17. **Author website** for journals with the following additional clauses:
All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx . As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.
Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
18. **Author website** for books with the following additional clauses:
Authors are permitted to place a brief summary of their work online only.
A hyper-text must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.
Central Storage: This license does not include permission for a scanned version of the

material to be stored in a central repository such as that provided by Heron/XanEdu.
19. **Website** (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. or for books to the Elsevier homepage at http://www.elsevier.com
20. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. **Other Conditions**:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501085127.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Rightslink Printable License https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID...
5 of 5 8/7/2013 8:18 AM

The following is the copyright permission to reuse a figure from Darwin et al. (2008):

Dear Mr. Varner,

Thank you for your inquiry regarding the use of ACI-copyrighted material. You have ACI's permission to reuse the attached figure. Because rights for the figure were released to ACI upon publication, there is no need to also obtain permission from the authors. Please provide a statement similar to "Reprinted with permission from the American Concrete Institute," and credit the original authors, as appropriate.

Please let me know if you require any further documentation of this permission, or if you have any questions or concerns.

Best Regards,

Ashley

Ms. Ashley A. Poirier
Associate Editor
American Concrete Institute
38800 Country Club Drive
Farmington Hills, MI 48331 USA
Phone: (248) 848-3753

Fax: (248) 848-3701

E-mail: Journals.Manuscripts@concrete.org

Website: http://mc.manuscriptcentral.com/aci

From: Jonathan Varner <jvarner@k-state.edu>
To: Journals.manuscripts@concrete.org
Date: 07/30/2013 02:00 PM
Subject: Copyright permission for figure from report "Effects of Deicers on Concrete Deterioration"

Hello,

My name is Jon Varner and I am a graduate student at Kansas State University under Dr. Kyle Riding in the Civil Engineering Department. I am writing to ask permission to use the attached figure in my Master's thesis and the report for the Kansas DOT based on the research included in my thesis.

The citation for the article is as follows:

Darwin, D., Browning, J., Gong, L., and Hughes, S.R. (2007). "Effects of Deicers on Concrete Deterioration." ACI Materials Journal, 105(6), 622-627

The figure attached is from the full report rather than the article itself. Would the authors' permission be required as well?

Thank you,

Jon Varner

The following is the copyright permission to reuse a figure from Dubberke and Marks (1985):

Dear Mr. Varner:

The Transportation Research Board grants permission to reproduce one figure from the paper, “The Effect of Deicing Salt on Aggregate Durability,” by W. Dubberke and V. Marks, in your Master’s thesis, as identified in your request of July 30, 2013, subject to the following conditions:

1. Please cite paper publication in Transportation Research Record 1031 , Figure 5,
p. 30. Copyright, National Academy of Sciences, Washington, D.C., 1985.

2. Please acknowledge that the material is reproduced with permission of the Transportation Research Board.

3. None of this material may be presented to imply endorsement by TRB of a product, method, practice, or policy.

Every success with your Master’s thesis. Please let me know if you have any questions.

Sincerely,

Javy Awan

Director of Publications
Transportation Research Board

Phyllis Barber
Transportation Research Board
Publications Office
202 334-2972 phone
202 334-3495 fax
pbarber@nas.edu
-----Original Message-----
From: Jonathan Varner [mailto:jvarner@k-state.edu]
Sent: Tuesday, July 30, 2013 1:35 PM
To: Barber, Phyllis
Subject: TRR Journal Online Copyright Question

Hello,

My name is Jon Varner and I am a graduate student at Kansas State University. I am writing to ask permission to use the attached figure in my Master's thesis and the report for the Kansas DOT based on the research included in my thesis.

The following is the citation for the source article of the figure:

Dubberke, W. and Marks, V. (1985). "The Effect of Deicing Salt on Aggregate Durability." Transportation Research Record, No. 1031, 27-34

Is permission of the authors required as well?

Thank you,

Jon Varner