1	NEUTRON RADIOGRAPHY MEASUREMENT OF SALT SOLUTION ABSORPTION
2	IN MORTAR
3	Catherine L. Lucero, Robert P. Spragg, Dale P. Bentz, Daniel S. Hussey, David L. Jacobson, and
4	W. Jason Weiss
5	ACI member Catherine L. Lucero is a civil engineer at the Concrete, Geotechnical and
6	Structural Laboratory of the US Bureau of Reclamation in Denver, CO. She received her BSCE
7	from the University of New Mexico and her MSCE from Purdue University.
8	ACI member Robert P. Spragg is a PhD candidate at Purdue University. He received his BSCE
9	and MSCE degrees from Purdue University.
10	ACI member Dale P. Bentz is a chemical engineer in the Materials and Structural Systems
11	Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD. He is a
12	member of ACI committees 232, Fly Ash; 308, Curing Concrete; and 546, Concrete Repair. His
13	research interests include experimental and computer modeling studies of the microstructure and
14	performance of cement-based materials.
15	Daniel S. Hussey is a Physicist at the National Institute of Standards and Technology, which he
16	first joined as a National Research Council Postdoctoral Fellow. He received his PhD in Physics
17	from Indiana University, Bloomington, and his BS in physics from the University of New
18	Hampshire. His research interests are focused on neutron imaging and optics and the application
19	of neutron imaging and scattering techniques to problems of porous media.

David L. Jacobson is a Physicist at the National Institute of Standards and Technology, which
he first joined as a National Research Council Postdoctoral Fellow. He received his PhD in

Physics from the University of Missouri, Columbia, and his BS in physics from Westminster
College (Missouri). His research interests are focused on neutron interferometry, imaging and
optics.

Jason Weiss, FACI, is the Edwards Professor of Engineering and Head of the school of Civil
and Construction Engineering at Oregon State University. He earned a BAE from Penn State
University and a MS and PhD from Northwestern University. His research interests include
shrinkage, early age behavior, cracking and moisture transport in concrete.

29

ABSTRACT

30 Some concrete pavements in the US have recently exhibited premature joint deterioration. It is 31 hypothesized that one component of this damage can be attributed to a reaction that occurs when 32 salt-laden water is absorbed in the concrete and reacts with the matrix. This study examines the 33 absorption of CaCl₂ solution in mortar via neutron imaging.

Mortar specimens were prepared with water to cement ratios, (*w/c*), of 0.36, 0.42 and 0.50 by mass and exposed to chloride solutions with concentrations ranging from 0 % to 29.8 % by mass. Depth of fluid penetration and moisture content along the specimen length were determined for 96 h after exposure. At high salt concentration (29.8 %), the sorption rate decreased by over 80 % in all samples. Along with changes in surface tension and viscosity, CaCl₂ reacts with the cement paste to produce products (Friedel's salt, Kuzel's salt, or calcium oxychloride) that block pores and reduce absorption.

INTRODUCTION

42 Concrete pavements represent a large portion of the transportation infrastructure. While many of 43 these pavements provide excellent long-term performance, some pavements, particularly in the 44 northern region of the US, have recently exhibited premature joint deterioration. This damage 45 can shorten the life of an otherwise well-functioning pavement or can necessitate costly repairs. 46 Recently, studies have been conducted to examine causes, early detection, and mitigation of joint 47 deterioration [1]–[6].

48 Other research has focused on the development of approaches to predict how long freeze-thaw 49 damage will take to occur. These models use fluid absorption to aid in the determination of the 50 degree of saturation [7]. The degree of saturation influences the freeze-thaw performance of 51 concrete [8], [9]. The addition of salts to the pore fluid can increase the degree of saturation due to the higher equilibrium relative humidity of the solution [10], [11]. The addition of salts will 52 53 alter properties of the fluid such as surface tension and viscosity, therefore altering the transport 54 properties such as absorption. The fluid viscosity and surface tension both increase with an 55 increase in concentration of salts, but the viscosity more so than the surface tension, which will 56 decrease the rate of absorption. Furthermore, salt can also precipitate out of solution and block 57 pores, preventing further fluid ingress and increasing the local degree of saturation [12].

In many cold climates, salt solutions are used on concrete roads and sidewalks to minimize the formation of ice by lowering the freezing temperature of the solution. However, calcium chloride $(CaCl_2)$ can react with the calcium aluminate phases (C₃A) of cement clinker or monosulfate (Afm) to create Friedel's salt [13], [14]. The calcium sulfo-aluminate phases (Afm and ettringite) can further react with chloride-based salts to form Kuzel's salt [15]. Additionally, calcium

chloride can react with calcium hydroxide to form calcium oxychloride at room temperature
(Equation 1). All three products can precipitate and grow in the voids, reducing fluid ingress, as
well as reducing the volume of empty pores, thereby increasing the local degree of saturation.

$$66 \quad 3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O \qquad Equation 1$$

A standardized test method for quantifying absorption of water in concrete is ASTM C1585 [16]. This test was developed for water and does not provide corrections for fluids with viscosities and surface tensions that differ from those of deionized water. Additionally, the absorption behavior is influenced by the initial conditioning [17]. According to the standard, the absorption, *I* $(mm^3/mm^2 [in^3/in^2])$, can be computed as shown in Equation 2:

72
$$I = \frac{m_t}{a \cdot \rho}$$
 Equation 2

where m_t is the change in specimen mass (g [lb]) at the time *t* after exposure to the fluid, *a* is the exposed surface area of the specimen (mm² [in²]) and ρ is the density of water (g/mm³ [lb/in³]). Additionally, ASTM C1585 instructs users to plot the results of the test as mm³ [in³] of water absorbed normalized by the surface area of the specimen in mm² [in²] versus the square root of time. This calculation provides a result in units of mm [in] that many mistakenly interpret as the depth of water ingress. However, the test does not account for the total pore volume, which can affect the interpretation of the results.

80 The initial rate of absorption, or sorptivity as defined by ASTM C1585, S_i (mm/s^{1/2} [in/s^{1/2}]) is

81 the slope of the absorption versus the square root of time up to 6 h. The secondary sorptivity, S_s

 $82 \quad (mm/s^{1/2} [in/s^{1/2}])$ is the slope of the absorption versus the square root of time achieved between 1

d and 7 d. However it should be noted that these times are dependent on the sample height and
fluid properties, both of which are specified in the ASTM C1585 test method [11], [18], [19].

While Equation 2 is used for absorption and the ASTM method for determining S_i and S_s are useful for qualifying the absorption behavior of concrete, it may not be representative of the actual depth of penetration into the specimen. The rate at which the fluid travels is dependent on the fluid properties (such as surface tension, viscosity and density) and the volume of pores, as well as their connectivity in the paste [18], [20]–[22]. To overcome this shortcoming, some have used the intrinsic absorption as defined in Equation 3 [19].

91
$$I_{int} = \frac{m_t}{a \cdot \rho \cdot \Phi \cdot (1 - D_0)} \cdot \sqrt{\frac{\gamma_w \eta_s}{\gamma_s \eta_w}}$$
Equation 3

92 where I_{int} (mm [in]) is the intrinsic absorption, Φ is the volume fraction of porosity, D_0 is the 93 volume fraction of the initial degree of saturation, η_w and η_s are the viscosities of water and 94 solution (mN•s/m² [lbf-s/in²]), respectively; and γ_w and γ_s are the surface tensions of water and 95 solution (mN/m [lbf/in]), respectively. The quantity under the square root represents the 96 theoretical influence of fluid surface tension and viscosity on the absorption.

97 Neutron imaging is an accurate and powerful method of monitoring fluid penetration in porous 98 media and has been used by many researchers to study fluid permeation in concrete [23]–[25]. 99 The gray level of a pixel in a radiograph is proportional to the number of neutrons that made it 100 through the object. Hydrogen has a large neutron attenuation coefficient, meaning materials rich 101 in hydrogen appear dark in images. This nondestructive test method can be used to monitor the 102 actual depth of fluid penetration continuously for long periods of time. The volume of water in 103 the system can be accurately quantified, in addition to the ability to visually monitor fluid

movement in situ [26]–[28]. This allows for the calculation of the degree of saturation in the
system which is directly related to long term performance, particularly during exposure to freezethaw cycles.

107

RESEARCH SIGNIFICANCE

108 One approach to achieving sustainable concrete construction is to increase its service life and 109 minimize the need for costly repairs. The deterioration of joints in pavements is one example 110 where foundational efforts are needed to better understand the contributing phenomena and to 111 develop functional approaches to reducing damage and cracking. This experimental study 112 investigates the fundamental transport of calcium chloride solutions into mortar, permitting a 113 quantitative description of the saturation (and salt) profile of the exposed specimen. 114 Understanding how these salts penetrate into and react with the concrete will promote the 115 development of mitigation strategies to effectively reduce and perhaps one day eliminate 116 premature joint deterioration.

117

EXPERIMENTAL INVESTIGATION

118 Sample Preparation

119 Mortar specimens were mixed in accordance with ASTM C192/C192M-13 using the mixture 120 proportions in Table 1. All materials were weighed to the nearest 0.01 g [0.00002 lb]. Both 121 ASTM C150 Type I and Type V cements were used in this study. The composition of each 122 cement is listed in Table 2. It is expected that mortars made using Type V cement will produce 123 less Friedel's and Kuzel's salts when exposed to $CaCl_2$ due to their lower amount of aluminates 124 (C₃A), although these compounds may still form due to the increased presence of C₄AF [13], 125 [29].

126 The mortar was cast in prism molds with nominal dimensions of 76.2 mm by 101.6 mm by 406.4 127 mm [3 in by 4 in by 16 in]. After setting, the mortar prisms were removed from their molds, 128 sealed, and kept at 23 °C \pm 1 °C [73.4 °F \pm 1.8 °F] until they reached 60 % hydration. The 129 curing time to reach the desired degree of hydration was estimated using isothermal calorimetry. 130 The time to reach 60 % hydration was 27 d, 78 h, 55 h, and 21 d for mixtures 1 through 4, 131 respectively. The mortar prism was cut with a wet saw to 76.2 mm [3 in] wide by 50 mm ± 1.1 132 mm [2.0 in \pm 0.04 in] high by 20 mm \pm 1.2 mm [0.79 in \pm 0.05 in] thick slices. Since the field of 133 view of the neutron camera (75 mm [2.95 in]) was smaller than the nominal width of the 134 specimen, the width of individual specimens was not measured. The cut specimens were then 135 placed in a chamber at 23 °C [73.4 °F] and 50 % relative humidity (RH) for 1 month. 136 Equilibrium was determined when the change in mass was less than 0.02 % for a 15 d period 137 [17]. Four sides of the specimens were then wrapped in aluminum tape to prevent moisture loss. 138 The top and bottom surfaces of the 50 mm [2.0 in] high specimens were subsequently exposed 139 for absorption tests.

140 Additional 76.2 mm wide by 50 mm high by 20 mm [3 in by 2.0 in by 0.79 in] samples of each 141 mixture were oven dried and vacuum saturated to 100 % degree of saturation. A group of 142 additional mortar specimens with a w/c of 0.42 and Type I ordinary Portland cement (OPC) were 143 conditioned differently in order to compare the degree of saturation as determined from neutron 144 images and by mass measurements. Samples were conditioned to degrees of saturation between 145 30 % and 90 % by saturating samples and letting them dry in air for various amounts of time. 146 One sample for each degree of saturation shown in Figure 1b was prepared. Once dried to the 147 desired moisture content (mass), each sample was rewrapped in aluminum tape and allowed to 148 re-equilibrate for at least 24 h.

149 Calcium chloride solutions were prepared as percent of CaCl₂ to water by mass. Solutions 150 ranging from 0 % (deionized water) to 29.8 %, the eutectic concentration of calcium chloride and 151 water, were used for this study in order to include the spectrum of concentrations that may be 152 seen in pavements in the field. The fluid properties of each solution are summarized in Table 3 153 [11], [30]. The viscosity of the solution increases by a factor of 3.3, while the surface tension 154 only increases by a factor of 1.13 over the full range of concentrations investigated in the present 155 study. The sorptivity of a fluid is proportional to the square root of the ratio of the surface 156 tension to the viscosity [20], so the relatively larger increase in viscosity will result in an overall 157 decrease in sorptivity.

158 Neutron Imaging

159 Imaging was performed at the Neutron Imaging Facility at the National Institute of Standards 160 and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, Maryland. The 161 imaging facility is located at Beam Tube 2 as shown in Figure 2. The thermal neutron source is a 162 20 MW [18969 Btu/s] heavy-water fission reactor operated at 37 °C [98.6 °F]. A collimation ratio (L/D) of 450 and a neutron fluence rate of 1.4×10^7 cm⁻¹s⁻¹ [3.55 x 10⁷ in⁻¹s⁻¹] were used for 163 164 the sorption experiments. A scientific complimentary oxide semiconductor (sCMOS) camera 165 viewed a gadolinium oxysulfide scintillator through a Nikon* 85 mm f/1.8 lens with a PK-11a extension tube to create a neutron detector with an effective pixel pitch of $30 \,\mu m$ [3.94 x 10^{-5} in]. 166

167 The experiment was set up such that five samples could be imaged in each test series. The

168 samples were placed on a motorized table so that they could be repositioned in the beam line

169 without the beam being turned off, as shown in Figure 3. Nine images of each sample were taken

170 with an exposure time of 60 s to serve as reference images of the specimen at 50 % RH before

171 being exposed to the chloride solutions. Nine images of similar geometry samples cut from the

same prism in the oven dried and fully saturated conditions were also taken to determine thedegree of saturation during absorption.

After the reference images were captured, fluid ingress could be measured. The ponding reservoirs on top of the samples were filled with approximately 30 mL [1.0 fl. oz. (US)] of solution and the mortar began absorbing the fluid. Three images were captured of each sample before the stage moved to the next position to image the next sample. Including the time to move the table to each position, approximately 30 min elapsed between each set of images per specimen.

180 Image Processing and Analysis

Images were combined with a median filter in groups of 9 for the reference images or 3 for images taken during absorption. 30 flat field (open beam) and dark (closed beam) images were also taken and combined with a median filter. The use of a median filter (in time) eliminated the appearance of streaks due to gamma rays and fast neutrons depositing energy directly into the sCMOS.

186 The images of the mortar in the wet state at time *t* after exposure to fluid were normalized to the

187 reference image before exposure to fluid and converted to binary form as shown in Figure 4a and

4b. The depth of penetration was measured at 10 points, excluding the edges, equally spaced at 7

189 mm [0.28 in] according to Figure 4c, along the water front as shown in Figure 4d.

190 Beam hardening effects, where the effective attenuation coefficient decreases due to an increased

- 191 mass of high energy neutrons in the effective cross section, can be seen in neutron images
- 192 containing relatively large quantities (thicknesses) of water [26], [31]. These effects can make
- 193 quantifying water difficult. However, with total water thicknesses less than about 5 mm [0.20 in],

the relationship between optical density and water thickness remains approximately linear [26],
[32]. The optical density is defined as

196
$$OD = -\ln\left(\frac{I}{I_0}\right)$$
 Equation 4

197 where OD is the optical density, I is the measured intensity and I_0 is the intensity of the flat field.

Figure 1a illustrates a calculation of optical density as a function of pore volume in mortar for different sample thicknesses. The approximate volume fraction of the pores at 60 % degree of hydration was determined using Powers Model and is summarized in Table 4 [33]. The theoretical capillary porosity for 0.36, 0.42, and 0.50 *w/c* mortars ranged from approximately 19 % to 24 % and is indicated in the gray shaded region of Figure 1a. The volume fraction was then applied to various thicknesses of mortar to determine the extent of beam hardening that can be expected.

205
$$OD(t_w) = \mu_w t_w + \beta_w t_w^2$$
 Equation 5

where t_w is the thickness of water, μ_w is 0.38483 mm⁻¹ [9.69 in⁻¹], and β_w is -0.00947 mm⁻² [6.10 in⁻²], as taken from [26]. When using a 20 mm [0.79 in] thick mortar sample as in the case of this study, beam hardening will not be significant as $t_w \le 4.8$ mm [0.19 in]. This indicates that the relationship between the optical density and the water content can be assumed to be linear between oven dried mortar and 100 % saturated mortar.

211 The optical density can be normalized by the sample thickness to define the composite

attenuation coefficient of the mortar (μ_{mortar}) [32]. By normalizing to the thickness of the sample

213 (*t_{sample}*), the optical densities from multiple mortar samples can be compared to each other.

214
$$\mu_{mortar} = \frac{OD_{mortar}}{t_{sample}}$$
 Equation 6

The degree of saturation in the mortar is calculated from the radiographs using the optical density normalized to the sample thickness of an oven dried sample (S=0) and a completely saturated sample (S=1) as calculated in Equation 7

218
$$S = \frac{\mu_{mortar} - \mu_{DRY}}{\mu_{SAT} - \mu_{DRY}} \times 100\%$$
 Equation 7

where μ_{DRY} and μ_{SAT} are the attenuation coefficients of the mortar in the oven dried and saturated states, respectively.

Figure 1b is a plot of degree of saturation (*S*) obtained via neutron radiographs versus the degree of saturation determined gravimetrically. A good one-to-one correlation exists between the degrees of saturation calculated from the radiographs to the actual degree of saturation determined by mass. The error associated with the calculated value of *S* is largely attributed to the variation of sample thickness.

226

EXPERIMENTAL RESULTS AND DISCUSSION

227 **Depth of Fluid Penetration**

228 The average depth of penetration was measured every 30 min for the first 12 h of exposure to the

- chloride solution. After 12 h, the depth of penetration was measured at 25 h (300 s^{1/2}) and 40 h
- 230 (400 s^{1/2}). The results from each series (mixtures 1-4) are plotted in Figure 5.
- 231 In general, the rate of fluid penetration decreases as the concentration of chlorides in the solution
- increases as shown in Figure 5. This is consistent with previous studies [11], [12], [19], [34]
- where the rate of salt solution absorption decreases as the concentration of salts increase. When

normalized to the sorptivity of water, there is a clear decrease in sorptivity with an increase in chloride concentration as shown in Figure 6. The theoretical influence of the altered fluid properties (surface tension and viscosity), i_{fluid} , is calculated by Equation 8 [11], [20] and is plotted as a function of calcium chloride concentration in Figure 6.

238
$$i_{fluid} = \sqrt{\frac{\gamma_s \eta_w}{\gamma_w \eta_s}}$$
 Equation 8

239 When exposed to 10 % CaCl₂, mortar prepared with Type V cement remains on the theoretical 240 line, meaning the specimen sorptivity is only influenced by the fluid properties. Mortar prepared 241 with Type I cement also shows a decrease in absorption due to fluid properties when exposed to 242 10 % CaCl₂ solution, however the value of normalized sorptivity deviates from the theoretical 243 curve due to a decrease in porosity from the reaction between C_3A and calcium chloride resulting 244 in the precipitation of Friedel's and Kuzel's salts [13], [19]. At room temperature, calcium 245 oxychloride can form when the CaCl₂ concentration is over 12 % by mass [35]. When exposed 246 to solutions with 20 % and 29.8 % CaCl₂, all samples experienced a significant decrease in 247 sorptivity beyond that predicted by the change in fluid properties. This additional decrease in 248 sorptivity is the effect of the formation of calcium oxychloride, in addition to the formation of 249 Friedel's and Kuzel's salts in the Type I mortar [2], [19], [36]. Although salt formation cannot 250 be directly detected with neutron radiography, the hindered rate of fluid ingress is likely 251 attributed to the formation of calcium oxychloride and Friedel's salt that occupies space in the 252 pores and effectively decreases the local pore volume of the matrix. Table 5 summarizes the 253 sorptivity (rate of fluid penetration), the normalized sorptivity and the percent difference 254 between the experimental normalized sorptivity and the theoretical value.

255 Change in Degree of Saturation

The change in moisture content was monitored continuously for 10 h to 12 h. Since the samples were conditioned to 50 % RH, the initial degree of saturations were approximately 20 %, 16 %, 15 %, and 18 % for Mixtures 1 through 4 respectively. The following figures monitor the change in degree of saturation with respect to the distance from the wetting edge. The degree of saturation was calculated using Equation 7.

261 Figure 7a and 7b exhibit moisture profiles with a steep gradient at the wetting front that maintain 262 a constant shape as time increases, as expected [18], [32]. However, in Figure 7c and 7d, there is 263 a clear increase in the change in degree of saturation at the far end of the sample after the water 264 front reaches that edge, as indicated by the local peak in the 10 h data at a distance of about 48 265 mm. All the small pores (gel and capillary pores [33]) quickly fill as the water front advances 266 due to the high capillary pressure in these pores, and once the water front reaches the edge of the 267 sample, larger pores (entrapped and entrained air) begin to fill slowly as the mortar continues to 268 absorb water [18].

The increase in salt concentration to 10 % by mass does not greatly influence the change in degree of saturation. However, as noted in the previous section, it does decrease the rate of fluid penetration in mortars prepared with Type I cement. The moisture profiles have similar gradients at the wetting front as compared to deionized water. Again, in Figure 8d, there is an increase in the degree of saturation at the far edge of the sample after the moisture front reached that edge.

With higher chloride concentrations, such as the 20 % by mass shown in Figure 9, the slope of the fluid front becomes less sharp. In addition, there is a gradient throughout the entire distance of the wetted portion, rather than a relatively constant change in moisture content followed by a sharp decrease at the wetted front. In the case of deionized water and 10 % CaCl₂ solution in Figure 7 and Figure 8, the moisture content through the wetted portion was generally constant.
This could be due to the change in fluid properties with highly concentrated solutions. The
viscosity of CaCl₂ solution doubles when the solution concentration is increased from 10 % to 20
% by mass [10]. It can also be due to the formation of calcium chloroaluminate phases (Friedel's
and Kuzel's salts) decreasing the pore volume. When these phases form and fill porosity, the
resulting thickness of water measured will decrease.

284 Finally, at very high concentrations of CaCl₂, 29.8 % by mass, it is clear that the penetration of 285 fluid has been greatly hindered in all mortar samples including the one prepared with the Type V 286 cement. In Figure 10, there is a two-part moisture front. There is a highly saturated portion near 287 the exposed surface followed by a sharp decrease in moisture content for the remainder of the 288 wetted portion. There may be a build-up of chlorides near the exposed surface that accounts for 289 the peaks seen within the first 5 mm (0.20 in). Chlorine has an attenuation coefficient that is 290 approximately one third that of hydrogen [37] so it could influence the attenuation of neutrons if 291 there are large quantities accumulated. The wetting front gradually declines, which is a much 292 different behavior compared to that of the mortars exposed to lower concentrations of calcium 293 chloride.

In many of the mortars, the fluid front reached the edge of the sample within 10 h (See Figure 7

and Figure 8). By 24 h, the deionized water, 10% CaCl₂, and 15% CaCl₂ solutions had

296 completely penetrated the mortar. The mortar continued to absorb fluid after 24 h until

297 monitoring stopped at 96 h. This slow uptake in fluid corresponds to the secondary sorptivity in

ASTM C1585. Figure 11 shows the continued increase in the degree of saturation after the fluid

reached the edge of the sample between 24 h and 96 h. The rate of absorption is much slower at

300 longer times (days) due to the low capillary suction in the larger voids [38]. The measured

entrapped air volume of the 0.42 Type I sample was higher than that of the 0.36 Type I sample
(See Table 4), which results in less matrix porosity and therefore a lower degree of saturation
when the small pores are initially filled.

304

CONCLUSIONS

305 This study utilized neutron radiography to measure the depth of fluid penetration and the degree 306 of saturation in four mortars (Type I cement with w/c's of 0.36, 0.42, and 0.50 and Type V 307 cement with a w/c of 0.42) exposed to varying concentrations of CaCl₂. The addition of chlorides 308 influences the transport properties of fluid in mortar due to changes in the fluid properties such 309 as surface tension, viscosity and density. In addition, CaCl₂ salt solutions can react with the 310 cement paste resulting in the formation of expansive reaction products such as Friedel's salts, 311 Kuzel's salts and calcium oxychloride that can fill in the porosity and potentially damage the 312 matrix. At a low concentration (10 % by mass), mortars prepared with Type I cement 313 experienced a reduction in sorptivity between 20 % and 38 % due to a change in fluid properties 314 and the creation of Friedel's and Kuzel's salts, whereas the mortar prepared with Type V cement 315 only reduced in sorptivity by 10 %, due to the change in fluid properties. Cements containing 316 aluminates (C_3A) will react with CaCl₂ even at low concentrations to produce pore-blocking salts 317 that reduce the subsequent rate of absorption. These pore-blocking salts also reduce the effective 318 pore volume and increase the degree of saturation which can lead to premature freeze-thaw 319 damage in pavement joints. At high concentrations, all mortars experienced a dramatic decrease 320 (between 80 % and 87 %) in sorptivity due to the change in fluid properties (increases in 321 viscosity and surface tension) and the formation of calcium oxychloride.

322 The neutron radiographs enabled the fluid ingress depth and change in degree of saturation to be 323 accurately calculated. From this information, the shape or gradient of the wetting front could be 324 monitored. The wetting front became clearly less sharp as the concentration of chlorides 325 increased. In addition, the phenomenon of pore-blocking with chlorides was observed at high 326 concentrations (29.8 %). In this scenario, there is a build-up of chlorides close to the fluid source 327 and a sharp decrease in the amount of fluid past the build-up. This implies that the pores have 328 decreased in volume, therefore the volume of fluid that can penetrate past that barrier decreases 329 as does the rate of further ingress.

* Certain trade names and company products are mentioned in the text or identified in an
illustration in order to adequately specify the experimental procedure and equipment used. In no
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for the purpose.

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REFERENCES

336 [1] W. Jones, Y. Farnam, P. Imbrook, J. Spiro, C. Villani, J. Olek, and W. J. Weiss, "An

337 Overview of Joint Deterioration in Concrete Pavement: Mechanisms, Solution Properties, and
338 Sealers," West Lafayette, Indiana, 2013.

L. Sutter, K. Peterson, G. Julio-Betancourt, D. Hooton, T. Van Dam, and K. Smith, "The
Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete,"
Pierre, South Dakota, 2008.

342 [3] D. Harris, P. Imbrock, and W. J. Weiss, "Using Ground-Penetrating Radar to Detect

Indicators of Premature Joint Deterioration in Concrete Pavements," in Transportation Research
Board 94th Annual Meeting, 2015.

345 [4] D. Harris, Y. Farnam, R. P. Spragg, P. Imbrock, and W. J. Weiss, "Early Detection of

Joint Distress in Portland Cement Concrete Pavements," West Lafayette, Indiana, No. SPR 3623,
2015.

- 348 [5] K. Raoufi, T. Nantung, and W. J. Weiss, "Numerical Analysis of Saw Cutting: The
- Influence of Environmental Conditions," Am. Concr. Institute, ACI Spec. Publ., no. 266 SP, pp.
 87–99, 2009.
- 351 [6] K. Coates, S. Mohtar, B. Tao, and W. J. Weiss, "Can Soy Methyl Esters Reduce Fluid

352 Transport and Improve the Durability of Concrete?," Transp. Res. Board, vol. 2113, pp. 22–30,
353 2009.

354 [7] D. P. Bentz, M. A. Ehlen, C. F. Ferraris, and E. J. Garboczi, "Sorptivity-based Service

355 Life Predictions for Concrete Pavements," in 7th International Conference on Concrete

356 Pavements–Orlando, Florida, USA, Sept, 2001, vol. 1, pp. 9–13.

357 [8] G. Fagerlund, "The International Cooperative Test of the Critical Degree of Saturation

Method of Assessing the Freeze/Thaw Resistance of Concrete," Mater. Struct., vol. 10, no. 4, pp.
231–253, 1977.

360 [9] W. Li, M. Pour-Ghaz, J. Castro, and J. Weiss, "Water Absorption and Critical Degree of

361 Saturation Relating to Freeze-Thaw Damage in Concrete Pavement Joints," J. Mater. Civ. Eng.,

362 vol. 24, no. 3, pp. 299–307, 2012.

- 363 [10] C. Villani, R. Spragg, M. Pour-Ghaz, and W. Jason Weiss, "The Influence of Pore
- Solutions Properties on Drying in Cementitious Materials," J. Am. Ceram. Soc., vol. 97, no. 2,
 pp. 386–393, Oct. 2013.
- 366 [11] R. P. Spragg, J. Castro, W. Li, M. Pour-Ghaz, P.-T. Huang, and J. Weiss, "Wetting and
- 367 Drying of Concrete Using Aqueous Solutions Containing Deicing Salts," Cem. Concr. Compos.,
- 368 vol. 33, no. 5, pp. 535–542, May 2011.
- 369 [12] C. Villani, Y. Farnam, T. Washington, J. Jain, and W. J. Weiss, "Performance of
- 370 Conventional Portland Cement and Calcium Silicate-Based Carbonated Cementitious Systems
- 371 During Freezing and Thawing in the Presence of Calcium Chloride Deicing Salts," J. Transp.
- 372 Res. Rec., no. 15–2312, pp. 48–54, 2015.
- 373 [13] A. K. Suryavanshi, J. D. Scantlebury, and S. B. Lyon, "Mechanism of Friedel's Salt
- Formation in Cements Rich in Tri-calcium Aluminate," Cem. Concr. Res., vol. 26, pp. 717–727,
 1996.
- 376 [14] Y. Farnam, D. P. Bentz, A. Hampton, and W. J. Weiss, "Acoustic Emission and Low
- 377 Temperature Calorimetry Study of Freeze and Thaw Behavior in Cementitious Materials
- 378 Exposed to Sodium Chloride Salt," J. Transp. Res. Rec., vol. 2441, pp. 81–90, 2014.
- 379 [15] T. R. Jensen, A. N. Christensen, and J. C. Hanson, "Hydrothermal Transformation of the
- 380 Calcium Aluminum Oxide Hydrates CaAl₂O₄•10H₂O and Ca₂Al₂O₅•8H₂O to Ca₃Al₂(OH)₁₂
- 381 Investigated by in Situ Synchrotron X-ray Powder Diffraction," Cem. Concr. Res., vol. 35. pp.
- 382 2300–2309, 2005.
- 383 [16] ASTM Standard C1585-13, "Standard Test Method for Measurement of Rate of
- 384 Absorption of Water by Hydraulic-Cement Concretes." ASTM International, West
- 385 Conshohocken, PA, 2013.

- 386 [17] J. Castro, D. Bentz, and J. Weiss, "Effect of Sample Conditioning on the Water
- Absorption of Concrete," Cem. Concr. Compos., vol. 33, no. 8, pp. 805–813, Sep. 2011.
- 388 [18] C. Hall and W. D. Hoff, Water Transport in Brick, Stone and Concrete, 2nd ed. CRC
 389 Press, 2009.
- 390 [19] Y. Farnam, T. Washington, and J. Weiss, "The Influence of Calcium Chloride Salt
- 391 Solution on the Transport Properties of Cementitious Materials," Adv. Civ. Eng., vol. 2015, p.
- 39213, 2015.
- 393 [20] S. Kelham, "A Water Absorption Test for Concrete," Mag. Concr. Res., vol. 40, no. 143,
 394 p. 106, 1988.
- G. Sant and W. J. Weiss, "Using X-Ray Absorption to Assess Moisture Movement in
 Cement-Based Materials," J. ASTM Int., vol. 6, no. 9, p. 15, 2009.
- 397 [22] M. Pour-Ghaz, F. Rajabipour, J. Couch, and J. Weiss, "Numerical and Experimental
- 398 Assessment of Unsaturated Fluid Transport in Saw-Cut (Notched) Concrete Elements," ACI
- 399 Spec. Publ., pp. 73–86, 2009.
- 400 [23] F. C. de Beer, J. J. le Roux, and E. P. Kearsley, "Testing the Durability of Concrete with
- 401 Neutron Radiography," Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers,
- 402 Detect. Assoc. Equip., vol. 542, pp. 226–231, Apr. 2005.
- 403 [24] P. Trtik, B. Münch, W. J. Weiss, A. Kaestner, I. Jerjen, L. Josic, E. Lehmann, and P.
- 404 Lura, "Release of Internal Curing Water from Lightweight Aggregates in Cement Paste
- 405 Investigated by Neutron and X-ray Tomography," Nucl. Instruments Methods Phys. Res. Sect. A
- 406 Accel. Spectrometers, Detect. Assoc. Equip., vol. 651, no. 1, pp. 244–249, Sep. 2011.
- 407 [25] L. Hanžič and R. Ilić, "Relationship between Liquid Sorptivity and Capillarity in
- 408 Concrete," Cem. Concr. Res., vol. 33, no. 9, pp. 1385–1388, Sep. 2003.

- 409 [26] D. S. Hussey, D. Spernjak, a. Z. Weber, R. Mukundan, J. Fairweather, E. L. Brosha, J.
- 410 Davey, J. S. Spendelow, D. L. Jacobson, and R. L. Borup, "Accurate Measurement of the
- 411 Through-Plane Water Content of Proton-Exchange Membranes Using Neutron Radiography," J.
- 412 Appl. Phys., vol. 112, no. 10, p. 104906, 2012.
- 413 [27] P. Zhang, F. H. Wittmann, T. Zhao, E. H. Lehmann, and P. Vontobel, "Neutron
- 414 Radiography, a Powerful Method to Determine Time-Dependent Moisture Distributions in
- 415 Concrete," Nucl. Eng. Des., vol. 241, no. 12, pp. 4758–4766, Dec. 2011.
- 416 [28] S. E. Oswald, M. Menon, A. Carminati, P. Vontobel, E. Lehmann, and R. Schulin,
- 417 "Quantitative Imaging of Infiltration, Root Growth, and Root Water Uptake via Neutron
- 418 Radiography," Vadose Zo. J., vol. 7, no. 3, p. 1035, 2008.
- 419 [29] Y. Bu, D. Luo, and W. J. Weiss, "Using Fick's Second Law and the Nernst-Planck
- 420 Approach in the Prediction of Chloride Ingress in Concrete Materials," Adv. Civ. Eng. Mater.,
 421 2014.
- 422 [30] M. R. Conde, "Properties of Aqueous Solutions of Lithium and Calcium Chlorides:
- 423 Formulations for use in Air Conditioning Equipment Design," Int. J. Therm. Sci., vol. 43, no. 4,
- 424 pp. 367–382, Apr. 2004.
- 425 [31] R. K. Hassanein, "Correction Methods for the Quantitative Evaluation of Thermal
- 426 Neutron Tomography," Swiss Federal Institute of Technology Zurich, 2006.
- 427 [32] C. L. Lucero, D. P. Bentz, D. S. Hussey, D. L. Jacobson, and W. J. Weiss, "Using
- 428 Neutron Radiography to Quantify Water Transport and the Degree of Saturation in Entrained Air
- 429 Cement-Based Mortar," Phys. Procedia, vol. 69, pp. 542–550, 2015.
- 430 [33] T. C. Powers and T. L. Brownyard, "Studies of the Physical Properties of Hardened
- 431 Portland Cement Paste," PCA Bull. Portl. Cem. Assoc., vol. 43, pp. 1–356, 1948.

- 432 [34] K. Hong and R. D. Hooton, "Effects of Cyclic Chloride Exposure on Penetration of
- 433 Concrete Cover," Cem. Concr. Res., vol. 29, no. 9, pp. 1379–1386, 1999.
- 434 [35] Y. Farnam, S. Dick, A. Weise, J. Davis, D. Bentz, and W. J. Weiss, "The Influence of
- 435 Calcium Chloride Deicing Salt on Phase Changes and Damage Development in Cementitious
- 436 Materials," Cem. Concr. Compos., vol. 64, pp. 1–15, 2015.
- 437 [36] K. Peterson, G. Julio-Betancourt, L. Sutter, R. D. Hooton, and D. Johnston,
- 438 "Observations of Chloride Ingress and Calcium Oxychloride Formation in Laboratory Concrete
- 439 and Mortar at 5 °C," Cem. Concr. Res., vol. 45, pp. 79–90, 2013.
- 440 [37] A.-J. Dianoux and G. Langer, Neutron Data Booklet. Philadelphia, PA: Old City
- 441 Publishing, 2003.
- 442 [38] N. S. Martys and C. F. Ferraris, "Capillary Transport in Mortars and Concrete," Cem.
- 443 Concr. Res., vol. 27. pp. 747–760, 1997.

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- 476 Fig. 9 Degree of saturation when exposed to 20 % by mass CaCl₂ solution for mortar with (a)
- 477 w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I
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- 480 (a) w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I
- 481 *cement, and (d) w/c of 0.42 and Type V cement. (Note change in x-axis scaling)*
- 482 *Fig.* 11 Increase in degree of saturation of mortars exposed to deionized water up to 96 h.

Mix ID	Type I Cement, kg/m ³ (lb/yd ³)	Type V Cement, kg/m ³ (lb/yd ³)	Water, kg/m ³ (lb/yd ³)	Fine Aggregate (SSD), kg/m ³ (lb/yd ³)	w/o
1	632.62 (1066.3)		227.74 (383.86)	1363.11 (2297.59)	0.3
2	581.01 (979.32)		244.02 (411.31)	1368.34 (2306.41)	0.4
3	524.01 (883.24)		262.01 (441.63)	1363.11 (2297.59)	0.5
4		581.01 (979.32)	244.02 (411.31)	1363.11 (2297.59)	0.4

Table 1 - Mixture proportions for the four mortars used in absorption experiments

Table 2 - Chemical and physical properties of ordinary Portland cement

	Percent by Mass (%)		
Component	Type I	Type V	
SiO ₂	19.3	21.3	
Al ₂ O ₃	5.2	2.6	
Fe ₂ O ₃	2.9	4.2	
CaO	64.0	63.2	
MgO	2.6	4.5	
SO ₃	3.3	2.8	
C ₃ S	63.4	64.0	
C_2S	8.4	13.1	
C ₃ A	9.0	0.0	
C ₄ AF	8.7	12.8	
Blaine Fineness [cm ² /g]	3680	3160	
(in ² /lb)	(259000)	(222000)	

491 Table 3 - Fluid properties at 25 °C for concentrations of CaCl₂ solutions used in this study

[11], [30].

		Viscosity via	Surface Tension via Du Noüy	
$CaCl_2$		rheometer,	tensiometer,	Theoretical
Concentration	Density, kg/m ³	$mN \cdot s/m^2 (10^{-7})$	mN/m (10 ⁻⁴	Normalized
(% by mass)	(lb/ft^3)	lbf-s/in ²)	lbf/in)	Sorptivity
0	997 (62.2)	0.905 (1.13)	72.8 (4.16)	1.00
10	1087 (67.86)	1.045 (1.52)	75.02 (4.28)	0.94
20	1189 (74.23)	1.675 (2.43)	79.47 (4.54)	0.77
29.8	1291 (80.59)	2.975 (4.31)	85.88 (4.90)	0.60

494Table 4 - Calculated components of porosity according to Powers model [33]

	Mixture No.			
-	1	2	3	4
Capillary Porosity	0.071	0.097	0.128	0.099
Gel Porosity	0.073	0.065	0.058	0.066
Chemical Shrinkage	0.024	0.022	0.019	0.022
Measured Air	0.020	0.035	0.040	0.026
Total Calculated Porosity	18.8 %	21.8 %	24.4 %	21.3 %

				Normalized	% Deviation
Mixture	Sample	CaCl ₂	Sorptivity ¹	Sorptivity	from Theoretical
No.	Description	Solution (%)	$(mm/s^{1/2})$	$(S_{solution}/S_{water})$	Value
		0	0.214 ± 0.006	1.00 ± 0.03	0.0
1	w/c = 0.36,	10	0.138 ± 0.002	0.64 ± 0.01	28.9
1	Type I	20	0.097 ± 0.002	0.45 ± 0.01	41.0
		29.8	0.039 ± 0.002	0.18 ± 0.01	69.7
		0	0.277 ± 0.003	1.00 ± 0.01	0.0
2	w/c = 0.42,	10	0.210 ± 0.003	0.76 ± 0.01	16.3
Z	Type I	20	0.144 ± 0.003	0.52 ± 0.01	32.3
		29.8	0.035 ± 0.003	0.13 ± 0.01	78.9
		0	0.311 ± 0.019	1.00 ± 0.06	0.0
2	w/c = 0.50,	10	0.235 ± 0.009	0.76 ± 0.03	16.2
3	Type I	20	0.160 ± 0.006	0.52 ± 0.02	32.9
		29.8	0.051 ± 0.003	0.16 ± 0.01	72.4
		0	0.361 ± 0.007	1.00 ± 0.02	0.0
4	w/c = 0.42,	10	0.327 ± 0.007	0.91 ± 0.02	0.3
4	Type V	20	0.224 ± 0.004	0.62 ± 0.01	19.1
		29.8	0.074 ± 0.004	0.20 ± 0.01	65.8

Table 5 - Summary of measured sorptivity and normalized sorptivity for mortar samples exposed to CaCl₂ solutions.

 1 1 mm/s^{1/2} = 0.039 in/s^{1/2}



Fig. 1 - (a) Influence of mortar thickness on optical density. The shaded region is the total porosity of the four mortar samples used. (b) Relationship between the degrees of saturation as determined by neutron radiographs and by mass measurements. Error bars indicate +/- one standard deviation in the experimental measurements.



Fig. 2 - Plan view of the Neutron Imaging Facility at NIST



Fig. 3 - Experimental set up for chloride ponding tests.



Fig. 4 - Image analysis process for determining the average depth of penetration. (a) Normalized images were (b) converted to binary. (c) A mask of vertical lines was subtracted from the binary images to result in (d) 10 measurable lines of the fluid front.



Fig. 5 - Average depth of penetration of four concentrations of $CaCl_2$ solution for mortars composed of (a) w/c of 0.36 and Type I cement, (b) w/c of 0.42 and Type I cement, (c) w/c of 0.50 and Type I cement, and (d) w/c of 0.42 and Type V cement. Dashed lines represent a linear best fit. Coefficient of variation is less than 7 % for measured depths.



Fig. 6 - Normalized sorptivity with an increase in CaCl₂ concentration in the ponded fluid. Sorptivity values were normalized to those of DI water for each respective mortar.



Fig. 7 - Degree of saturation when exposed to deionized water for mortar with (a) w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I cement, and (d) w/c of 0.42 and Type V cement.



Fig. 8 - Degree of saturation when exposed to 10% by mass CaCl₂ solution for mortar with (a) w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I cement, and (d) w/c of 0.42 and Type V cement.



Fig. 9 - Degree of saturation when exposed to 20 % by mass CaCl₂ solution for mortar with (a) w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I cement, and (d) w/c of 0.42 and Type V cement.



Fig. 10 - Degree of saturation when exposed to 29.8% by mass CaCl₂ solution for mortar with (a) w/c of 0.36 with Type I cement, (b) w/c of 0.42 with Type I cement, (c) w/c of 0.50 with Type I cement, and (d) w/c of 0.42 and Type V cement. (Note change in x-axis scaling)



Fig. 11 - Increase in degree of saturation of mortars exposed to deionized water up to 96 h.