1 Using a Saturation Function to Interpret the Electrical Properties of Partially Saturated Concrete

- 2 Jason Weiss,¹ Ken Snyder,² Jeff Bullard,² and Dale Bentz²
- 3 1 Purdue University, West Lafayette, IN
- 4 2 National Institute of Standards and Technology, Gaithersburg, MD
- 5 Abstract

6 Electrical properties are frequently measured in the concrete construction industry as a part of 7 mixture gualification and guality control testing. While there are several factors that influence the 8 electrical response of concrete, one of the most important factors is its degree of saturation. Although 9 current standard tests rely on the concrete being saturated, this can be difficult to accomplish, is time 10 consuming, and can artificially increase the degree of hydration of the test sample in comparison to that 11 of concrete in field structures (when the test samples are stored in water). While some studies have 12 measured the electrical response of concrete for samples with different moisture content (i.e., stored at 13 different relative humidities), a single expression has not been proposed that predicts how drying 14 changes the electrical response. This paper suggests that a saturation function should be considered as 15 a possible method to account for, and to correct for, less than complete saturation in concrete. This 16 function would provide one term that accounts for changes in pore fluid volume, pore solution 17 concentration, and pore fluid connectivity. While preliminary, this approach has several potential 18 benefits: 1) it could enable testing of partially saturated concrete, thus saving time; 2) it could be used 19 to predict properties under different exposure conditions; 3) it may facilitate more comprehensive 20 service life models; and 4) it may enable a wider use of embedded sensor technology.

21 1. Background

22 Several test methods exist in the construction industry that use measures of the electrical 23 properties of concrete as an indicator of potential durability performance. The so-called rapid chloride 24 permeability (RCP) test (e.g., AASHTO T277/ASTM C1202) is one example of an electrical test for 25 concrete. For nearly three decades, the concrete profession has qualified concrete mixtures using the 26 RCP testing procedure. While rapid in comparison to long-term ponding tests, the RCP test procedure 27 applies an electrical potential to the test sample for 6 h and requires that the sample be vacuum 28 saturated prior to testing. Several researchers have suggested that the testing time could be 29 dramatically shortened without compromising the quality of the data. Snyder et al. (2000) illustrated 30 that there was no need for the 6 h measurement because values after 1 min or 5 min provide an equally 31 valid indication of the electrical resistivity of the concrete. Other researchers have also confirmed that 32 the test can be performed with shorter test times (Shane et al. 1999, Riding et al. 2008). In fact, 33 shortening the test would improve the quality of the results, as it reduces the potential for Joule 34 heating, which artificially increases the measured response of charge passed over time (Julio-Betancourt 35 and Hooton 2004). Since the time of the preparation of this paper, ASTM committee C09 has accepted a 36 new test method to implement this more rapid measurement protocol (ASTM C1760). But, even if the 37 measurement time is reduced, the sample preparation time is still inconveniently long. RCP testing (or

ASTM C1760) requires saturation of the sample, a task which is time consuming, labor intensive, and difficult to accomplish in many cases. The cost of testing (in terms of time and money) could be significantly reduced if reliable measurements could be made on partially saturated specimens. Such a measurement also provides value in that it can provide information on the transport properties under partially saturated conditions.

43 Similarly, time might be saved by using test geometries and methods other than the rapid 44 chloride permeability test. Surface measurements of electrical properties are popular (FM-5-578 2004) 45 and AASHTO has recently developed a provisional standard (TP95-11) based on the Wenner four probe 46 surface resistance test (Morris et al. 1996, Berke and Hicks 1992, Kessler et al. 2005, UNE 2008a, Jackson 47 2011, Rupnow and Icenogle 2011). Although this test procedure can be performed in less than 2 min, it 48 frequently requires the storage of samples in lime saturated water. While storage in water is intended 49 to ensure that the samples are saturated, low-permeability concretes may not maintain saturation even 50 after long immersion times, due to self-desiccation (internal drying). Likewise, samples stored in air, 51 even humid air, are not fully saturated. Furthermore, storage in water may provide additional curing 52 and/or leaching that are not representative of what may be happening in actual field structures.

53 Other test procedures have also been proposed for rapid electrical testing. Specifically, a test 54 procedure has been proposed that measures a bulk resistivity through cylinders (Whittington et al. 55 1981, Newlands et al. 2008, UNE 2008b, Spragg et al. 2011). Tests could be conducted on samples of 56 other geometries or even between embedded electrodes (Monfore 1968, McCarter et al. 1981, Hansson 57 and Hansson 1983, Christensen et al. 1994, Tumidajski et al. 1996, Gu et al. 1992, Raupach and Scheissl 58 1997, Scheissl et al. 1999, Sellevold et al. 1997, Shane et al. 1999, Weiss et al. 1999, Rajabipour et al. 59 2007, Poursaee et al. 2009, Castro et al. 2010). Each of these methods uses a different electrode 60 configuration and sample size, thereby requiring a separate geometric correction factor; however, the 61 fundamental principles of the tests are similar. Details on many of the geometric correction factors are 62 available in the literature (e.g., Rajabipour 2006).

63 It is interesting to note that, when the appropriate geometric corrections are made and the 64 samples are uniform (i.e., relatively homogenous) and properly conditioned, an intrinsic material 65 property (conductivity or resistivity) is obtained that is independent of sample geometry. Therefore, all 66 of these methods have great promise for moving the field towards qualification and quality control test 67 methods that are simple and related to durability performance, but it should be noted that their results 68 can be dramatically influenced by the degree of saturation of the concrete (Monfore 1968, Scheissl et al. 69 1999, Andrade et al. 2011). This paper will focus on understanding how the moisture content (i.e., 70 degree of saturation) influences the overall measured electrical response. Specifically, this paper 71 suggests that a universal expression could be used to interpret measurements for partially saturated 72 concrete.

73 2. Electrical Conductivity Expression for Saturated Concrete

The electrical conductivity (inverse of resistivity) of concrete depends on four factors: the conductivity of the solution in the pores, the volume of saturated pores (porosity), their connectivity 76 within the microstructure (tortuosity), and the degree of saturation. Although there are several 77 expressions that could be used to estimate the electrical response of a composite like concrete 78 (Torquato 2002), the two most commonly used are a modified parallel law (Garboczi 1990) and Archie's 79 equation (originally developed in 1942 and reprinted in 2003). Of the two, Archie's equation for the 80 electrical conductivity of a rock soaked (saturated) in brine provides a useful starting point:

$$\frac{\sigma_r}{\sigma_h} = a\phi^m \tag{1}$$

81 where *a* is a parameter that depends upon the rock type, σ_r is the rock conductivity, σ_b is the brine 82 conductivity, and ϕ is the pore volume fraction (porosity). The exponent *m* is a fitting parameter that is 83 referred to as the cementation factor. It should be noted that the cementation factor refers to how the 84 microstructure is formed, and is not related to the actual cementitious content of the material.

85 3. Electrical Conductivity Expression for Partially Saturated Concrete

86 Several researchers have developed expressions similar to equation 1 for partially saturated 87 concrete. These modifications consist of reinterpreting the pore volume as only the volume of the pore 88 fluid (Weiss 1999, Andrade et al. 2011). While that simple correction may be expedient, it leads to 89 some confusion between pore volume and fluid-filled pore volume. Further, additional complications 90 arise since several factors in Eq. 1, including the pore solution conductivity and solution connectivity, 91 change as the degree of saturation changes. As such, previous work has accounted for each factor 92 individually (Rajabipour et al. 2007); however this can be very time consuming and does not lend itself 93 to easy use for quality control testing.

An alternative approach is to start with the expression that characterizes the pore structure of the concrete called the formation factor (a uniquely defined parameter for a material with a given composition and degree of hydration) and to incorporate the effects of partial saturation. For a fully saturated concrete, the ratio of the pore solution conductivity at saturation σ_p^o to the concrete conductivity at saturation σ_c^o is the formation factor *F* (Snyder, 2001):

$$\frac{\sigma_p^o}{\sigma_c^o} = F$$
^[2]

For a partially saturated concrete, the concrete conductivity σ_c decreases as the saturation level of the concrete decreases. This is due, in part, to the reduction in the pore fluid volume but also due to changes in the connectivity of the connected pathways and changes in the pore solution in the system (Rajabipour et al. 2007). For a concrete, the relationship between the concrete conductivity and the saturation could be accounted for using an expression that will be referred to as the saturation factor, f(S):

$$\frac{\sigma_c}{\sigma_p} = \frac{1}{F} f S$$
[3]

Furthermore, if one assumes that the pore solution at saturation (σ_p^{o}) is known, the pore solution conductivity at values other than saturation (e.g., due to drying) can be (at first approximation) related to the degree of saturation as:

$$\sigma_p = \frac{\sigma_p^o}{S}$$

108 Combining equations 3 and 5 results in equation 5:

$$\sigma_c = \frac{\sigma_p^o}{S} \quad \frac{1}{F} \quad f \quad S \tag{5}$$

While the left hand side of the equation is the conductivity of the concrete as a function of saturation, the right side of the equation has three terms. The first term accounts for the pore solution conductivity (due to the mixture design and subsequent concentration due to water loss), the second term accounts for the total pore space and the third term accounts for the connectivity of the fluid in the pore space. Each term is independent of the others, and all of the parameters are related to well defined properties of the matrix and the solution filling its pores.

115 The saturation function is used in other transport problems and could be formulated in a number of 116 ways (Millington and Quirk 1961, Martys 1999, Samson and Marchand 2008, 117 (http://en.wikipedia.org/wiki/Archie%27s law)). Although there is flexibility in how the saturation 118 function is formulated, the constraint is that at saturation (S=1), the function's value is unity (f(S=1)=1). 119 One viable function that has been used to describe the influence of saturation is a power-law 120 relationship:

$$f S = S^n \tag{6}$$

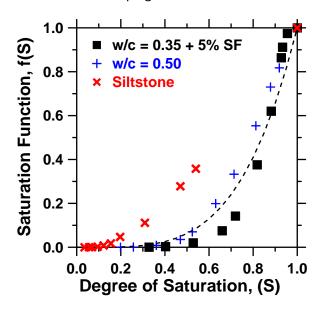
where *n* is a fitting parameter called the saturation coefficient. As described later in this paper, *n* is typically of the order of 1.5 to 3 for rocks, while it may be slightly higher for cement and concrete (i.e., in the range of 3.5 to 5 for the paste and mortar samples discussed in this paper and 5 for the computer

124 simulations discussed in this paper).

125 It should also be mentioned that the degree of saturation (S) is frequently determined using the 126 difference in mass before and after drying at 100°C normalized by the equivalent difference in mass for 127 a saturated system. This mass-based form of the degree of saturation is used since it is easy to 128 determine experimentally in the laboratory. But, the mass-based determination is equal to the 129 saturation in terms of fluid volume only if the filling liquid is water. For concentrated electrolytes such 130 as concrete pore solutions, there may be merit in interpreting S as a volumetric degree of saturation 131 (volume of the fluid as compared with the overall volume of fluid that can be held by the pore system of 132 the sample at saturation).

Figure 1 shows a plot of the saturation function S^n along with estimates based on experimental 133 134 data from Rajabipour et al. (2007), calculated from Eq. 3 using known values for the pore solution 135 conductivity at each step. In figure 1, the degree of saturation was determined on a mass basis. As may 136 be expected, the cement system behaves slightly differently than the siltstone that has larger pores, few 137 if any 'ink bottle pores', and a more open pore network. The saturation coefficient for the siltstone is 138 approximately 2 (which is a value consistent with that reported in the geological literature 139 (Schlumberger Oilfield Glossary 2011)). However, for the cement-based system with a ratio of water 140 mass to cement mass (w/c) of 0.50, the value of the saturation coefficient is approximately 3.5, and the 141 saturation coefficient approaches 5 for the system containing silica fume (w/c = 0.35 + 5 % silica fume).

The saturation function shown as the dashed line in Figure 1, using equation 6, assumes n = 4. It should be noted that the saturation function shown in Figure 1 is equivalent to the normalized conductivity (ratio of the conductivity of the concrete to the conductivity of the pore solution). As such, data like those in Figure 1 are currently quite rare in the concrete literature, as the changes in the pore solution with saturation must be included when developing such data.



147

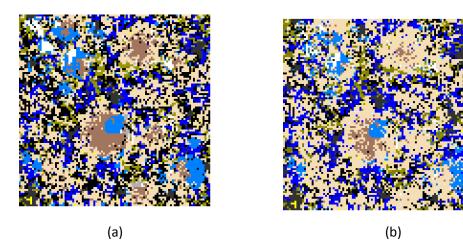
Figure 1: Experimentally Measured Saturation Coefficients for Siltsone and Cementitious Materials.(Containing data from Rajabipour 2006)

150 4. Saturation Functions from Simulation (Considering pore fluid volume and connectivity)

151 The Virtual Cement and Concrete Testing Laboratory software (VCCTL), used to predict degree 152 of hydration, microstructure development, and physical properties of cement paste, mortar, or concrete 153 (Bullard et al., 2008), was adapted in this study to estimate the form of a saturation function. One 154 advantage of the numerical simulations is that they automatically account for the pore solution 155 conductivity, a property which may be difficult to measure experimentally in many partially saturated 156 cementitious samples for three reasons. First, it becomes difficult to extract the pore solution using the 157 pressurized approach like the one proposed by Barneyback and Diamond (1981) in partially saturated 158 conditions, due to the very low volume of available pore fluid. Second, the loss of water by drying can 159 also increase the ionic concentration of the solution, which concurrently increases the pore solution conductivity (Rajabipour et al. 2007). Finally, pore solutions can be susceptible to rapid carbonation, 160 161 which will also significantly alter their conductivity (Rajabipour 2006).

Using the VCCTL, 3D virtual microstructures of cement paste were generated that were chemically and physically representative of the real systems considered in this paper. Hydration and microstructure development, under either saturated or sealed moisture conditions, were simulated out to ages of 1 d, 2 d, 3 d, 7 d, 28 d, 90 d, and 365 d. The 3D microstructures at each age were input into a finite difference model that calculated the net charge flux across the microstructure in response to a fixed applied electric field. The relative conductivity of the microstructure was computed by dividing the charge flux by the electric field (Ohm's law). In addition, the formation factor, F, was calculated by saturating the capillary pore volume (for the sealed curing condition specimens) and repeating the calculation of effective conductivity.

Figure 2 shows the simulated cement paste microstructures for a sealed mortar with a w/c of 0.42 and an aggregate volume fraction of 55 % at 3 d (Figure 2a) and at 365 d (Figure 2b). Over time, the capillary porosity of the system decreases due to hydration. In addition, since the system is sealed, the vapor-filled space increases due to chemical shrinkage and self-desiccation. To estimate the saturation function, the conductivity of the sealed mortar was compared with the sealed mortar that was 'resaturated' by altering the conductivity of the vapor-filled space to be equivalent to that of the pore solution.



178

179

Figure 2: Microstructural images developed using the VCCTL model for a mortar with a w/c of 0.42 and an aggregate volume of 55 % at a) 3 d and b) 365 d hydrated under saturated conditions. The phases are color-coded as follows: black = capillary porosity, brown = alite, light blue = belite, white = ferrite, beige = C-S-H gel, dark blue = CH, and green = ettringite and monosulfoaluminate combined.

184 It should be noted that two types of porosity are generally considered to exist in a hydrated cement paste system. The capillary pores are larger pores (shown in black in Figure 2) which remain 185 from the original space occupied by mix water that has not filled in during hydration. The gel pores are 186 187 smaller pores that are created within hydration products. In the VCCTL model, microstructure is 188 represented as a 3D digital image where each voxel, a 1 μ m cube, is assigned a particular cement phase. 189 Therefore, capillary pores are computed directly from the voxels that represent pores in the simulation, 190 but the gel pores are assumed to occupy 38 % of the volume of any C-S-H voxel. This compares 191 favorably and is consistent with the calculations from a Powers' model type approach (Powers and 192 Brownyard 1942). An advantage of the VCCTL model as compared with the Powers' calculations is that 193 it provides a 3D spatial distribution of the porosity, including its tortuosity, which can be used in 194 conductivity computations. A disadvantage is that the capillary pores have a lower size limit of 1 μ m 195 because of the finite voxel size. This lower limit is relatively coarse compared with the smaller capillary 196 pores in a typical hydrated portland cement, although comparisons of capillary porosity correlation

197 functions determined on model and real microstructures for a w/c=0.47 cement paste are quite 198 favorable (Bentz 2006).

199 Figure 3a shows results from the VCCTL simulation of a paste with a w/c of 0.50 and a degree of 200 hydration of 65 % yielding a similar formation factor (24.2) as that from the experimental data shown in 201 Figure 1. A series of simulations were subsequently performed where fluid was systematically removed 202 from the capillary pores to simulate the influence of a change in the degree of saturation caused by 203 drying, by emptying the largest pores within the 3D microstructure first, consistent with the algorithm 204 currently employed for self-desiccation of microstructures hydrated under sealed conditions. While the 205 general trend between the experiment and the simulation is similar, it can be noticed that the 206 simulation shows a more dramatic influence of drying on the saturation function than is observed 207 experimentally (n = 5 for the simulations, while n = 3.5 for the experiment shown in Figure 1).

Figure 3b plots the simulated saturation function for a series of sealed specimens with different w/c's. The saturation function was determined by using the conductivity of a sealed mortar and the conductivity of that sealed mortar after being 'resaturated', (i.e., by altering the conductivity of the vapor-filled space to be equivalent to that of the pore solution). The results in Figure 3b represent mortars with a wide range of w/c (0.30 to 0.45) and ages of 3 d to 365 d, along with the 0.50 paste that was dried after reaching 65 % hydration (as shown in Figure 3a). The results of these simulations appear to collapse reasonably close to the same line (n=5).

215 While these results indicate the potential that a single function may work for cementitious 216 systems (with *n* equals approximately 4 from the limited experimental data), it should be noted that an 217 exhaustive examination of all cement compositions, particle size distributions and degrees of hydration 218 were not considered, as small changes in *n* may be observed. It is recommended that experiments be 219 performed over a wide range of concrete mixture compositions to determine the best choice for this 220 saturation coefficient.

221

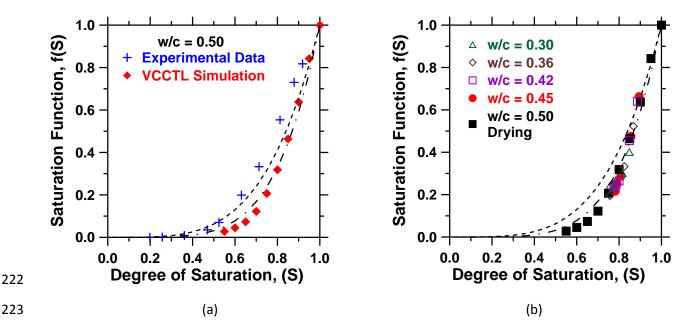


Figure 3: a) A Saturation Function Interpreted for VCCTL computer simulations b) Calculated saturation functions obtained from a series of simulated microstructures. The dashed curve corresponds to a saturation coefficient n=4 and the dotted and dashed line corresponds to a saturation coefficient n=5.

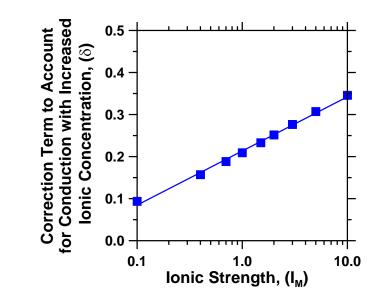
227 5. Correction for High Pore Solution Concentration on Drying

228 The parameter S appearing in Eq. 4 approximates the influence of the water loss from the pore solution 229 which increases concentration and conductivity (e.g. due to drying). It is mentioned that equation 4 is a 230 good first approximation for the pore solution conductivity; however, it does not account for the nonlinear relationship between conductivity and concentration that arises from ionic interactions. A 231 232 more thorough expression can be developed based on the work of Snyder (2001). While the full 233 derivation that is provided in Snyder (2001) was used in the analysis here, a simplified version is 234 presented that produces nearly identical results where the conductivity of the solution is assumed to be 235 proportional to the ionic strength (I_M, based on molar concentration) of the solution with a single 236 correction parameter for high ionic strengths:

237
$$\sigma \propto \frac{I_M}{1+G \ \overline{I_M}}$$
[7]

where G is the conductivity parameter (assumed to be approximately 0.4 $(mol/L)^{-1/2}$ for a typical pore solution). Starting at saturation, as the specimen dries, the ionic strength is inversely proportional to the saturation (this is the same as increasing the concentration). The ratio of the pore solution conductivity to the initial pore solution conductivity is given in equation 8. The expression in equation 8 can be approximated by a power-law relationship where the degree of saturation is raised to a correction exponent, δ -1 where the value of δ is a function of the pore solution ionic strength as shown in Figure 4.

245
$$\frac{\sigma_p}{\sigma_p^o} \cong \frac{1}{s} \quad \frac{1+G}{1+G} \frac{\overline{I_M}}{\overline{I_M}} = S^{\delta-1}$$
[8]



246

Figure 4: A Correction term (δ) to account for the ionic interactions in a pore solution, having an ionic strength I_M when the sample is saturated, as it becomes more concentrated due to drying

249 Combining equations 2, 3, and 8 yields a result for the ratio of the conductivity of drying concrete to

250 saturated concrete accounting for the saturation coefficient and the concentration of the pore solution

251 due to drying, where δ is based on the ionic strength:

$$\frac{\sigma_c}{\sigma_c^o} = S^{n-1+\delta}$$
[8]

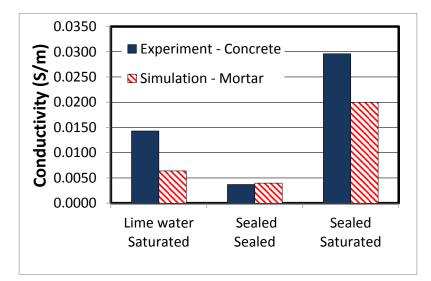
Therefore, once the value of δ has been determined by either direct measurement of the pore fluid ionic strength or by estimation based on the mixture design (i.e., the ionic strength), and assuming that n is known for a material or there exists a universal value of *n* for concrete, one can use equation 8 to estimate the change in a concrete conductivity due to changes in its degree of saturation.

256 6. Example Application 1 - Comparing Sealed and Saturated Curing Conditions

257 To illustrate the need for a method that enables electrical conductivity measurements to be 258 corrected based upon the degree of saturation in the concrete, the variation in conductivity was 259 measured from a series of concrete cylinders that were cast along with a bridge deck, made with an 260 ordinary portland cement concrete having a w/c of 0.39. These cylinders were demolded at 24 h and were stored for a year (DiBella et al. 2011). The concrete cylinders were conditioned in one of three 261 262 ways after demolding. First, some samples were stored in lime water after demolding to simulate water 263 curing. Second, other samples were sealed in a double layer of thermally sealed plastic bags. The 264 samples that were sealed in bags were removed from the bags and tested in the sealed state. The 265 degree of saturation for the concrete sealed in a bag after 1 year was measured to be 0.56, which 266 corresponds to a relative humidity of approximately 85 % to 90 % (Li et al. 2012). Third, after initial 267 testing, the sealed concrete samples were then cut to size for RCP testing and water saturated under vacuum in accordance with the ASTM C1202 procedures. Before conducting the 6-h measurement in 268 269 ASTM C1202, the resistivity was measured using plates on either side of the concrete disk (52 mm tall by 270 102 mm in diameter). At an age of 365 d, the measured conductivity of the concrete stored in lime 271 water was 0.0143 S/m. In contrast, the sealed concrete conductivity was 0.0037 S/m, and after being 272 resaturated, its conductivity was 0.0296 S/m, which is eight times greater than before resaturation. 273 These values are shown in Figure 5. Therefore, the measured conductivity strongly depends on how the 274 sample was cured and conditioned prior to testing.

275 This sensitive dependence of conductivity on sample storage and preparation implies that there 276 are at least two potential pitfalls when interpreting these kinds of measurements, both of which can 277 cause an underestimation of the conductivity. First, if a conductivity measurement were made on a 278 partially saturated sample, one could naively (and mistakenly) believe that the material has a 279 conductivity (diffusivity) that is nearly an order of magnitude better (i.e., lower) than it actually is (when 280 saturated). The second pitfall is to neglect the effect of storage conditions. The concrete stored in lime 281 water has approximately half the conductivity of the concrete that was sealed during curing and 282 saturated at the time of testing. Therefore, a sample stored in lime water in the laboratory would 283 appear to be performing much better than the same concrete in the field if the curing/sealing 284 compounds were working perfectly (and the concrete was saturated when sealed and when tested).

285 A mortar similar to that used in the experiments shown in Figure 5 was modeled using the 286 VCCTL (w/c of 0.39 and an aggregate volume of 55 %). The simulation should not be compared directly 287 to the field concrete since it was performed on mortar and did not include entrained air. The simulation 288 is still helpful, however, since it can provide some useful insights regarding trends and for interpreting 289 the results as a function of their curing conditions and the saturation function. The simulated 290 normalized conductivity obtained using the VCCTL is 0.00047 for the lime water saturated specimen, 0.000266 for the sealed specimen, and 0.00134 for the sealed sample that was resaturated. The 291 292 conductivity of the pore solution was estimated using an equivalent sodium content of 0.67 293 (http://concrete.nist.gov/poresolncalc.html; Bentz (2007)) with a resulting pore solution conductivity 294 between 12.4 S/m and 14.9 S/m. These estimated mortar conductivities are also shown in Figure 5.

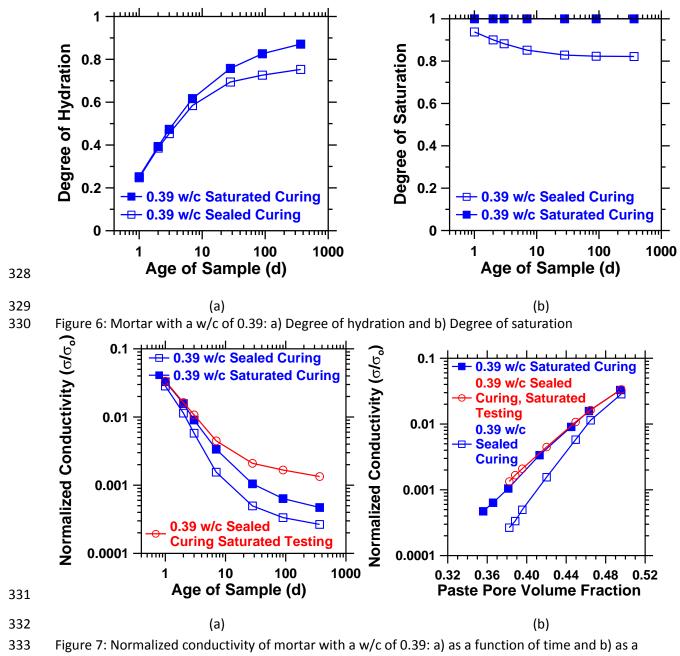


295

Figure 5: Measured electrical conductivity from RCP tests using a field concrete and simulated mortar with a w/c of 0.39 under different curing and sample conditioning (A maximum coefficient of variation of 3.2% was observed for the experiments)

299 In comparing the sample that was continuously stored in lime water with the sample that was 300 sealed and saturated at each age, the overall conductivity of the continually saturated sample is lower, 301 presumably due to the differences in the extent of hydration. Figure 6a shows the simulated degree of 302 hydration as a function of time as obtained from the VCCTL simulations. As one may expect, the system 303 that is saturated has a higher degree of hydration (87 % at one year) than a system that is simply sealed 304 cured (75 % at one year) (Bentz and Stutzman 2006). In this particular experiment, the lime-water cured 305 sample will have a lower porosity (albeit a relatively small decrease from 38 % of the paste to 36 % of 306 the paste volume fraction). It should be noted, however, that this small reduction in porosity is actually 307 a relatively large reduction in the fraction of the capillary porosity. For the mixtures being discussed, 308 nearly 65 % of this porosity at this degree of hydration is gel porosity. Figure 6b illustrates the degree of 309 saturation in the simulated mortars. While the saturated sample from the simulation remains at 100 % 310 saturation, the sealed sample has a degree of saturation that progressively decreases to approximately 311 0.81 at an age of 1 year. It should be noted that the VCCTL simulation did not include entrained air 312 which would comprise approximately 20 % of the paste volume for this mixture. If the degree of 313 saturation for the concrete sample is adjusted to account for entrained air, the degree of saturation of 314 the concrete cylinder is more similar to that of the simulation (approx. 0.76 vs. 0.81).

315 The normalized conductivity for the simulated mortar is plotted as a function of time in Figure 7a. This is similar to results previously shown by Bentz (1998). It can be noticed that the samples have a 316 317 similar conductivity at early ages as one may expect; however over time substantial differences in 318 conductivity begin to develop. To better illustrate the influence of the degree of hydration on the resulting pore structure, the normalized conductivity is plotted in terms of total pore volume in Figure 319 320 7b. Figure 7b shows that a single curve begins to appear that describes the specimens with water 321 (saturated) curing and the samples with sealed curing when they are tested in a saturated state. This 322 again confirms that the 'formation factor' (a normalized conductivity/pore solution conductivity) is a material property that varies with degree of hydration (or pore volume) for the saturated system. The primary difference between the samples cured under lime water and the samples that were sealed and resaturated is that the samples that are cured under lime water exhibit more hydration, thereby achieving a lower porosity and a lower normalized conductivity than the sealed/resaturated sample at the same age (Figure 7b). Again, this is consistent with the experimental observations.



function of the pore volume in the paste as computed using Powers' model

The results from Application 1 show that while the electrical conductivity may be a simple property to measure, it can be significantly influenced by curing conditions (sealed versus lime water 337 saturated) and sample preparation (testing the sealed sample versus testing the sealed sample that was 338 resaturated).

339 7.0

Example Application 2 - Measurements Made on Samples Exposed to Drying

340 In addition to using electrical property measurements on quality control samples, several 341 researchers have measured electrical properties in concrete systems exposed to drying or wetting 342 (Schießl 1999, Weiss et al 1999, 1999b, Sellevold 2000, Andrade et al. 2011). While the drying process 343 takes place over a long time period and may set up moisture gradients inside of the concrete (Weiss et 344 al. 1999 and Rajabipour et al. 2005), moisture gradients are not considered here. The saturation 345 approach may be useful in estimating the response of a concrete equilibrated to different levels of 346 drying.

347 Figure 8 illustrates equation 8 plotted as a function of relative humidity (RH) for a series of 348 concretes with a w/c of 0.4 that were allowed to dry for nearly a year (Weiss et al. 1999). The equation 349 with a saturation coefficient of n = 4 provides a reasonable shape response at higher humidities, but this relationship begins to break down for RH less than approximately 60 %. At these lower relative 350 351 humidities, the saturation function is low (approximately 0.1) and the capillary pore water is likely lost, 352 suggesting that the main conduction pathway likely changes from the large capillary pore network to the 353 gel pores or along the walls of the capillary pores. If this is true, the breakdown of the relation valid at 354 higher RH is not surprising.

355 The data for samples with a w/c of 0.4 and having no chemical admixtures (Schiessl et al. 1999) 356 were compared with equation 8 and a saturation coefficient of 3.9 was obtained for concrete with a w/c357 of 0.4 for data at relative humidities greater than 60 %. A similar assessment of the data reported by 358 Andrade et al. (2011) would be consistent with saturation coefficients that are approximately 3.5. These 359 coefficients are similar to those observed from the numerical simulations reported in Figures 3 and 4 360 and from the plain pastes in Figure 1. This suggests that this approach may be applicable to drying 361 samples. Figure 8b illustrates the desorption isotherm to relate relative humidity and the degree of 362 saturation. It also illustrates the saturation function (assuming two different values for the saturation 363 coefficient (i.e., n = 4 and n = 5)). This illustrates that once the relative humidity drops below 65 % to 70 364 % RH, the saturation function is very low.

365 As such, it appears that it may be quite reasonable to design an experiment where the 366 saturation coefficient is determined for a concrete mixture by measuring the conductivity of a sample 367 with two different degrees of saturation (provided they are relatively high). For example, this could 368 consist of measuring the conductivity of a sealed sample and then measuring the conductivity of the 369 same sample after vacuum saturation. Assuming the mass of the sample is measured along with the 370 electrical properties, the degree of saturation could be obtained by oven drying the sample after testing 371 and measuring its oven-dried mass. This could then provide an estimate of *n* for each mixture.

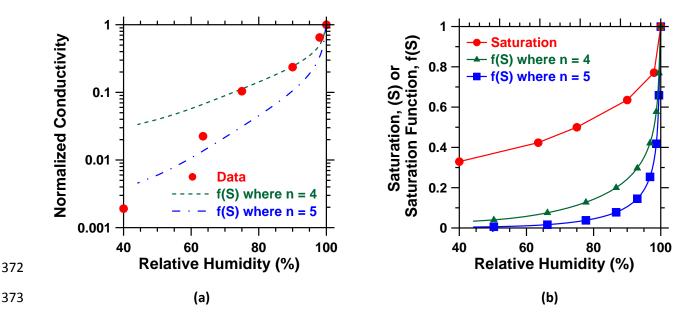
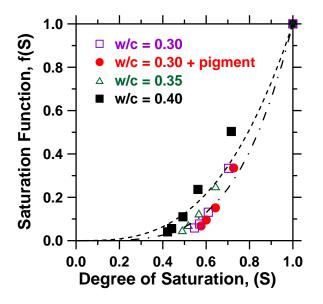


Figure 8: a) Normalized Conductivity as a Function of Drying and b) The Relationship Between RelativeHumidity and Saturation for the Data

376 A further illustration of this approach can be seen in Figure 9 where the surface resistivity was measured 377 on mortar specimens exposed to drying at 50 +/- 2% relative humidity (1 in. (25 mm) square cross 378 section and a 10.6 inch length (262.5 mm) (Bentz et al. 2012)). It can be noticed that despite the 379 samples not being in equilibrium during the test (i.e., the samples were drying and likely continuing to hydrate slightly) a similar trend emerges for the saturation function. The mixture with a lower w/c 380 381 would be expected to have a more uniform moisture content and follow the expected function a little 382 more closely than the samples with a higher w/c that likely show some influence of the moisture 383 gradients.



384

Figure 9: The application of the saturation function to mortar prisms during drying (The dashed line and dot-dash line denotes a n-1+ δ value of 3 and 4, respectively).

387

388 8.0 Summary

389 Tests that measure the electrical conductivity of concrete are sensitive to the degree of 390 saturation of the concrete. This paper explores the potential for testing partially saturated concrete and 391 correcting this data based on its measured degree of saturation to obtain the formation factor, which is 392 a material property. This could have substantial impact when rapid field tests or embedded sensors are 393 used to provide measures of properties related to durability performance. Similarly, this approach could 394 be used to solve the equally important problem of converting measured transport coefficients for 395 saturated concrete to values that would correspond to field conditions with a lower degree of 396 saturation.

397 This paper suggests that the general form of Archie's Law can be written in a way that describes 398 the electrical conductivity of partially saturated concrete, using a stand-alone saturation function. It 399 appears that the saturation function can be written as the degree of saturation raised to an exponent 400 called the saturation coefficient (n). A suggestion for the form of this equation is shown in equation 8 401 which accounts for both drying effects and changes in the pore solution concentration and conductivity 402 during drying. While the saturation coefficient varies from approximately 1.5 to 2.5 for many rocks 403 (shown in this paper for siltstone as 2), it is slightly higher for cement-based materials, ranging from 404 approximately 3.5 to 5.5 for the limited data from experiments. Simulations made using the VCCTL 405 show a coefficient of approximately 5; however these simulations also showed that the saturation 406 coefficient exhibited little variation with changes in the degree of hydration or the water to cement 407 ratio, over the ranges investigated. The use of a saturation value of 4 provided reasonable correlation 408 with the limited experimental data for the plain portland cement-based systems described in this paper.

409 The saturation function in equation 8 accounts for changes in pore solution, pore fluid volume 410 and pore connectivity. The saturation function was used in two examples where the electrical 411 properties were measured, the first being concrete exposed to sealed curing and the second being 412 concretes and mortars exposed to drying. Future studies should be conducted to better understand the 413 response of partially saturated concrete and to obtain experimental values for n for a wider range of 414 concrete mixture compositions. When this work is performed, it would be helpful to describe the pore 415 solution conductivity (or to report the sodium and potassium alkali contents of the cement), so that the 416 role of pore solution concentration can be estimated. It would also be helpful to provide the degree of 417 saturation of the concretes in addition to their measured internal relative humidity.

418 9.0 Acknowledgements

This first author is grateful for support from the Joint Transportation Research Program administered by the Indiana Department of Transportation and Purdue University. The contents of this paper reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein, and do not necessarily reflect the official views or policies of the Indiana Department of Transportation, nor do the contents constitute a standard, specification, or regulation.

424 10.0 References

- Andrade, M. C., Bolzoni, F. and Fullea, J. (2011). "Analysis of the relation between water and resistivity
 isotherms in concrete", Materials and Corrosion, Vol. 62(2), 130-138.
- 427 Archie, G. E. (2003). "The electrical resistivity log as an aid in determining some reservoir 428 characteristics", SPE Reprint Series, (9-16.
- ASTM C1202 (2010). Standard test method for electrical indication of concrete's ability to resist chloride
 ion penetration, ASTM International, West Conshohocken, PA.
- AASTHTO T277 (2007)., Standard method of test for electrical indication of concrete's ability to resist
 chloride ion penetration, American Association of State Highway and Transportation Officials,
 Washington, D.C.
- Barneyback, S. and Diamond, S.(1981). "Expression and analysis of pore fluids from hardened cement
 pastes and mortars ", Cem Concr Res 11, 279.
- Bentz, D.P. and Stutzman, P.E., "Curing, Hydration, and Microstructure of Cement Paste," ACI
 Materials Journal, 103(5), 348-356, 2006
- 438 Bentz, D. P. (2007). "A virtual rapid chloride permeability test", Cem Concr Compos, 29, 723-731.
- Bentz, D.P., "Quantitative Comparison of Real and CEMHYD3D Model Microstructures Using Correlation
 Functions," Cement and Concrete Research, 36 (2), 259-263, 2006.
- 441 Bentz, D. P., Stutzman, P., Sakulich, A., and Weiss, W. J., (2012), "Study of Early-Age Bridge Deck 442 Cracking in Nevada and Wyoming", NISTIR 7841, January 2012.
- Berke, N. S. and Hicks, M. C. (1992). "Estimating the Life Cycle of Reinforced Concrete Decks and Marine
 Piles Using Laboratory Diffusion and Corrosion Data", in,.
- Bullard, J. W., Ferraris, C. F., Garboczi, E. J., Martys, N., Stutzman, P. E. and Terrill, J. E. (2008). "Virtual
 Cement and Concrete." Chapter 10 in Innovations in Portland Cement Manufacturing. Edited by J.I.
 Bhatty, F.M. Miller, and S.H. Kosmatka. Portland Cement Association, Skokie, IL.
- Bentz, D.P. (1998) "Modelling Cement Microstructure: Pixels, Particles, and Property Prediction,"
 Materials and Structures, 32, 187-195Christensen, B. J., Coverdale, R. T., Olson, R. A., Ford, S. J.,
 Garboczi, E. J., Jennings, H. M. and Mason, T. O. (1994). "Impedance spectroscopy of hydrating
 cement-based materials: measurement, interpretation, and application", J Am Ceram Soc, 77, 27892804.
- Castro, J., Spragg,, R., Kompare, P. and Weiss, W. J. (2010). "Portland Cement Concrete Pavement
 Permeability Performance", Joint Transportation Research Program, Indiana Department of
 Transportation and Purdue University, West Lafayette, Indiana.

456 Dibella thesis

- 457 FM 5-578 (2004). "Florida method of test for concrete resistivity as an electrical indicator of its 458 permeability", Flordia Department of Transportation, Tallahassee, FL.
- Garboczi,, E. J. (1990). "Permeability, diffusivity, and microstructural parameters: A critical review", Cem
 Concr Res, 20, 591-601.
- Garboczi, E. J. (1998) Finite Element and Finite Difference Programs for Computing the Linear Electric
 and Elastic Properties of Digital Images of Random Materials. NISTIR 6269; 211 p. December 1998.
- Gu, P., Xie, P., Beaudoin, J. J. and Brousseau, R. (1992). « A.C. Impedance Spectroscopy 1 : A New
 Equivalent Circuit Model for Hydrated Portland Cement Paste », Cement and Concrete Research 22,
 833-840.
- Julio-Betancourt, G. A. and Hooton, R. D. (2004). "Study of the Joule effect on rapid chloride
 permeability values and evaluation of related electrical properties of concretes", Cem Concr Res, 34,
 1007-1015.
- Hansson, I.L.H. and Hansson, C. M. (1983). « Electrical resistivity measurements of Portland cement
 based materials », Cement and Concrete Research, Vol. 13(5), 675-683.
- Jackson,, N. M. (2011). "Results of round-robin testing for the development of precision statements for
 the surface resistivity of water saturated concrete", Ponte Vedra Beach, Florida.
- Kessler, R. J., Powers, R. G. and Paredes, M. A. (2005). "Resistivity Measurements of Water Saturated
 Concrete as an Indicator of Permeability", in: Corrosion 2005, NACE International, Houston, TX.
- Li, W., Pour-Ghaz, M., Castro, J., and Weiss, W. J., (2012) "Water Absorption and the Critical Degree of
 Saturation as it relates to Freeze-Thaw Damage in Concrete Pavement Joints," ASCE Journal of Civil
 Engineering Materials
- 478 Martys, N.S., "Diffusion in Partially-Saturated Porous Materials," Materials and Structures, 32, pp 555479 562 (1999).
- 480 Millington, R. J., and Quirk, J. P., (1961) 'Permeability of Porous Solids,' Transactions of the Faraday
 481 Society, 57, pp. 1200-1207
- 482 McCarter, W. J., Forde, M. C. and Whittington, H. W. (1981). "Resistivity characteristics of concrete",
 483 Proceedings of the Institution of Civil Engineers (London) Part 1 Design & amp; Construction, 71,
 484 107-117.
- 485 Monfore, G. E. (1968). "The electrical resistivity of concrete", Portland Cement Association, Research
 486 and Development Laboratories, Skokie, IL,.

- 487 Morris, W., Moreno, E. I. and Sagues, A. A. (1996). "Practical evaluation of resistivity of concrete in test
 488 cylinders using a Wenner array probe", Cem Concr Res, 26, 1779-1787.
- Newlands, M. D., Jones, M. R., Kandasami, S. and Harrison, T. A. (2008). ," Sensitivity of electrode
 contact solutions and contact pressure in assessing electrical resistivity of concrete", Mater Struct,
 41, 621-621-632.
- Powers, T. C., and Brownyard, T.L., (1942) 'Studies of the Physical Properties of Hardened Portland
 Cement Paste', Bulletin 22 Research and Development Laboratories of the Portland Cement
 Association, Chicago, Illinois (1948)
- Poursaee, A. and Weiss, W. J.(2009). « An automated electrical monitoring system (AEMS) to assess
 property development in concrete », Automation in Construction, Vol. 19(4), 485-490.
- Rajabipour, F., Weiss,, J. and Shane, J. D., Mason, T. O. and Shah, S. P. (2005) Procedure to interpret
 electrical
- Rajabipour, F. and Weiss, J. (2007). « Electrical conductivity of drying cement paste », Materials and
 Structures, Vol. 40(10), 1143-1160.
- Rajabipour, F. (2006). "Insitu electrical sensing and material health monitoring in concrete structures",
 Ph.D. Dissertation, Purdue University, West Lafayette, Indiana.
- Raupach, M. and Schiessl, P. (1997). « Monitoring system for the penetration of chlorides, carbonation
 and the corrosion risk for the reinforcement », Construction and Building Materials, Vol. 11(4), 207 214.
- Riding, K. A., Poole, J. L., Schindler, A. K., Juenger, M.C.G. and Folliard, K. J. (2008). "Simplified concrete
 resistivity and rapid chloride permeability test method", ACI Mater J, 105, 390-394.
- Rupnow,. T. D., and Icenogle, P. (2011). "Evaluation of surface resistivity measurements as an
 alternative to the rapid chloride permeability test for quality assurance and acceptance", Louisiana
 Department of Transportation, Baton Rouge, LA, pp. 68.
- Samson, E., and Marchand, J., (2007) 'Modeling the Transport of Ions in Unsaturated Cement-Based
 Materials,' Computers and Structures, 85, pp. 1740-1756
- Schissl, A., Weiss, W. J., Shane, J. D., Berke, N. S., Mason, T.O., and Shah, S. P., (2000) "Assessing the
 Moisture Profile of Drying Concrete Using Impedance Spectroscopy," Concrete Science and
 Engineering, Vol. 2, pp. 106-116
- Sellevold, E. J., Larsen, C. K. and Blankvoll, A. A. (1997). « Moisture State of Concrete in a Coastal
 Ridge », Special Publication, SP170-42, Vol. 170, 823-834.

- 518 Schlumberger (2011), Oilfield Glossary
- Shane, J. D., Aldea, C. D., Bouxsein,, N. F. Mason, T. O., Jennings, H. M. and Shah, S. P. (1999).
 "Microstrucutral and pore solution changes induced by the rapid chloride permeability test
 measured by impedance spectroscopy", Concr Sc Eng, 1, 110-119.
- 522 Shane, J. D. (2000). "Electrical conductivity and transport properties of cement-based materials 523 measured by impedance spectroscopy", Ph.D. Dissertation, Northwestern University, Evanston, IL.
- 524 Snyder, K.A., (2001) "The relationship between the formation factor and the diffusion coefficient of 525 porous materials saturated with concentrated electrolytes: Theoretical and experimental 526 considerations," Concrete Science and Engineering, 3 (12), 216-224, (2001).
- Snyder, K. A., Ferraris, C., Martys, N. S. and Garboczi, E. J. (2000). "Using impedance spectroscopy to
 assess the viability of the rapid chloride test for determining concrete conductivity", J NIST, 105,
 497-509.
- Spragg, R, Castro, J., Nantung, T., Parades, M, and Weiss, W. J., (2011) "Variability Analysis of the Bulk
 Resistivity Measured Using Concrete Cylinders," JTRP Report SPR-3509, FHWA/IN/JTRP-2011/21
 DOI: 10.5703/1288284314646
- Torquato, S. (2002). "Random heterogeneous materials: microstructure and macroscopic properties",
 Springer, New York, NY.
- TP95-11 (2011) Draft standard method of test for surface resistivity indication of concrete's ability to
 resist chloride ion penetration, American Association of State Highway and Transportation Officials,
 Washington, D.C.
- Tumidajski, P. J., Schumacher, A. S., Perron, S., Gu. P. and Beaudoin, J. J. (1996). « On the relationship
 between porosity and electrical resistivity in cementitious systems », Cement and Concrete
 Research, Vol. 26(4), 539-544.
- 541 UNE (2008a)
- 542
- 543 UNE (2008b)
- 544
- Weiss, W. J., Shane, J. D., Mieses, A., Mason, T. O. and Shah, S. P. (1999). "Aspects of monitoring
 moisture changes using electrical impedance spectroscopy", Second symposium on the importance
 of self desiccation in concrete technology, Lund, Sweden.
- 548 Whittington, H. W., McCarter, J., and Forde, M. C. (1981). "The conduction of electricity through 549 concrete", Mag Concr Res, 33, 48-60.