Electrical Resistivity Measurements in Cementitious Systems: Observations of Factors that Influence the Measurements

Robert Spragg (Corresponding Author) Graduate Research Assistant School of Civil Engineering, Purdue University 550 Stadium Mall Drive West Lafayette, IN 47907-2051 E-mail: rspragg@purdue.edu Phone: 765.494.7999

Chiara Villani Graduate Research Assistant School of Civil Engineering, Purdue University 550 Stadium Mall Drive West Lafayette, IN 47907-2051 E-mail: cvillani@purdue.edu Phone: 765.494.7999

Ken Snyder Leader, Supervisory Physicist Materials and Structural Systems Division National Institute of Standards and Technology 100 Bureau Drive, Stop 8615 Gaithersburg, MD 20899 E-mail: kenneth.snyder@nist.gov Phone: 301.975.4260

Dale Bentz Chemical Engineer Materials and Structural Systems Division National Institute of Standards and Technology 100 Bureau Drive, Stop 8615 Gaithersburg, MD 20899 E-mail: dale.bentz@nist.gov Phone: 301.975.5865

Jeffrey W. Bullard Materials Research Engineer Materials and Structural Systems Division National Institute of Standards and Technology 100 Bureau Drive, Stop 8615 Gaithersburg, MD 20899 E-mail: bullard@nist.gov Phone: 301.975.5725

and

Jason Weiss Professor and Director of Pankow Materials Laboratory School of Civil Engineering, Purdue University 550 Stadium Mall Drive West Lafayette, IN 47907-2051 E-mail: wjweiss@purdue.edu Phone: 765.494.2215

> Submitted on July 31, 2012 Re-submitted on November 16, 2012

Number of words: Body: 5,486; Figures: 2,000 (8x250) = Total: 7,486 (7,500 max)

1 ABSTRACT

2 The electrical resistivity of cement-based materials can be used as an indicator of its fluid transport properties, for 3 use in quality control or for service life prediction. Although electrical tests have the advantage of being easy and rapid to perform, there are several key factors that can influence the results: 1) specimen geometry, 2) specimen 4 5 temperature and 3) sample storage and conditioning. This paper addresses these issues and compares the 6 measurements from several commercially available testing devices. First, the role of sample geometry is explained 7 using three common geometries: surface, uniaxial and embedded electrodes. If the geometry is properly accounted 8 for, measurements from different test geometries result in electrical resistivity values that are similar. Second, the 9 role of sample temperature is discussed for both pore solution and uniaxial tests on cylinders. Third, the paper 10 examines the importance of sample curing, storage, and conditioning. Sample storage and conditioning influences both the degree of hydration and the degree of saturation. The role of sample volume to solution volume is discussed 11 12 as this may influence alkali leaching and pore solution conduction. This paper is intended to identify factors that 13 influence the results of the rapid electrical test measurements and to help identify areas of future research that are needed so that robust specifications and standard test methods can be developed. This will enable electrical tests to 14 15 be used to provide rapid, accurate, repeatable measurements of concrete's electrical properties. 16

17 BACKGROUND

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19 A Brief Background of Electrical Tests in Cementitious Materials

20 The electrical properties of cement-based materials have been investigated for nearly a century (1-3). One practical 21 use of electrical measurements is the standard test that is commonly referred to as the rapid chloride permeability 22 test (RCPT) (4). The RCPT measures the charge passed in a saturated sample over time when a constant voltage is 23 applied. While widely used, the RCPT has a few shortcomings due to the relatively long sample preparation time, its 24 destructive nature, and sample heating, which influences the results (5-8). Given these limitations, there is growing 25 interest to develop non-destructive resistivity measurements that can replace the RCPT. The benefit of resistivity tests is that they can be low cost, repeatable, and rapid to perform (7, 9, 10). AASHTO and ASTM are in the process 26 of developing standard test methods for surface resistivity testing (11, 12), and a multi-user study was conducted to 27 28 assess the variability of two rapid resistivity tests (9, 10). While substantial research has focused on electrical methods over the last thirty years to describe material structure and transport properties (13-19), comparatively little 29 30 research has focused on the role of sample conditioning and sample geometry. This paper serves to highlight 31 important features that may need to be captured in the ongoing development of standard test methods. 32

33 The Influence of Sample Geometry

34 Several different sample geometries have been used to measure the electrical properties of concrete. This section 35 describes these geometries and discusses how they can be related to one another. The most commonly used 36 geometries are shown in Figure 1. The first geometry is referred to as surface resistivity as shown in Figure 1a. The 37 surface resistivity test uses a four electrode configuration where an alternating current is passed between the outer 38 probes and the voltage is measured between the inner probes (In this paper a standard 100 mm diameter x 200 mm 39 long cylinder specimen is used with a probe spacing of 38 mm (11)). The second geometry is typical of a uniaxial 40 test where a set of plate electrodes are placed at the ends of a cylindrical specimen and used to measure the 41 resistance through the cylinder, shown in Figure 1b. This test was conducted using the testing procedure described 42 by Spragg et al. (10). The third geometry evaluated in this study used a set of embedded stainless steel rods (in this 43 paper a standard 150 mm x 300 mm test cylinder was used with two embedded threaded rods as shown in Figure 1c 44 and described by Castro et al. (20)).

The tests highlighted in this study are based on measuring the electrical resistance between electrodes on a sample. This electrical resistance can be related to the geometry independent property known as resistivity using the approach shown in Equation 1:

$$\rho = Rk \tag{1}$$

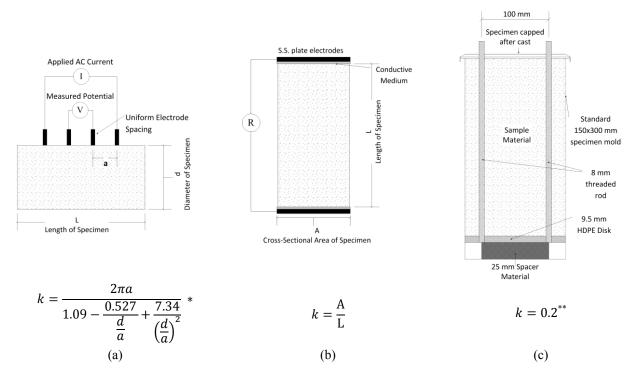
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where ρ is the material resistivity, *R* is the measured resistance, and *k* is the geometry correction factor. This factor can be determined numerically (14, 21) or experimentally (10, 22) and is shown in Figure 1 for the geometries

52 described above. In addition to these geometries, a wide range of electrode geometries and specimen sizes can be

1 used for this type of testing, provided the geometry factor can be determined, with examples provided in the 2 literature (14, 22-24).

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5 **FIGURE 1** Testing geometries and geometric correction factors (*k*) for cylindrical specimens: a) surface, b) 6 uniaxial, c) embedded electrode geometries. *valid for specimens with $d/a \le 4.0$ and $L/a \ge 5.0$; ** valid only for this 7 specimen geometry 8

9 The Influence of Sample Temperature

The temperature of the sample can substantially influence the measured resistivity (3, 25-28). An increase in the temperature of the sample results in an increase in the mobility of the ions in the pore solution and a decrease in measured resistivity. While several approaches have been proposed to account for temperature, the correction investigated by the authors is a variation of the Arrhenius Law:

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$$\rho_{t-\text{Ref}} = \rho_t \cdot \exp\left[\frac{E_{\text{A-Cond}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{Ref}}}\right)\right]$$
(2)

where ρ_{t-Ref} (ohm m) is the resistivity at a reference temperature (23 °C in the U.S.), ρ_t (ohm m) is the resistivity at the testing temperature, E_{A-Cond} (kJ/mol) is the parameter known as the activation energy of conduction, R (8.314 J/(mol·K)) is the universal gas constant, T (K) is the testing temperature, and T_{Ref} (K) is the reference temperature of 23 °C. Although changes in temperature can influence the rate of hydration of cement-based materials, this correction is intended to account for the influence of temperature on the electrical measurements and hydration effects are dealt with separately (28). This work will investigate the influence of temperature on both the pore solution and sample resistivities.

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24 The Influence of Sample Conditioning – Storage and Conditioning

Another important factor that can influence electrical measurements is how the samples are stored and conditioned.

To best illustrate this approach, the NIST developed Virtual Cement and Concrete Testing Laboratory (VCCTL)

- model was used to simulate a mortar with a w/c of 0.42 with three curing conditions considered: 1) sealed during curing and testing, 2) sealed during curing and saturated during testing, and 3) saturated during curing and testing.
- Details on how these simulations were performed can be found in the literature (29, 30). There are two primary
- factors that influence this response: the degree of hydration of the cement and the degree of saturation of the sample.

The uniaxial mortar resistivity (ρ_c) values calculated from these simulations, normalized by the resistivity of the fluid in the pores (ρ_o), are shown in Figure 2. The sample that was sealed both during curing and testing had the greatest resistivity. The sample that was sealed during curing and saturated at the time of testing had the lowest resistivity. While the pore structure and degree of hydration of both samples is the same, the difference can be explained by the moisture content (or degree of saturation) of the sample. An approach has been proposed to account for changes in resistivity in partially saturated concrete using Equation 3 (30):

$$\rho^* = \rho S^{n-1+\delta} \tag{3}$$

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9 where ρ^* is the resistivity at saturation, ρ is the resistivity at a given level of saturation of *S* (which is between 0 and 1), n is fitting parameter termed the saturation coefficient, and δ describes the the ionic strength of the pore solution 11 and how it changes during drying. For the mortar used in this study (the physical experiments), the degree of 12 saturation was varied between 85 % and 100 % and it was observed that an exponent (n-1+ δ) of 4.15 best fit the 13 data, which compares well to the data presented by Weiss et al. (30) from the simulations.

14 Figure 2 also shows that the storage of samples in lime water results in a greater degree of hydration than 15 that achieved in samples that were sealed. The data points in Figure 2b provide evidence that different degrees of 16 hydration occur due to sample conditioning, while Figure 2a presents these measurements at the same specimen age. 17 This implies that storing a sample underwater in the lab may result in a substantially different degree of hydration 18 than what may be occur in a field structure. It can be noticed that the sample that is continually saturated and the 19 sample that is sealed and saturated at the time of testing have a similar resistivity for the same degree of hydration; 20 however, the sample that is continually saturated has a higher degree of hydration at the same age. In Figure 2c, 21 these model results suggest that, for a given sample, the resistivity at any degree of saturation can be estimated from 22 a single measurement, given that the relative change in the pore solution conductivity can also be predicted. These 23 models also suggest that resistivity measurements can be evaluated in terms of the fraction of saturated porosity in 24 the paste, as shown in Figure 2c, with results similar to those reported by Weiss et al. (30).

It has also been hypothesized that for samples that are cured under saturated lime-water, the volume of solution in which the samples are stored can influence resistivity measurements. This may be due to possible pore solution concentration or dilution via leaching. This work will carefully investigate the influence of the volume of storage solution to sample size that is used for saturated lime-water curing.

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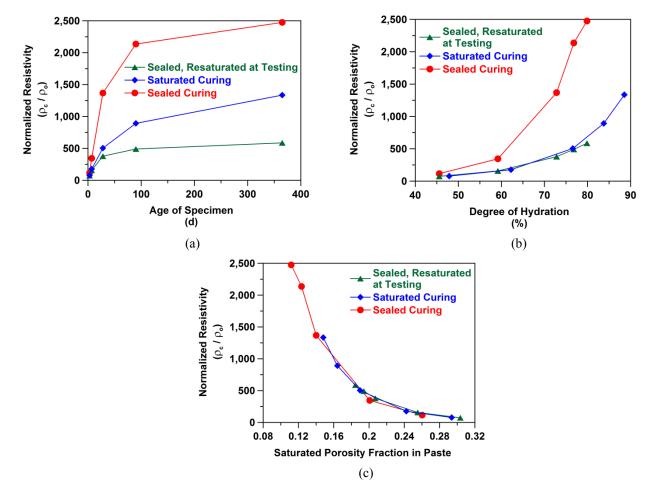


FIGURE 2 VCCTL simulations of the same w/c=0.42 mortar mixture evaluated for three curing conditions (data are shown at ages of 3 d, 7 d, 28 d, 90 d and 365 d and are presented normalized by the resistivity of the fluid in the pores).

5 MATERIALS

6 The samples described in this paper were made using a mortar and a paste, each with a water to cement ratio of 0.42

by mass. The mortar mixture consisted of 55 % aggregate by volume, made with a fine aggregate with a specific gravity of 2.61 and an absorption capacity of 2.20 % by dry mass. A Type I ordinary portland cement with a Blaine

9 fineness of 375 m²/kg, a specific gravity of 3.17, and an estimated Bogue composition of 60 % C₃S, 10 % C₂S, 9 %

10 C₃A, and 10 % C₄AF by mass was used. The cement contained an alkali content of 0.35% Na₂O and 0.77% K₂O.

11 Based upon the chemical composition, the ultimate theoretical heat release was calculated to be 512 J/g, using the

12 tabulated heat of hydration of each Bogue phase (31, 32).

This study evaluated samples that were stored in a lime-saturated solution. This solution was always used at a lime dosage rate of 3.0 g / L of solution to ensure a saturated solution. At saturation, the solubility of pure calcium hydroxide is 1.2 g / L of water.

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17 EXPERIMENTAL EQUIPMENT USED FOR RESISTIVITY TESTING

18 Sample resistance was measured using four different commercially available resistivity meters. Each meter used an

alternating current (AC), but operated at a different frequency. The Proceq Resipod was used for surface resistivity

- testing (Figure 1a) at a fixed probe tip spacing of 38 mm and uniaxial resistivity testing (Figures 1b) using the
- 21 uniaxial resistivity testing kit available from Proceq, and operating at a frequency of 40 Hz. The M.C. Miller 400D
- was used in uniaxial resistivity testing (Figures 1b) at a frequency of 80 Hz. The uniaxial measurements (Figures 1b)
- 23 using the RCON meter were performed at a single frequency (1 Khz), with the exception of the equivalent circuit

model discussed in Section 4.5. To quantify the effect of a single frequency measurement, the Solatron 1260A impedance spectrometer across a frequency range of 1Hz to 10MHz.

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EXPERIMENTAL RESULTS AND DISCUSSION

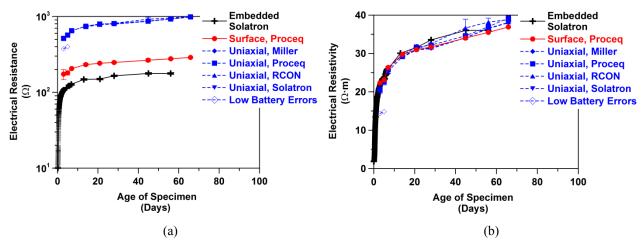
6 **Corrections for Geometry**

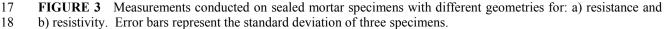
Measurements of electrical resistance were made on sealed specimens, i.e. specimens heat sealed in double plastic bags between testing, and the results are shown in Figure 3a. It can be noticed that when the appropriate correction for geometry is applied (using Equation 1 and values highlighted in Figure 1) to calculate the electrical resistivity, the results obtained from different specimens of different geometries are quite comparable, as shown in Figure 3b.

It is interesting to note that a few of the early age uniaxial measurements using the Miller resistivity meter (highlighted using hollow diamond symbols in the figure) show a much lower resistance. These lower measurements were traced to low battery levels and when the battery was replaced for a second set of experiments, the results were comparable with other experiments. This however shows the value in having a standard, unchanging reference sample that can be used each day to confirm that the meter is working properly.

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20 **Pore Solution Contribution**

The resistivity of the sealed mortar was measured and is plotted against the degree of hydration (DOH), determined from isothermal calorimeter measurements (33), and shown in Figure 4a. The resistivity is nearly a linear function of the DOH, which is similar to previously reported data (14, 20, 34).

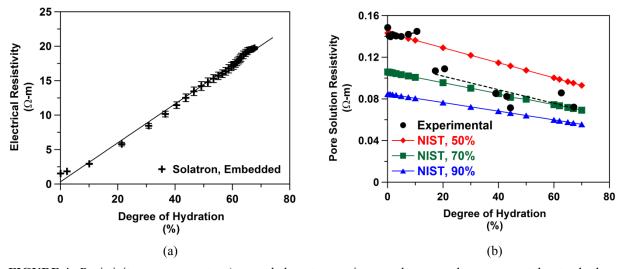
The pore solution is the primary conducting phase in cement-based materials, and has a resistivity several orders of magnitude lower than the solids and vapor phases (14). To study how the pore solution changes with hydration, the pore solution was extracted from paste specimens with a w/c = 0.42. Solutions were extracted at ages of 10 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, and 7 h while still in the fresh state by a Millipore pressure filtering system, using nitrogen gas at pressures up to 200 kPa (35). Extractions performed on hardened samples were conducted at ages of 1 d, 3 d, 5 d, and 7 d using a high pressure die at pressures up to 380 MPa as described by Barneyback et al. (36). The extracted solutions were then measured for resistivity using a pore solution cell described by Castro (33).

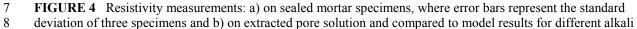
31 The experimentally measured pore solutions were compared to a model (37) which was developed into an 32 online tool by Bentz (http://concrete.nist.gov/poresolncalc.html)(38). This model predicts the electrical properties of 33 the pore solution using only the masses of the water, cement and supplementary materials; the chemical composition 34 of those materials (i.e., their Na₂O, K₂O and SiO₂ mass percentages); and the estimated degree of hydration. The model estimates the composition of the pore solution and then evaluates the electrical properties of this pore 35 solution. One assumption, however, that has to be made in this model is the proportion of alkalis that initially 36 37 dissolve in the solution. While a value of 75 % is a typical default value that can be employed, assumed values of 50 %, 70 %, and 90 % are shown in Figure 4b along with the experimental results. Initially, a value of 50 % of the 38 39 alkalis dissolving in solution appears appropriate; however, between a degree of hydration of 10 % and 20 % this

value suddenly increases to 70 %. It is interesting that this appears to relate to the shoulder of heat release curve that was observed for this system and which generally relates to the renewed reaction of the calcium aluminate phase of the cement. Several methods currently exist to rapidly assess the pore solution resistivity including pore solution extraction, estimation using an approach like the NIST website, and embedded sensors (14, 20). Research is ongoing to better understand the correlation between these results.



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9 dissolution percentages.

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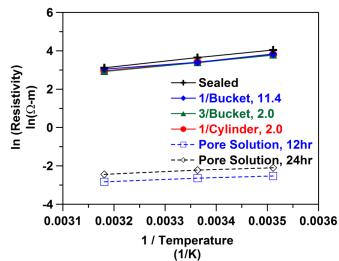
11 Influence of Temperature

Temperature can also influence the measured electrical response. For example, the resistivity measured using the same mature sample can differ by as much as 80 % when the temperature of the sample fluctuates between 10 °C and 45 °C. This is primarily due to the increased ionic mobility of the material's pore solution and can be described using an Arrhenius approach (Equation 2).

The activation energy of conduction (E_{A-Cond}), can be determined using the slope of a plot of the natural logarithm of resistivity and the inverse of temperature as shown in Figure 5. The slope of the best fit line is multiplied by the negative of the universal gas constant [-8.314 J/(mol·K)] to determine the activation energy of conduction.

20 Figure 5 shows results for mature mortar cylinders (closed symbols) and extracted pore solution (open 21 symbols). The sealed specimens exhibit an activation energy of conduction of 23.4 ± 0.13 kJ/mol, the specimens 22 stored in volume to solution ratio of 2.0 exhibit an average value of 21.5 ± 0.08 kJ/mol, and the specimens stored in 23 a solution to sample ratio of 11.4 exhibit a value of 19.9 ± 0.42 kJ/mol. Previously reported values for the activation 24 energy of conduction in mortar specimens have included 18.7 ± 2.5 kJ/mol, values in excess of 20, and ranges of 16 25 -30 kJ/mol (14, 26, 28). The activation energy of conduction was also measured on pore solution extracted from specimens at ages of 12 h and 24 h, resulting in values of 8.7 ± 0.18 kJ/mol and 7.7 ± 0.12 kJ/mol respectively. 26 27 Previously reported results for synthetic and extracted solutions have ranged from 8.98 kJ/mol to 13.8 kJ/mol (14, 28 20, 28).

This difference between measured activation energies of conduction obtained on extracted pore solution and uniaxial cylinders appear to suggest the microstructure of a material can also influence these measurements, as previously noted by Rajabipour *(14)*. This may be due in part to the confinement provided by the pore space, pore constriction, surface/absorption effects, or changes in the pore fluid volume during heating and cooling; however additional work is needed to fully understand the reasons for these changes.



1 2 FIGURE 5 Activation energy of conduction measured on uniaxial samples (closed points) and extracted pore 3

solution (hollow points) using electrical impedance spectroscopy. Linear fits show an average R^2 of 0.996.

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5 **Influence of Sample Storage and Conditioning**

6 As previously mentioned, the conduction of the electrical current occurs primarily through the pore fluid in the 7 cementitious system. While the pore solution changes during hydration, the pore solution may also change if ions 8 leach from the sample to the surrounding solution. As such, a series of tests was conducted where the ratios of the 9 volumes of the lime saturated solution to sample (Sol/Sam) varied (2.0 and 11.4). The Sol/Sam of 2.0 can be 10 obtained when using a standard 100 mm x 200 mm testing specimen by using; one specimen in a standard 150 mm x 300 mm mold or 3 samples in 5-gallon bucket. The Sol/Sam of 11.4 can be obtained when using a single specimen 11 12 in a 5-gallon bucket.

13 The samples were stored in a lime-saturated solution as described above and was monitored for electrical 14 resistivity. The nominal resistivity of the lime saturated solution is 12.6 Ω -m. The measured resistivity of solution 15 in the system where the Sol/Sam was 11.4 initially increased to a value of 16 Ω -m at approximately two weeks, 16 before it began to decrease, reaching 13.8 Ω -m after 2 months. The measured resistivity of solution in the system 17 where the Sol/Sam was 2.0 initially decreased to a value of 2 Ω -m by approximately one week, while it slowly 18 decreased to 1.3 Ω -m after 2 months. Initial data seems to suggest this is due to ion leaching and dilution effects, but 19 future research will investigate this in more detail.

20 In addition to monitoring the resistivity of the solution, resistivity measurements were measured on the 21 sample using: surface and uniaxial geometries at a frequency of 40 Hz, and uniaxial resistivity measured over a 22 range of frequencies. Figure 6 shows the resistivity for the samples measured using the different storage conditions. 23 It can be noticed that the resistivity of the sealed sample is higher than the samples stored in the solution with a 24 Sol/Sam of 2.0. This can be explained by the fact that the samples in solution have a higher degree of saturation.

25 It is interesting to note that the samples stored with Sol/Sam of 11.4 where the resistivity was measured at 26 low frequency more closely resembles the measurements conducted on sealed samples than other samples that are 27 lime-water cured (Figure 6b). Testing at a variable frequency (Figure 6c) provides similar results for specimens 28 stored in both Sol/Sam with less than 1 % difference.

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30 At early ages up to 7 d, the surface resistivity measurements have more variability than the uniaxial measurements, evidenced by standard deviations that are up to 2.7 times higher for surface measures using 8 31 32 samples. (Figure 6a and 6b), while at later ages the effect of storage solution volume seems to be reduced. This can 33 likely be attributed to the effects of leaching of surface alkalis in both solution volumes. The results obtained to date suggest that at later ages, the influence of storage solution volume on surface measurements and uniaxial 34 35 measurements at variable frequencies (Figures 6a and 6c) is generally within the variability of the measurement, 36 while uniaxial measurements at fixed frequencies show differences from 10 to 30 % between storage solutions 37 (Figure 6b).

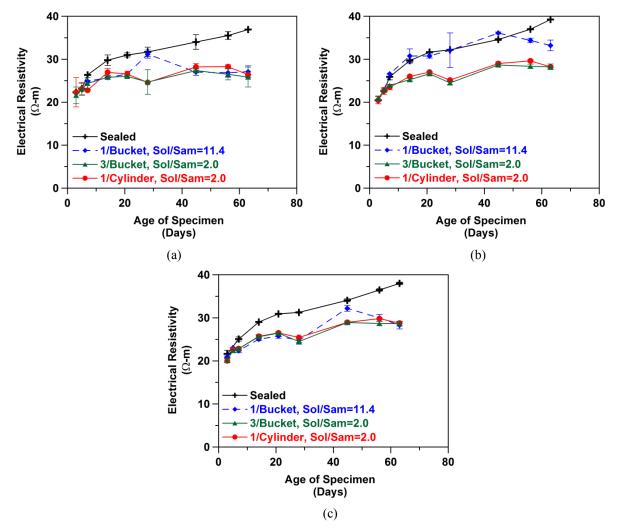


FIGURE 6 Resistivity measurements using differing solution to sample ratios: a) surface b) uniaxial 40 kHz frequency and c.) uniaxial multi-frequency measurements. Error bars represent the standard deviation of a minimum of three specimens.

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5 Influence of Measurement Frequency on Total Impedance

6 Because saturated cementitious systems behave like resistor-capacitor circuits, resulting in a phase difference 7 between the applied current and the measured voltage (impedance), and there is a noticeable difference in 8 impedance at different frequencies; the real component of the impedance at zero phase angle is the true uniaxial 9 resistance. Because the phase is (almost never) zero, the meters report the total impedance Z_0 : the real and 10 imaginary components added in quadrature. To compare the response of the different meters, an electrical circuit (Figure 7) was used and the responses are shown in Figure 7a; the Proceq was configured for uniaxial resistivity. 11 12 The Solatron meter provides a response over a wide range of frequencies, and the values are shown using circular 13 symbols (every 10th symbol is shown). The Miller and Proceq meters were tested at a single frequency and are 14 shown by the triangle and the diamond-shaped symbols, respectively. The phase angle, shown with hollow points 15 and dashed lines is also used to highlight the frequency dependence. While the measured response of the meters 16 shown in Figure 7a compare well with one another, the data demonstrate why the resistance reported from each unit 17 will not be the same, as they are measured at different frequencies.

The frequency dependence of the electrical response also exists in uniaxial mortar specimens as shown for a specimen stored in Sol/Sam of 2.0 conditions at an age of 45 d in Figure 7b. While there is not a significant difference between the measurements of the single frequency meters and the impedance spectra, there is a difference seen in the resistivity that would be reported among these different meters. This can be explained through the

22 influence of frequency, while the two fixed meters operate in the range of 80 Hz to 100 Hz, the measurements used

by the Solatron have the lowest imaginary impedance at 794 Hz which would be where the uniaxial resistance would be reported. Note that the Proceq and Miller devices report values approximately 5 % lower than the true uniaxial value determined by the Solartron.

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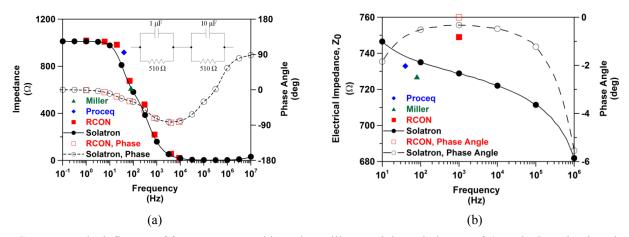


FIGURE 7 The influence of frequency on total impedance illustrated through the use of a) equivalent circuit and
 b) a uniaxial measurement on a mortar cylinder at an age of 45 d.

A variable frequency was also used to interpret uniaxial resistivity measurements for samples stored using different sample to solution volumes. It can be noticed that the frequency responses change as the specimen ages, as shown in Figure 8 for 5 d and 65 d samples, respectively. Specimens with a larger Sol/Sam exhibit more variability between samples, which is even more pronounced at later ages. This may be explained by the impedance response across the frequency range. This is especially evident in the phase angle measurements, where the larger storage volume appears to have two local minima contrasted with the other specimen conditions, which is largely pronounced at later ages, but can also be seen even as early as five days.

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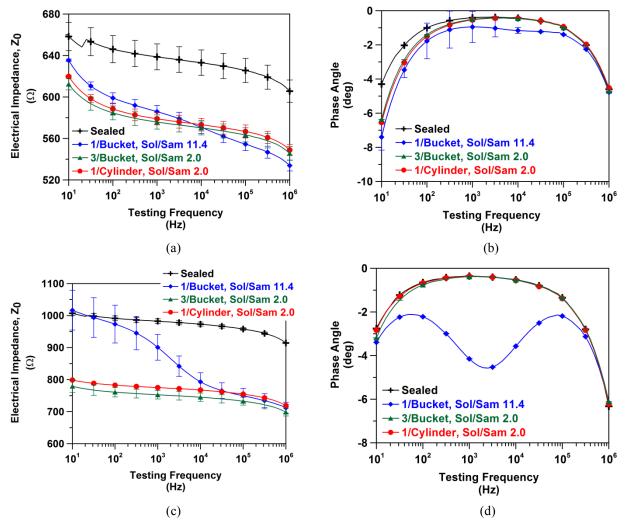


FIGURE 8 Frequency and phase angle responses of specimens with different Sol/Sam: a and b) 5 d and c and d)
 65 d. Error bars represent the standard deviation of three specimens.

4 CONCLUSIONS

5 There are several key factors that should be considered in standardizing tests for the electrical resistivity of cement-6 based materials. First, different specimen geometries can be used; however, the measured resistance should be 7 converted to the resistivity using an appropriate geometry correction factor. Second, the temperature of the specimen 8 during the test can also influence resistivity measurements, so a relatively narrow temperature range of the test 9 specimens (e.g., ± 2 °C) should be specified in standard test methods. The temperature dependence can be partially 10 attributed to the increased mobility of the ionic species of the pore solution. It was shown that both pore solution 11 resistivity and specimen resistivity measurements follow an Arrhenius relationship, with different activation 12 energies of conduction (E_{A-Cond}). Third, it was shown that sample storage and conditioning is also important, as it 13 can influence the degree of hydration, the degree of saturation, and the pore structure and solution through leaching. 14 Differences in resistivity can develop due to sample storage conditions (sealed versus saturated). It was noticed that 15 when hardened specimens were stored in different solutions of different volumes inconsistent results were obtained. 16 This appears to be related to pore solution dilution which appears to alter the measured frequency spectra. As such, testing at variable frequencies has the ability to reduce these effects, but for testing at a fixed frequency the solution 17 18 volume surrounding the sample should be tightly controlled. A solution to sample volume ratio of 2.0 appears to be 19 an appropriate recommendation at this time. Future studies are underway to investigate this potential dilution effect 20 and the potential gradients that develop in the material that can lead to sample inhomogeneity (39).

1 ACKNOWLEDGEMENTS

This work was supported in part by the Joint Transportation Research Program administered by the Indiana Department of Transportation and Purdue University (Project SPR 3509). 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 Federal Highway Administration and the Indiana Department of Transportation, nor do the contents constitute a standard, specification, or regulation. The authors thank Giatec Scientific for supplying a unit for testing.

9 **DISCLAIMER**

Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement or recommendation by the National Institute of Standards and Technology or Purdue University, nor does it indicate that the products are necessarily the best available for the purpose.

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