



AN ABSTRACT OF THE THESIS OF

Joseph H Biever for the degree of Master of Science in Civil Engineering presented on September 12, 2022.

Title: Measuring and Correcting the Electrical Resistivity of Concrete Pore Solution in Fresh Mixtures

Abstract approved:

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A vital aspect of concrete construction is quality assurance and control (QA/QC). Engineered structures must meet pre-determined and agreed-upon strength and durability requirements. Concrete falls into a specific category of infrastructure material because in most cases, these strength and durability requirements cannot be found until the material has at least partially cured (7-28 days). Recent research has suggested that fresh concrete electrical resistivity may be a possible indicator of critical hardened concrete properties; therefore, it can be used to supplement existing QA/QC protocols of concrete.

The electrical properties of fresh and hardened concrete have been investigated for more than 80 years. However, two key aspects of measuring fresh concrete resistivity in the field have not been extensively studied. The main goal of this thesis is to answer the following two questions: (1) how can the electrical resistivity of concrete pore solution be measured practically in the field and (2) would aggregates affect these measurements.

The first part of this thesis statistically compares techniques for fresh concrete resistivity extraction and measurement. These procedures must be cost-effective, easy to upscale for industry, and yield faster results. The centrifuge approach of extraction and conductivity probe for measuring resistivity are found to be the most practical

techniques for potential field use. Additionally, it is found that pore solution extraction and measurement can be performed 30-90 minutes after mixing without significantly affecting the resistivity. Finally, a practical method is proposed to determine the resistivity from a diluted cement paste sample when the extracted pore solution volume is inadequate for accurate measurement.

The second part of this thesis examines the influence of fine aggregates on the pore solution of fresh mortars. Specifically, this chapter considers the dilution of pore solution due to the water content of aggregates, and the potential adsorption of pore solution ions on the surface of aggregates. Results indicate that aggregates may play a significant role in the chemistry of a fresh mortar system. A test method is proposed to identify aggregates that are a significant ionic influence on the pore solution system, and a methodology is proposed that corrects for the change in ion concentration of a fresh pore solution due to the dilution and adsorption of aggregates.

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Measuring and Correcting the Electrical Resistivity of Concrete Pore Solution in  
Fresh Mixtures

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Joseph H Biever

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Joseph H Biever, Author

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## CONTRIBUTION OF AUTHORS

Dr. W. Jason Weiss (advisor), Dr. O. Burkan Isgor (advisor), and Krishna Siva Teja Chopperla (post-doctorate advisor), were involved in the writing of chapter 2.

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## 1 GENERAL INTRODUCTION

### *1.1 Introduction*

The very first ready-mix concrete delivery was made to Baltimore, Maryland over 100 years ago in the year 1913 (1). Through years of research and development, concrete material has seen incremental improvements in strength, durability, workability, and cost-effectiveness. Test methods for quality assurance and quality control (QA/QC) of concrete, however, are nearly a century old. The industry is approaching a crossroads, where advancements in material testing and modelling may potentially satisfy the limitations seen in current QA/QC practice. Concrete has changed to meet the demands of modern-day ecological, durability, and materials concerns, and older test methods have not evolved to account for these factors.

ASTM C94 (2) is a widely-used contractual agreement that calls for a number of QA/QC measurements upon delivery of ready-mix concrete. These measurements include the slump, unit weight, temperature, and air content. ASTM C94 also calls for cylindrical samples to be taken on-site and cured for 7-28 days to determine the compressive strength of the delivered concrete (2). While these factors are meant to give an interpretation of the concrete quality, they do not measure critical concrete parameters such as the water to cementitious materials ratio (w/cm), nor do they quantify the durability of the delivered material. They are also not helpful for making quick decisions on the acceptance of delivered concrete on site. Simply stated, QA/QC techniques that have worked in the past may need to be reconsidered with more complicated mixture designs and materials.

Multiple first steps have been made to improve QA/QC programs in fresh concrete. For example, w/cm of concrete is one of the most variable characteristics of ready-mix concrete yet is also one of the most influential. W/cm can determine the overall strength, permeability, and consistency of a delivered mixture (3). W/cm, however, can

vary due to incorrect aggregate moisture content calculated, batch plant tolerances, residual water in ready-mix drums, or added water in transit or on site. Approaches such as the AASHTO T318-15 microwave oven drying method (4) and the Phoenix method (5) utilize evaporation techniques to determine the w/cm of fresh concretes upon delivery. These new approaches, however, have downsides. AASHTO T318-15 takes 40 minutes, is labor intensive, and results can vary  $\pm 0.05$  from actual w/cm (4). The phoenix method dries samples faster (8 minutes) and reduces variability to  $\pm 0.01$ , however requires a portable furnace to process samples (5). Most other advancements in concrete QA/QC programs are performed on hardened concrete. One of these techniques that has significantly benefitted industry is the incorporation of hardened concrete resistivity measurement as a means for determining w/cm and durability characteristics.

### 1.1.1 Background on Electrical Properties

Electrical resistivity is a measurement of a material's ability to resist electrical current. In the field of concrete material science, electrical resistivity has been used as early as 1928 to monitor the setting of concrete (6). The resistivity of a concrete is determined by its liquid and solid phases (7). The liquid phase of a concrete is known as the pore solution and is composed of water and dissolved ions from cementitious materials. The pore solution is significantly more conductive than the solid phases of concrete by many orders of magnitude (7,8). Other components of the concrete system such as aggregates and cementitious materials act as insulators, forcing the electrical current to make a path through the connected pores containing pore solution. Resistivity is therefore heavily dependent upon the porosity and shape of interconnections, which is known as the tortuosity (9). Because of this, resistivity measurement is an indicator of the microstructure characteristics of a concrete. A parameter known as the formation factor (F) is a way to quantify the volumetric fraction of the conductive component in the system.

$$F = \frac{\rho_b}{\rho_{ps}} = \frac{1}{\varphi\beta} \quad (1.1)$$

Where  $F$  is defined as the ratio of the bulk concrete resistivity ( $\rho_b$ ) to the pore solution resistivity ( $\rho_{ps}$ ) and is inversely related to the product of porosity ( $\phi$ ) and pore connectivity factor ( $\beta$ ). The formation factor has been related (mainly in hardened concrete) to many durability properties in concrete (7,10-12). Some examples include the use of formation factor to assess transport properties such as water absorption (13,14), chloride ingress (15-17), or permeability (18) of hardened concrete. Using the resistivity to determine these durability properties is highly advantageous, as resistivity can be rapidly determined, and is a very inexpensive test to perform. Due to its usefulness and practicality, industry has begun to use resistivity properties to measure durability.

Standards such as ASTM C1760 (19), AASHTO TP119 (20) and AASHTO T 358 (21) have made resistivity a useful tool for industry (22). Specifications such as AASHTO R 101 (previously known as PP 84 (23) specify minimum formation factor for mature concrete to limit chloride ingress in concrete. These standards all outline test methods for hardened concrete. Because  $F$  is a measurement of the microstructure of a concrete, however, it may also be applied to fresh concrete systems.  $F$  values will be significantly different than hardened due to the unmaturing and non-hydrated system, however they give similar insight to the future pore structure of the concrete. Measuring the fresh resistivity is also highly attractive to industry, as it reduces testing costs and allows for immediate results on-site. In response, several studies (24-28) have examined the use of electrical properties of fresh concrete as a potential QA/QC tool.

A benefit to fresh concrete resistivity measurement is its potential to measure not just durability, but other key parameters such as the water-to-cementitious materials ratio ( $w/cm$ ). Whittington et al. reported that paste bulk resistivity increases with an increasing  $w/cm$  ratio (7), and Li et al. suggested that at a specific age of hydration, paste bulk resistivity and the  $w/cm$  of cement paste follow a power trend relationship ( $Y=Ax^B$ ), which is dependent upon cementitious material composition. Mancio et al. also reported a clear trend with  $w/cm$  and resistivity using an in-situ probe method to measure paste resistivity (29).



Other studies have examined the impact of supplementary cementitious materials content on the resistivity of cement paste. Bekir et al. examined the change in resistivity with setting in cement systems containing SCMs like fly ash, silica fume, and blast furnace slag (30). Bekir et al. reported that resistivity of the cement paste increased with increasing SCM content (30). Sallehi et al. performed similar experiments, recording F values for differing fresh cementitious paste systems containing fly ash, silica fume, and additionally a superplasticizer (25). Outside of these studies, minimal research has been done regarding the electrical resistivity of fresh cementitious systems.

Many other parameters outside of w/cm, SCM, and superplasticizers can affect the resistivity of a fresh concrete system. For example, the temperature can change the ion mobility, ion interactions, and ion concentration in pore solution (31,32), increasing the resistivity as the temperature decreases. Additionally, admixtures like accelerators, retarders, and corrosion inhibitors may also impact the resistivity of a system. The effect of these admixtures on resistivity has not been investigated. Most notably, aggregate may have a significant impact fresh concrete resistivity. Wei and Xiao investigated the change in bulk resistivity for fresh concretes of different volume fractions, but did not investigate the formation factor at young ages (33).

Most fresh cementitious studies choose to focus on cement paste because pore solution resistivity is believed to be the most influential aspect of fresh concrete resistivity (7). In most cases for fresh systems, it is more worthwhile to investigate the changes that may occur in the pore solution of cementitious materials as they are the primary contributors of ions in pore solution. This is best described by using the modified parallel law (Equation 1.2).

$$\frac{1}{\rho_c} = \frac{1}{\rho_{ps}} \phi_{ps} \beta_{ps} + \frac{1}{\rho_{cm}} \phi_{cm} \beta_{cm} + \frac{1}{\rho_{agg}} \phi_{agg} \beta_{agg} + \frac{1}{\rho_{air}} \phi_{air} \beta_{air} \quad (1.2)$$

where  $\rho_c$  is the resistivity of the concrete,  $\rho_{(p)}$  is the resistivity,  $\phi_{(p)}$  is the volume fraction, and  $\beta_{(p)}$  is the connectivity parameter of each phase ( $p$ ). Each phase of a concrete (pore solution, cementitious materials, aggregate, and air) impacts the electrical resistivity of the system based on their volume fraction. Concrete aggregates, however, typically have a resistance in the order of  $10^4$ - $10^8$  ohm.cm (34), and are therefore assumed to be electrically insulating (7,34). Similarly, the vapor phase and cementitious binder have typical resistivities of  $10^{19}$  ohm.cm and  $10^7$  ohm.cm, respectively (35). Therefore, it is typically assumed that the contribution of these phases to the resistivity of the system is minimal, and the pore solution is the main influence to measured resistivity as shown in Equation 1.3.

$$\frac{\rho_{ps}}{\rho_{cm}} \approx \frac{\rho_{ps}}{\rho_{agg}} \approx \frac{\rho_{ps}}{\rho_{air}} \approx 0 \quad (1.3)$$

Due to the high resistivity of the other phases of a fresh concrete, studies often simplify the system and study just the pore solution of cement paste (Equation 1.4).

$$\frac{1}{\rho_c} = \frac{1}{\rho_{ps}} \phi_{ps} \beta_{ps} \quad (1.4)$$

Although aggregates are typically disregarded as inert components of the pore solution system, they have been proven to interfere with resistivity measurements in some scenarios. In hardened concrete, for example, the influence of aggregates on the resistivity of concrete has been investigated, specifically for the interfacial transition zone (ITZ) due to its potential to increase the resistivity of mortar or concrete (34,36-38). Additionally, aggregates with a high porosity have been studied for their influence on resistivity measurements (39,40). The previous studies (34,36-38,40) mainly focused on the effect of different aggregates and aggregate contents on bulk resistivity of hardened mortar or concrete. Limited work (41) has been done on examining aggregate's influence on the pore solution of mortar or concrete.

Aggregates may influence a fresh mortar or concrete pore solution in two ways. One influence is aggregate water content. In practice, batching facilities compensate for the water content of aggregates by adjusting the amount of water added to concrete

mixtures. This concept is not new but is an important component to consider. Dilution-resistivity relationships like those outlined in Snyder's et al. paper (42) can also be used to correct for this water content. A second potential influence that aggregates may have on pore solution is ion adsorption. Aggregates may gain surface charge depending upon the pH of the surrounding solution and the mineralogy, which may potentially lead to adsorption of counterions on aggregate surfaces for macroscopic electrical neutrality (43). This effect on pore solution has not been researched and may have a significant influence on the pore solution chemistry of a fresh mortar or concrete.

### 1.1.2 Resistivity Measurement Background

Practical methods exist to measure bulk resistivity of fresh cementitious systems (7,31,32,44-47); however, no standardized methods exist to measure the properties of the pore solution in fresh cementitious materials. Numerous different techniques have been used in research. For example, Rajabipour et al. (48) developed pore solution sensors; however, these have a time lag which is not a concern at later ages though it may be an issue in measuring fresh concrete. Further, these sensors have yet to be mass produced. Thermodynamic modeling is another tool that has been successfully used for long-term properties; however, these models struggle to provide strong predictions for fresh mixtures as they are based on long term equilibrium calculations and early ages are dominated by kinetic effects and dissolution properties (49-60). Direct measurement methods that use chemical composition to calculate resistivity such as ion chromatography (61), titration (62), or inductively coupled plasma spectroscopy (ICP) (63,64) take significant time and require multiple samples, making them expensive and impractical for field applications. Pore solution resistivity has been able to be calculated using chemical composition obtained using X-ray fluorescence (XRF) with an error of 3.75% (65,66). This, however, requires the solution to be extracted and tested in a laboratory environment.

Similarly to pore solution resistivity measurement, extraction of fresh pore solution is also not standardized. Various techniques have been used in past research. Marisol et al. used a high pressure nitrogen press to extract the pore solution from cement pastes (66). Sallehi et al. used a vacuum apparatus and filter to extract the pore solution from cement paste (25). These methods are difficult to use in the field, as they require equipment like pumps and compressed nitrogen. As such, a need exists for a practical method to extract pore solution from fresh cementitious systems. Further, a need exists to rapidly determine the resistivity of this pore solution to make fresh concrete a viable alternative to current QA/QC programs.

## ***1.2 Research Objectives***

The primary objectives of this study are as follows:

- To develop a field test method for extracting and measuring the pore solution of fresh concrete, and statistically compare this method to commonly used techniques in laboratories and research facilities.
- Perform a statistical investigation into the effect of mixing time on the resistivity of fresh cement paste pore solution.
- Develop a procedure to dilute and back-calculate for the resistivity of a fresh pore solution if there is too little pore solution to test the resistivity.
- To develop a test method to investigate the effect of aggregates on the chemistry of a pore solution system due to dilution and potential surface adsorption of ions.
- Relate the developed aggregate test methods to mortars in an effort to determine the potential changes that aggregates may have on the pore solution of mortars and concrete.

## ***1.3 Thesis Organization***

This thesis consists of four chapters:

Chapter 1 provides background and literature review on the limitations of current concrete QA/QC programs, and the potential for fresh concrete resistivity measurements to improve the quality of delivered concrete. Finally, this chapter discusses the main objectives and organization of the thesis

Chapter 2 investigates new field measurement techniques for determining the bulk and pore solution resistivity of concrete in the field. It also discusses a new procedure to calculate the original resistivity of a diluted pore solution sample, and statistically compares the mixing time of concrete and when the best time to take resistivity measurements of fresh concrete may be.

Chapter 3 discusses the two potential impacts that an aggregate may have on a fresh concrete pore solution. The chapter contains tests of 16 aggregates, comparing their impacts on both the resistivity and the ion concentrations of mortar pore solutions. A test method is proposed to test aggregates, and a mathematical relationship is discussed that can relate the results of the test method to mortars in order to estimate the impact that ion adsorption may have on mortars and concretes.

Chapter 4 presents the main findings of the thesis and states the general conclusions of the study. Suggestions on the future of fresh concrete pore solution research is also discussed.

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## 2 PRACTICAL ELECTRICAL RESISTIVITY MEASUREMENT OF PORE SOLUTION IN FRESH CEMENTITIOUS MIXTURES

### **Abstract**

This study compares techniques to extract pore solution from fresh mixtures to measure the resistivity of the extracted solution. The centrifuge approach for extracting pore solution and conductivity probe for determining pore solution resistivity are practical and have the potential to be used in the field. Pore solution extraction can be done between 30 and 90 minutes after mixing without a statistically significant difference in the measured resistivity. A practical method is proposed to determine the pore solution resistivity from the diluted cement paste samples when the extracted pore solution quantity is not adequate for accurate measurements with a conductivity probe.

### **2.1 Introduction**

Over ten billion tons of concrete are produced worldwide each year (1). In the US alone approximately 75,000 ready mixed concrete trucks are used to deliver around 371 million cubic yards of concrete (2). The concrete mixtures that are delivered at the construction site are often checked for their slump, unit weight, air content, and temperature, as part of a contractual process defined by ASTM C94 (3). These measures are often used to demonstrate that the mixture delivered is consistent with the concrete that was purchased.

Compressive strength and water-to-cementitious material ratio (w/cm) are often used as surrogate indicators of a concrete's durability to various exposure states (corrosion, freeze-thaw damage, salt attack) as demonstrated by ACI 318 (4). While this is common in construction, the use of strength and w/cm may be insufficient in many cases to address durability issues. This is becoming increasingly challenging as mixture proportions are being altered to address concerns for economy, sustainability, and new material constituents. Simply stated, rules of thumb that have worked in the past that relate compressive strength and durability may need to be reconsidered with

more complicated mixture designs and materials. As such, the QC/QA protocols that have been used in the past may need to be updated to account for concrete durability and performance. AASHTO took a major step in this direction by developing a model specification, AASHTO R101 (5) and has the CEB-FIP model code (6). Both of these approaches identify transport processes of concrete as critical factors.

It should be noted that the compressive strength of hardened concrete is measured after a specific period of time like 7 or 28 days, which is not helpful to make quick decisions on the acceptance of delivered concrete at the site. Measuring factors such as w/cm on site as part of QC/QA protocols could be useful. Approaches such as the AASHTO T318-15 microwave oven drying method (7) and the Phoenix method (8) utilize evaporation techniques to determine the w/cm of fresh concretes. Additionally, fresh concrete resistivity properties to determine w/cm have been explored by several authors (9-12). However, no standard methods exist to determine w/cm of fresh concrete using electrical properties.

Another durability indicator that is typically measured on hardened concrete and has become a part of specifications such as AASHTO R101 (previously noted as PP 84) (13), the Standard Practice for Developing Performance Engineered Concrete Pavement Mixtures, is the formation factor (F) of concrete. For example, AASHTO R101 specifies minimum formation factor for mature concrete for limiting transport in concrete such as chloride ingress. Similar approaches were proposed for the use of concrete resistivity; however, one limitation of using resistivity is it can be heavily influenced by the chemistry of the fluid in the pores (14). To overcome this, F can be used to eliminate the pore solution effects as it can be determined from the bulk resistivity ( $\rho_b$ ) and pore solution resistivity ( $\rho_o$ ) (15-20) as shown in Equation 2.1.

$$F = \frac{\rho_b}{\rho_o} \cong \frac{1}{\varphi\beta} \quad (2.1)$$

F is inversely related to the product of porosity ( $\varphi$ ) and pore connectivity factor ( $\beta$ ); therefore, it is a highly useful durability indicator for concrete. While the formation

factor has been used to assess transport properties such as water absorption (21), permeability (22), or chloride ingress (23,24) of hardened concrete it may also have value for fresh concrete.

Recently, several studies (25,26) have focused on determining formation factor of fresh cement pastes and its properties. Sallehi et al. (26) calculated the formation factor of a variety of cementitious pastes containing OPC and supplementary cementitious materials (SCM) such as fly ash, silica fume, and slag. They found the formation factor of fresh cement pastes is correlated to the porosity, tortuosity, and w/cm of cement pastes (14). It was shown that for a given paste mixture, formation factor decreases with increase in porosity or w/cm. Sant et al. (27) evaluated the variations in the electrical response of fresh systems. Castro et al. (28,29) examined the early age electrical measurements in fresh concrete as a potential QC/QA tool by testing the ability of the tool to determine water added or admixture variations. A pore solution sensor was developed and evaluated by Rajabipour et al (30). Castro et al. (28) noticed specifically that the conductivity was able to pick up both changes in the paste volume and the pore solution.

Practical methods exist to measure bulk resistivity of fresh cementitious systems (12,31-36); however, no standardized methods exist to measure the properties of the pore solution in fresh cementitious materials. The National Institute of Science and Technology's (NIST) calculator (37) that uses mixture proportions and oxide compositions to calculate pore solution resistivity provides a good starting point, however, it may not be accurate for fresh cementitious systems as it does not consider sulfate ion concentrations to calculate pore solution conductivity and assumes 75% of alkalis dissolve into pore solution at early ages (37). Rajabipour et al. (30) developed pore solution sensors; however, these have a time lag which is not a concern at later ages though it may be an issue in measuring fresh concrete. Further, these sensors have yet to be mass produced. Thermodynamic modeling is another tool that has been successfully used for long-term properties; however, these models struggle to provide strong predictions for fresh mixtures as they are based on long term equilibrium

calculations and early ages are dominated by kinetic effects and dissolution properties (38-49). Direct measurement methods that use chemical composition to calculate resistivity such as ion chromatography (50), titration (51), or inductively coupled plasma spectroscopy (ICP) (52,53) take significant time and require multiple samples, making them expensive and impractical for field applications. Pore solution resistivity has been able to be calculated using chemical composition obtained using X-ray fluorescence (XRF) with an error of 3.75% (54,55). This however, requires the solution to be extracted and tested in a laboratory environment. As such, a need exists for a practical method to extract pore solution from fresh cementitious systems. Further, a need exists to rapidly determine the resistivity of this pore solution.

This paper investigates procedures to extract pore solution and to measure pore solution resistivity for use in the field. In addition, this study includes determination of the effect of time from mixing on the pore solution resistivity. This paper also investigates a practical method to determine the pore solution conductivity/resistivity from the diluted cement paste sample when the extracted pore solution quantity is not adequate to make accurate measurements.

### **Research Significance**

Obtaining the pore solution of a delivered concrete could have QC/QA benefits. For example, it may be used to assess if an admixture has been added or as a step determining the w/cm of the delivered concrete. This paper outlines a technique to obtain pore solution and to measure its electrical resistivity in the field. This approach is compared with the existing methods. This paper also discusses predicting the pore solution resistivity from diluted cementitious pastes in cases when limited solution can be extracted. This may provide a method for eventual use as a part of a QC/QA program.

## **2.2 *Materials and Methods***

### 2.2.1 Materials

An ASTM C150 Type I ordinary portland cement (OPC) was used in this study (56). The specific gravity of this cement was 3.15, and the Blaine fineness was 420 m<sup>2</sup>/kg. The water used in all mixtures was ASTM D1193 Type II deionized (DI) water. Table 2.1 lists chemical composition of the OPC used in this study.

*Table 2.1 - Chemical composition of OPC.*

Cement Oxides and LOI	OPC
	Percent by mass (%)
Silicon Dioxide (SiO <sub>2</sub> )	19.9
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	4.6
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.2
Calcium Oxide (CaO)	62.0
Magnesium Oxide (MgO)	3.8
Sulfur Trioxide (SO <sub>3</sub> )	2.8
Alkalis (Na <sub>2</sub> O+0.658*K <sub>2</sub> O)	0.57
Loss on Ignition (LOI)	1.6
Bogue phase composition	Percent by mass (%)
Tricalcium Silicate (C <sub>3</sub> S)	57.0
Dicalcium Silicate (C <sub>2</sub> S)	14.0
Tricalcium Aluminate (C <sub>3</sub> A)	7.0
Tetracalcium Aluminoferrite (C <sub>4</sub> AF)	10.0

This study examines cement pastes prepared at three different w/cm (0.35, 0.45, and 0.55). The cement pastes were mixed in a Renfert Inc. 1000 mL tabletop vacuum mixer for a total of three minutes at 400 RPM and 70% vacuum to minimize entrapped air, and they were agitated by mixing them for 90 seconds every 15 minutes until the testing time.

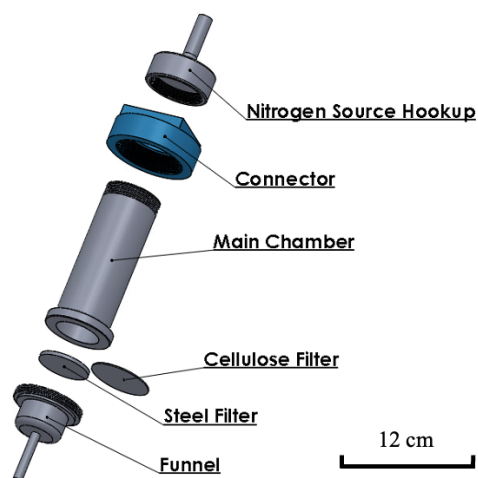
### 2.2.2 Pore Solution Extraction Methods

The two most prevalent techniques to extract fresh paste pore solution used previously are the nitrogen pressure extraction device and the vacuum pump (54,57). Both utilize applied pressure and a filter to extract the pore solution from a fresh cement paste. The reference method used in this study was nitrogen pressure extractor, as it is the easier



of the two methods which also minimizes carbonation (54). The method introduced in this study to obtain pore solution was centrifuge extraction and the solution obtained with this approach is compared with the nitrogen pressure extraction method.

*Nitrogen Pressure Extraction* - Figure 2.1 provides a labeled diagram of the nitrogen pressure extraction apparatus used in this study. It consists of several parts including a main chamber that holds the cement paste, steel filter and 0.45-micron cellulose filter to filter any solids, funnel that collects the extracted pore solution to transfer to a vial, and a part to attach the nitrogen gas cylinder to the main chamber using a connector. To extract the pore solution, the cement paste is placed in the main chamber which is pressurized with nitrogen at 200 kPa. This pressure causes the solution to be separated from the paste and it passes through the filter and is collected below the funnel.



*Figure 2.1 - Illustration of nitrogen pressure extraction apparatus (assembly diagram).*

The nitrogen pressure method of extraction takes approximately five minutes to obtain a sufficient amount of pore solution, which is around 8 mL. Between each measurement, the apparatus must be taken apart, cleaned, rinsed with DI water, dried, and a new filter must be inserted. It is only capable of testing one sample at a time. It also requires a nitrogen gas source, which makes it more cumbersome for field

applications. To avoid these concerns, an alternative method - centrifuge extraction of pore solution is studied.

*Centrifuge Extraction* - In this method, a centrifuge spins the samples at high-speed creating an acceleration that separates particles from the liquid phase according to their densities. A centrifuge can separate the pore solution from cement paste because cement particles are denser than the pore solution, causing them to separate due to centrifugal force. The benefits of using a centrifuge are portability, ease of use, and the number of samples it can run. The process requires very little space, low effort, needs only electrical power to operate and requires no cleaning is required between the uses as the tubes are self-contained and disposable.

In this work, centrifuge tubes (50 mL capacity) are filled with cement pastes, and five minutes later, four pore solutions are extracted from the cementitious materials. The pore solution is then decanted into another vessel for storage or immediate testing. The 50 mL centrifuge tubes are disposed of after decanting the pore solution. The apparatus used in this study can centrifuge four samples simultaneously, with potential to have additional samples tested in larger setups, allowing for testing to be performed much faster. The centrifuge method also yields more pore solution from a single cycle. An image of the centrifuge used in this study is pictured in Figure 2.2a, along with an image of the separated pore solution in Figure 2.2b.

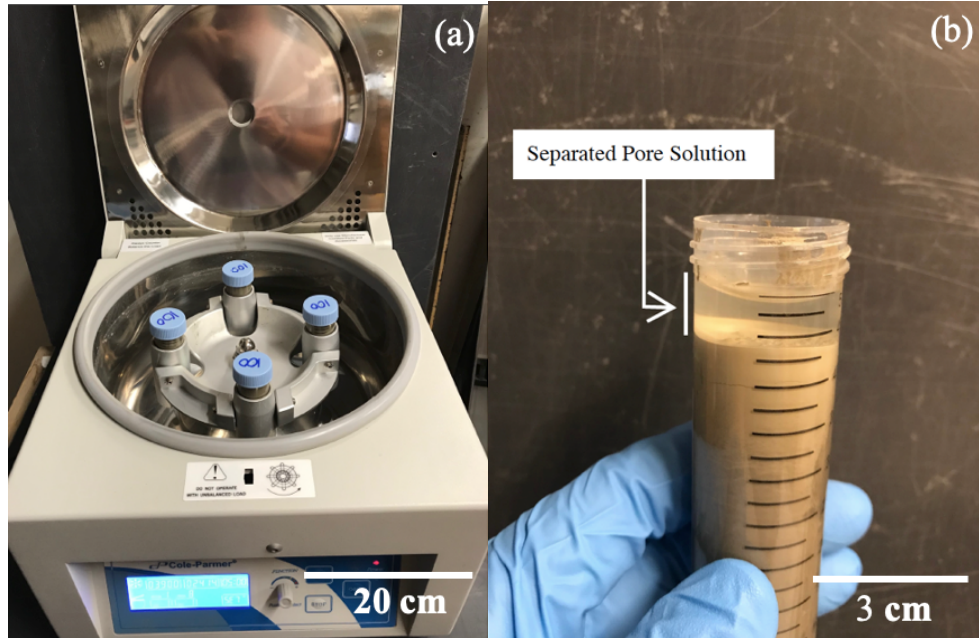
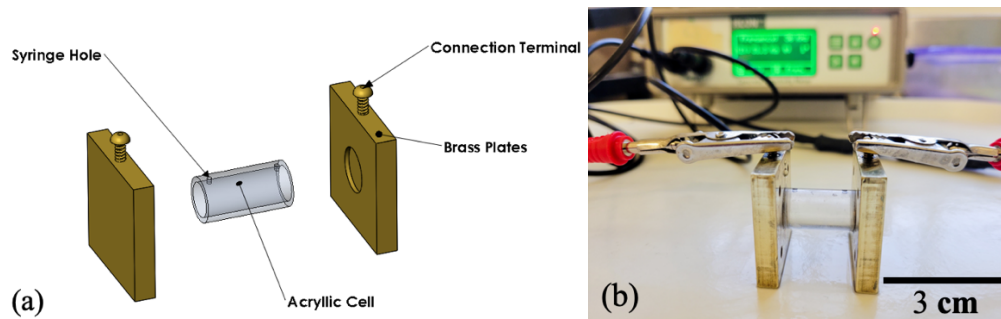


Figure 2.2 - (a) Picture of the centrifuge with 50 mL centrifuge tubes. (b) Image of specimen after cycled in centrifuge.

### 2.2.3 Pore Solution Resistivity Measurement Methods

Two pore solution resistivity measurement methods were considered in this study. The two methods include the resistivity cell (54,58-61) and conductivity probe (62,63). Measurement using a resistivity cell was used as a reference to compare and investigate the measurement using a conductivity probe.

*Cell Resistivity Measurement* - Electrical measurements of pore solution were taken by using a Giatec RCON concrete resistivity meter and running a current through a cell of known dimensions filled with the pore solution (58,64). Figure 2.3a and 2.3b show the details of the resistivity cell and brass plates.



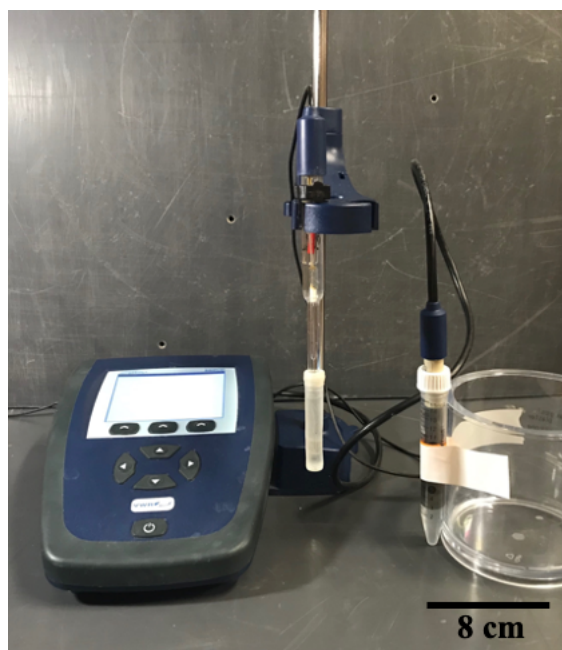
*Figure 2.3 - (a) Resistivity cell with conductive metal plates at both ends for circuit connections. (b) Assembled cell with resistivity meter.*

To perform a measurement, the acrylic cell is inserted into the indentation on either side of the brass plates. Pore solution is then injected with the syringe through the holes on the top of the acrylic cell. Alligator clips are attached to the connection points for the resistivity meter, and the impedance in ohms is recorded. Resistivity is then calculated by multiplying the impedance by the cosine of the phase angle and the geometry factor for the acrylic cell. For this resistivity cell, the geometry factor was found to be 2.76 mm, which was calculated by dividing the cross-sectional area of the cell (69.84 mm<sup>2</sup>) by the length of the cell (25.35 mm). To correct the measurement to standard temperature 23°C, the Arrhenius equation (Equation 2.2) was used with an activation energy of 13.9 kJ/mol (65-67).

$$\rho_0 = \rho_T e^{\left[\frac{-E_{a,\rho}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]} \quad (2.2)$$

$\rho_T$  is the resistivity measured at temperature T (K),  $\rho_0$  is the reference temperature (298.15 K),  $E_{a,\rho}$  is the activation energy for resistivity (kJ/mol), and R is the gas constant (kJ). This cell method is preferred for measuring pore solution properties of cured concrete as it requires less than 2 mL of pore solution. Many times, only around 2 mL of fluid can be extracted from fully hydrated concrete samples (58-61). There are several steps that must be taken with this method of electrical measurement to ensure accuracy. Cross-contamination between pore solution samples, oxidation of the brass plates, and air trapped in the acrylic cell must be minimized for an accurate measurement. The plates, syringe, and cell were rinsed with DI water between uses to prevent cross-contamination of pore solution samples. Wires need to be securely fastened, and connection points are cleaned to ensure proper current flow. The brass plates need to be cleaned and polished with a scouring product to remove the oxidized surface and rubbed with isopropyl alcohol to remove any chemical residue.

*Probe Resistivity Measurement* - An alternative to the cell method of measuring resistivity utilizes a commercial conductivity probe. The probe chosen for this study is a 3-pole platinum VWR conductivity electrode for a symphony series benchtop meter. The meter used in this study is a B40PCID symphony meter. The experimental setup can be seen in Figure 2.4.



*Figure 2.4 - B40PCID symphony benchtop meter with a pH probe (left) and resistivity probe testing a specimen (right).*

Probes can also contain a temperature sensor like the one used in this study to adjust the reading to room temperature (23°C). The conductivity probe was calibrated with a standard solution of 25 mS/cm before testing the pore solution samples. Measured conductivities of the solutions were later converted to resistivities. Conductivity probes are not commonly used to measure concrete pore solution as they require more than 2 mL of pore solution. However, sufficient pore solution can be extracted from fresh concretes and pastes as they are mostly unhydrated at an early age. Therefore, for early age studies, a conductivity probe is more desirable for its faster measurement times. A single reading took a minute to obtain, which was significantly faster than the cell resistivity method.

#### 2.2.4 Investigation of the Effect of Time from Initial Mixing on Pore Solution Resistivity

To analyze the possible effect of time from mixing on fresh pore solution resistivity, 0.35, 0.45, and 0.55 w/cm paste mixtures were prepared and measured their pore solution resistivities after 30, 60, and 90 minutes from initial mixing. Each mixture was agitated by mixing them every 15 minutes for 90 seconds prior to extraction and measurement of pore solution resistivity. The centrifuge method of extraction and probe method of resistivity measurement were used for all the samples.

#### 2.2.5 Prediction of Original Pore Solution Resistivity from Diluted Cement Paste

One of the possible challenges for the resistivity measurement of fresh cement paste pore solution (or concrete) is obtaining an adequate amount of pore solution from fresh mixtures. For these cases, a method is proposed that can be used to back-calculate the original pore solution resistivity (or conductivity) by measuring the conductivities of the extracted pore solutions of diluted fresh cement pastes (i.e., serial dilution). As additional water is added to dilute the fresh cement paste, more pore solution is yielded upon extraction by a centrifuge. Diluted fresh cement paste pore solution conductivity can be related to the original pore solution conductivity using the relationship between ion concentrations and solution conductivity that was discussed by Snyder et al. (68).

For diluting the fresh cement pastes, 60 g of fresh cement paste was measured into two different 50 mL centrifuge tubes. Different quantities of DI water were added to the centrifuge tubes to create different dilutions. Dilutions were calculated in terms of added water and were quantified using the dilution percentage shown in Equation 2.3. Seven different dilution points were tested for each paste sample, and all combinations of two points were examined to find the best selection of dilution points to predict the original pore solution conductivity with the least error. The procedure to choose the two dilution points measurements for the prediction of pore solution conductivity is further discussed in the results section.

$$D_P = \left[ \frac{V_{os} + V_{Aw}}{V_{os}} \right] 100 \quad (2.2)$$

where  $D_P$  is the dilution percentage,  $V_{os}$  represents the volume of original pore solution in the sample and  $V_{Aw}$  represents the volume of added water to the system for the dilution.

The centrifuge tubes with the added water and the cement paste were shaken for 60 seconds to sufficiently combine the added water with the paste, and they were run through the centrifuge to extract the pore solutions. The conductivity of each sample was then measured using the conductivity probe. The conductivity of an undiluted sample for each trial was also measured to act as a control for the experiment, which allowed to calculate percent error (difference between the measured and predicted pore solution conductivities). Using these measurements along with solution conductivity-ion concentration relationships from Snyder et al. (68), a relationship was found to theoretically predict the original pore solution conductivity. This relationship is represented as shown by Equation 2.4.

$$\sigma_{calc} = \sum_i C_i z_i \lambda_i \quad (2.3)$$

where  $C_i$  represents the molar concentration of each ion  $i$ ,  $z_i$  the valence number of each ion  $i$ , and  $\lambda_i$  the equivalent conductivity of each ion  $i$ . The equivalent conductivity of an ionic species can be calculated in a number of ways, but can be simplified by a single parameter model that is accurate to within 10% for pore solutions, as shown in Equation 2.5 (68).

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i I_M^{1/2}} \quad (2.4)$$

where  $\lambda_i^\circ$  is the equivalent conductivity of an ionic species at infinite dilution and  $G_i$  is conductivity coefficient. The values of these coefficients can be found in literature (69). The value  $I_M$  is the ionic strength on a molar basis and is described by Equation 2.6 (68).

$$I_M = \frac{1}{2} \sum_i z_i^2 C_i \quad (2.5)$$

Equations 2.4-2.6 can be combined to create an equation that relates the conductivities of the two pore solutions as a function of ion concentration. While the original ion concentrations are unknown, multiple data points allow these unknowns to be solved for with a system of equations. To create a function of pore solution conductivity in terms of concentration of pore solutions for diluted cement pastes, a new term for ion concentration was required in terms of the volume of added water for dilution. For each quantity of added water, it would quantify its change to the original concentration  $C_i$ . The following relationship was developed for determining an ion concentration at the dilution point:

$$C_{i.dilution} = \frac{C_i}{1 + \frac{V_{AW}}{V_{OS}}} \quad (2.6)$$

Pore solution of fresh cement paste (in the 30-90 minutes from initial mixing window) primarily consists of sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), hydroxide ( $\text{OH}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) ions (52). Because little to no hydration is expected to take place, calcium ( $\text{Ca}^{2+}$ ) concentration was assumed as insignificant at this early of an age. These ion concentrations were included in the function to solve for the original (undiluted cement paste sample) pore solution conductivity. The resulting function using Equations 2.4-2.7 is shown below in simplified form as Equation 2.8.

$$\sigma_{dilution(x)} = \sum_i \left[ \frac{C_i z_i}{1 + \frac{V_{AW}}{V_{OS}}} \right] \left[ \frac{\lambda_i^\circ}{1 + G_i \sqrt{\frac{1}{2} * \frac{C_K + C_{Na} + C_{OH} + 4C_{SO4}}{1 + \frac{V_{AW}}{V_{OS}}}}} \right] \quad (2.7)$$

To solve Equation 2.8, five unknown constants ( $C_K$ ,  $C_{Na}$ ,  $C_{OH}$ ,  $C_{SO4}$ ,  $V_{OS}$ ) must be determined. While these constants can be found by fitting the function to the five dilution points, the process can be simplified by reducing the number of unknown constants. For example,  $C_{OH}$  can be estimated using pH, which was measured for one



of the two pore solutions from the diluted samples, and the volume of added water of that pH measurement was noted for  $C_{OH}$  measurements that would be required. The activity of  $OH^-$  was then used to estimate the  $C_{OH}$  in the pore solution. In this work, the activity coefficient for  $OH^-$  was assumed as 0.7 based on the literature (70,71), but this assumption can be revised with additional information about the mixtures.  $C_{SO_4}$  was approximated using an equation developed by Taylor et al. (72) as shown in Equation 2.9.

$$C_{SO_4} = (0.06 \frac{l}{mol})(C_{Na} + C_K)^2 \quad (2.8)$$

An assumption was made that the ratio of  $Na_2O$  to  $K_2O$  of OPC would be equal to  $C_{Na}/C_K$  in the pore solution. Table 2.2 shows average percent by mass quantities of  $Na_2O$  and  $K_2O$  for a variety of portland cements (73) and SCMs [74].

*Table 2.2 - Mean of typical  $Na_2O$  and  $K_2O$  composition in portland cements and SCMs (% by mass) (73).*

Cement/SCM Type	Statistic:	$Na_2O$	$K_2O$
Type I	Mean	0.18	0.67
	SD	0.08	0.34
Type II	Mean	0.17	0.57
	SD	0.07	0.22
Type III	Mean	0.16	0.60
	SD	0.07	0.22
Type V	Mean	0.15	0.47
	SD	0.06	0.13
Un-Densified Silica Fume	Mean	0.41	0.34
	SD	0.55	0.27
Densified Silica Fume	Mean	0.32	0.63
	SD	0.39	0.14
Class-F Fly Ash	Mean	1.88	1.34
	SD	2.17	0.78
Class-C Fly Ash	Mean	1.98	0.58
	SD	1.45	0.26
Slag	Mean	0.32	0.45

	SD	0.12	0.13
Calcinated Clays	Mean	0.81	0.85
	SD	2.02	1.82

For the Type II cement used in this study, a ratio of 0.3 was used to develop the following relationship between ion concentrations as shown in Equation 2.10.

$$C_{Na} = 0.3 * C_K \quad (2.9)$$

A MATLAB code was prepared to solve Equations 7-9 and relate the measured conductivities of the two solutions from the diluted samples and pH of one of the solutions of diluted samples to find the original pore solution conductivity. This function solves for two unknowns ( $C_{Na}$  and  $V_{os}$ ) to provide the conductivity of the pore solution of the undiluted sample. To quantify the accuracy of the predictions generated by the MATLAB code, the percent difference in predicted and measured conductivity ( $\Delta\sigma$  %) was calculated. This calculation is represented by Equation 2.11.

$$\Delta\sigma \% = \left[ \frac{\sigma_m - \sigma_p}{\sigma_m} \right] 100 \quad (2.10)$$

where  $\sigma_m$  is the measured conductivity of the undiluted pore solution sample, and  $\sigma_p$  represents the predicted pore solution conductivity based on the fitted function to the points.

## 2.3 Results and Discussion

### 2.3.1 Extraction Methods Analysis

Table 2.3 shows the measured resistivity values of pore solution extracted using both the nitrogen pressure and centrifuge extraction methods. Statistical analysis was done using a t-test of two means to compare the extraction methods at each w/cm. Table 2.3 also shows the results of the analysis.

*Table 2.3 - T-test statistical comparison of differences in resistivity measurement means due to different pore solution extraction methods.*

w/cm	Extraction Method	Resistivity (ohm-m)	Standard Deviation (ohm-m)	Coefficient of Variation	P-Value
0.35	Nitrogen	0.222	0.004	0.019	0.241
	Centrifuge	0.225	0.003	0.015	
0.45	Nitrogen	0.258	0.004	0.017	0.145
	Centrifuge	0.262	0.002	0.006	
0.55	Nitrogen	0.294	0.002	0.008	0.372
	Centrifuge	0.295	0.001	0.003	

The calculated p-values across all three w/cm tests were greater than 0.05, implying that no statistically significant difference exists between the extraction test methods. The centrifuge method samples were easier to prepare, and disposable centrifuge tubes eliminated cleanup. It also yielded 3 mL more pore solution in 0.35 w/cm samples compared to the nitrogen pressure method. The centrifuge method provides flexibility to choose sample sizes. Additionally, four samples were extracted in 5 minutes using the centrifuge method, whereas only one sample was extracted using the nitrogen pressure method in 5 minutes. For these reasons, the centrifuge extraction method was found to be a more practical method for extracting pore solution from fresh cement pastes compared to the nitrogen pressure extraction method.

### 2.3.2 Resistivity Methods Analysis

Table 2.4 shows resistivity measurements made using both the resistivity cell and conductivity probe methods. The centrifuge method of extraction was used for this comparison for consistency in results. Statistical analysis was done using a t-test to compare the resistivity measurement methods. Table 2.4 also shows the results of the analysis.

*Table 2.4 - T-test statistical comparison of differences in resistivity measurement means using cell and probe methods.*

w/cm	Resistivity measurement method	Resistivity measurement (ohm-m)	Standard Deviation (ohm-m)	Coefficient of Variation	P-Value
0.35	Cell	0.265	0.002	0.008	0.059
	Probe	0.257	0.003	0.013	
0.45	Cell	0.300	0.010	0.033	0.233
	Probe	0.292	0.008	0.026	
0.55	Cell	0.350	0.010	0.027	1.023
	Probe	0.341	0.008	0.023	

Reported P-values of 0.059, 0.233, and 1.023 all indicated that there was no statistically significant difference between the mean resistivity measurements exists at a significance level of 0.05. The cell method of resistivity measurement was found to take around three minutes to make a single measurement, compared to around one minute for the probe to complete a resistivity measurement. Therefore, using the probe method for determining the resistivity of pore solution is recommended for making faster and accurate measurements.

### 2.3.3 The Effect of Time from Initial Mixing on Pore Solution Resistivity

Table 2.5 shows the pore solution resistivity measurements measured on 0.35, 0.45, and 0.55 w/cm cement pastes pore solutions at 30, 60, and 90 minutes after initial mixing. Analysis of variation (ANOVA) tests were performed to find if there was a statistically significant difference in the mean measured resistivities. The ANOVA results reported p-values greater than the significance interval of 0.05. Therefore, there is no statistically significant difference in pore solution resistivity at 30, 60, and 90 minutes after initial mixing. Similar observation was made in previous studies (11,26,27) where no noticeable difference in pore solution resistivity of fresh cement pastes was observed during the induction period of cement hydration.

*Table 2.5 - Statistical analysis of differences between resistivities of pore solutions extracted after 30, 60, and 90 minutes from initial mixing.*

w/cm	Time From Initial Mixing	Resistivity (ohm-m)	Standard Deviation (ohm-m)	Coefficient of Variation	P-Values (ANOVA results)
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(min.)					
0.35	30	0.206	0.0179	0.0869	0.604
	60	0.199	0.0127	0.0638	
	90	0.198	0.0124	0.0626	
0.45	30	0.253	0.0099	0.0391	0.621
	60	0.259	0.0014	0.0054	
	90	0.254	0.0028	0.0110	
0.55	30	0.289	0.0122	0.0422	0.606
	60	0.285	0.0041	0.0144	
	90	0.284	0.0032	0.0113	

This observation has practical implications. Ready-mix trucks typically arrive on site between 30 and 90 minutes after the mixture is first prepared at a batching plant. Because the statistical analysis shows the pore solution resistivity does not significantly change in this fresh state of concrete, testing can be simplified. All pore solution resistivity measurements taken within the 30 to 90-minute window from initial mixing will not require time adjustments.

#### 2.3.4 Prediction of Pore Solution Conductivity

Seven dilutions were tested in this study for each w/cm mixture. As the prepared MATLAB program uses resistivities of pore solutions of pastes at two dilutions to make a prediction of original pore solution resistivity, there were 21 combinations of two dilution points for the input to the function. To determine the best two dilution points in terms of predicting original pore solution conductivity accurately, all 21 combinations were tested. Table 2.6 shows the percent difference in predicted and measured conductivities of the samples with 0.35, 0.45, and 0.55 w/cm of the three best dilution combinations of all 21 combinations.

*Table 2.6 - Percent difference in predicted and original pore solution conductivity for 0.35, 0.45, and 0.55 w/cm samples when different combinations of two dilution points chosen.*

w/cm	Percent difference in predicted and original pore solution conductivity		
0.35	1.31*	-0.26**	3.52†

0.45	-1.35*	-1.11**	-1.27†
0.55	0.62*	4.34**	1.59†

\*Conductivities of diluted solutions with an average  $D_p$  of 120% and 144% were used for the prediction of the original pore solution conductivity

\*\*Conductivities of diluted solutions with an average  $D_p$  of 144% and 176% were used for the prediction of the original pore solution conductivity

†Conductivities of diluted solutions with an average  $D_p$  of 120% and 176% were used for the prediction of the original pore solution conductivity

The two dilution points that predicted the original pore solution conductivities most accurately were 120% and 144%. This is probably because these dilution levels were the most concentrated among the tested dilutions. However, if 120% dilution point is unattainable due to water content of the sample, 144% and 176% dilutions could also be used as the predictions did not change significantly (difference in average predicted and original pore solution conductivity was 0.8%).

Figure 2.5 shows the graphical output for each w/cm. The figure demonstrates using an average of 144% and 176% dilutions to back calculate for the original pore solution conductivity. Percent dilutions differ slightly for each w/cm, as each mixture has a different original water content.

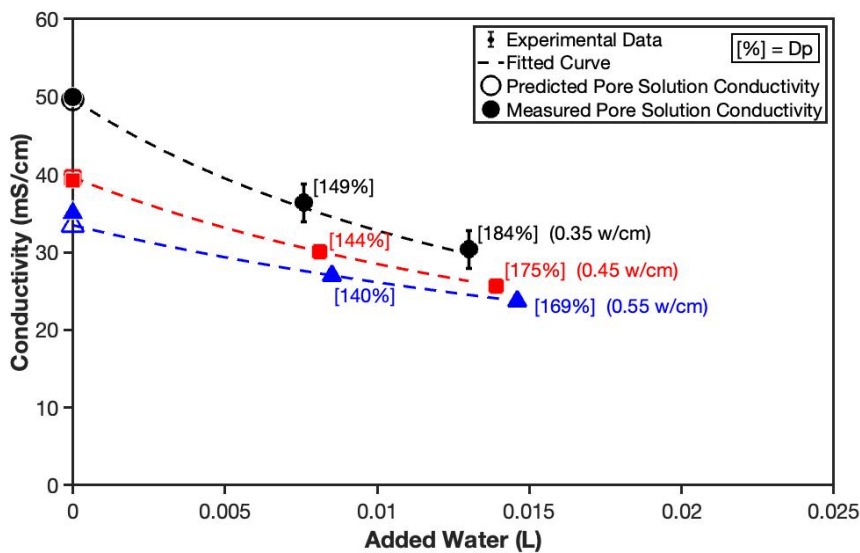


Figure 2.5 - Predicted conductivity from two diluted cement paste pore solution samples, unknowns:  $C_{Na}$ ,  $Vos$ . For 0.35 w/cm, difference in predicted and measured conductivities = -0.26%; For 0.45 w/cm, difference in predicted and measured

*conductivities = -1.1%; For 0.55 w/cm, difference in predicted and measured  
conductivities = 4.3%.*

For 0.35, 0.45, and 0.55 w/cm pastes, the predicted pore solution conductivity values were 50.13, 39.62, and 33.47 mS/cm, respectively. These predicted pore solution conductivity values translate to 0.199 ohm-m for 0.35 w/cm mixture, 0.252 ohm-m for 0.45 w/cm mixture, and 0.299 ohm-m for the 0.55 w/cm mixture. The measured values for 0.35, 0.45, and 0.55 w/cm pastes were 50.00, 39.18, and 34.99 mS/cm, respectively. The percent difference in the predicted and measured conductivity for 0.35 w/cm was -0.26%. For 0.45 and 0.55 w/cm samples, the percent difference in the predicted and measured conductivities were -1.11% and 4.34%, respectively. The higher error observed for 0.55 w/cm sample could be due to an overall higher dilution of the system due to the high water content of the cement paste. This method of resistivity determination has an error less than or similar to average error of 3.75% reported by resistivity calculation from ion concentrations determined using XRF (55). Also, the proposed approach is practical, more direct, and less expensive to use when compared to the resistivity calculated using the XRF method.

If the an assumption is made for the the ratio of  $\text{Na}_2\text{O}$  to  $\text{K}_2\text{O}$  of OPC such that it is equal to the ratio of  $C_K$  and  $C_{\text{Na}}$  of the pore solution cannot be made, both constants ( $C_K$ ,  $C_{\text{Na}}$ ) can be left as unknowns. The same function can be used to solve for the original pore solution conductivity. Figure 2.6 is the output for the MATLAB function with three unknowns ( $C_K$ ,  $C_{\text{Na}}$ ,  $V_{\text{OS}}$ ). This time, three dilution points were used as there are three unknown constants.

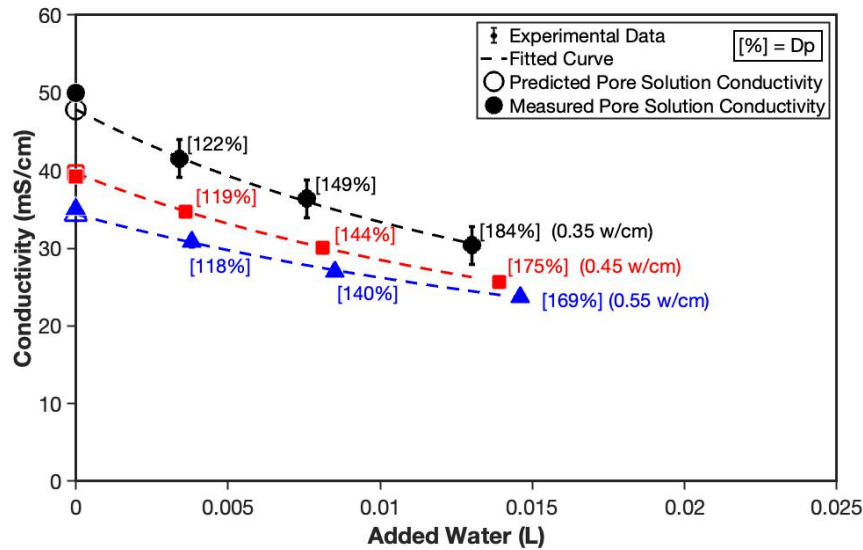


Figure 2.6 - Predicted conductivity from three diluted 0.35 w/cm cement paste pore solution samples, unknowns:  $C_K$ ,  $C_{Na}$ ,  $V_{OS}$ . For 0.35 w/cm, difference in predicted and measured conductivities = 4.3%; For 0.45 w/cm, difference in predicted and measured conductivities = -1.3%; For 0.55 w/cm, difference in predicted and measured conductivities = 1.7%.

Predicting pore solution conductivity using only one dilution was also explored. In order to do this, another assumption was made in addition to the previous assumptions to make number of unknowns equal to one.  $V_{OS}$  was assumed to be same as the amount of water added during the mixing process but calculated for the volume of the sample used. Therefore, the function only solves for one unknown -  $C_{Na}$ . Figure 2.7 shows the predicted and measured conductivities of the original solution and also the measured conductivities of the diluted solution of all three mixtures. It was observed that the percent difference in measured and predicted conductivities using single dilution approach ranges from 5-9%, which was higher when compared to the approach using two or three dilutions.



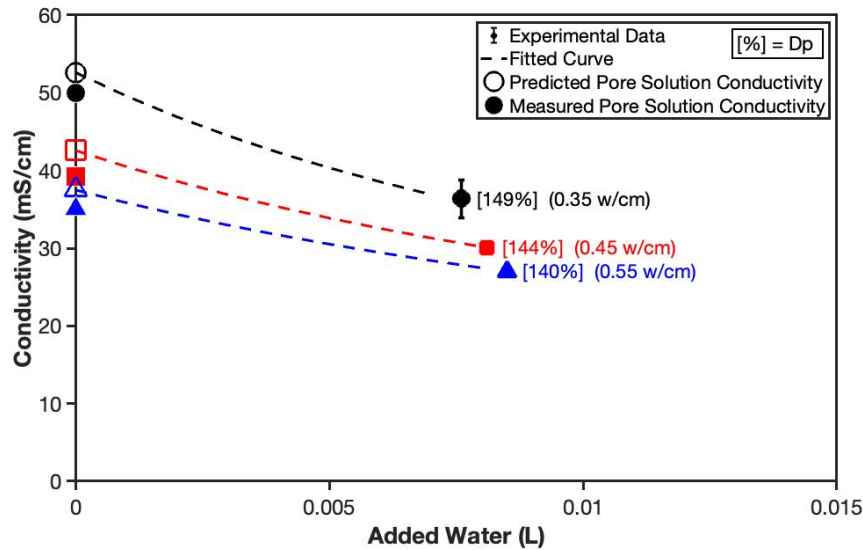


Figure 2.7 - Predicted conductivity from one diluted cement paste pore solution sample, unknown:  $C_{Na}$ . For 0.35 w/cm, difference in predicted and measured conductivities = -5.2%; For 0.45 w/cm, difference in predicted and measured conductivities = -8.7%; For 0.55 w/cm, difference in predicted and measured conductivities = -7.1%.

While this study used a constant 60 g of cement paste with added water for dilutions between 10-25 g, this can be upscaled for larger quantities for application to concrete or mortar. In the event of an insufficient amount of pore solution extraction to accurately measure conductivity using a probe, the proposed dilution approach allows the user to predict the original pore solution conductivity using the equations relating the ion concentrations and solution conductivity. It was observed that the proposed serial dilution method predicts the pore solution conductivity within 5% of the measured conductivity value.

#### 2.4 Conclusions

This paper discussed a method for extracting fresh cement paste pore solution and determining its resistivity. The proposed method was compared using statistical methods to both existing methods for extraction and pore solution resistivity/conductivity measurements. This paper also discussed the effect of time from initial mixing on the pore solution resistivity, and finally proposed a method of

predicting pore solution conductivity by the dilution of cement paste that can be used in the event of less amount of pore solution extraction. The conclusions that were drawn from the study are summarized below.

There was no statistically significant difference in the pore solution resistivities when a centrifuge is used for extraction as compared to nitrogen pressure extraction. The centrifuge method can perform multiple tests at a time rather than one, is easier to operate, and is more portable than the nitrogen pressure extractor. This approach has the potential to be scaled to mortar or concrete with a larger centrifuge.

ANOVA analysis showed statistically similar results between pore solution resistivity measured using a resistivity cell and conductivity probe. The probe method of measuring resistivity was found to be faster and more user friendly (especially for field application) compared to the cell method of measurement.

Statistical analysis of the measured pore solution resistivity showed that time from initial mixture of 30, 60, and 90 minutes were statistically similar; suggesting that the pore solution resistivity measurements can be done at any time between 30-90 minutes from mixing. This makes the measurements in the field more practical, as it allows pore solution resistivity tests to be calculated without factoring in corrections for the time from initial mixing.

This study also demonstrated that in the event of too little pore solution extracted for a pore solution resistivity measurement, a dilution procedure can be used to find the original pore solution resistivity. By preparing two dilutions of the fresh cement paste samples, measuring their pore solution conductivities, and using the ion concentration-solution conductivity relationship discussed by Snyder et al [68], the pore solution conductivity of the undiluted sample can be predicted within 5% of the measured pore solution conductivities.

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### 3 THE INFLUENCE OF AGGREGATE ON THE ELECTRICAL RESISTIVITY OF CONCRETE PORE SOLUTION IN FRESH MIXTURES

#### **Abstract**

This study examines the influence of fine aggregates on pore solution chemistry and electrical resistivity. Specifically, this paper considers the potential adsorption of chemical species on the aggregate surface. It was shown that fine aggregates can adsorb  $\text{Na}^+$  and  $\text{K}^+$  ions on their surface, which can change the ionic concentration balance of the pore solution and increase its resistivity, beyond the effect of dilution induced by aggregate pore volume and moisture.  $\text{K}^+$  adsorption was higher than  $\text{Na}^+$  adsorption by 128% on average. For 16 different aggregates obtained from various locations in the United States, the electrical resistivity of pore solution increased in a range from 4% to 145% in a mortar with an original pore solution resistivity of 25 ohm.cm. It is hypothesized that aggregate mineralogy and surface area were key factors affecting this variance. A methodology is proposed to identify the problematic aggregates and correct for the resistivity of pore solution.

#### **3.1 Introduction**

Electrical resistivity is a measurement of a material's ability to resist the flow of electrical current. In hardened concrete, resistivity is often used as an indicator for its ionic and moisture transport properties (1,2). As concrete durability is dependent upon transport of ions and moisture, resistivity can be correlated to durability using modeling concepts, as in the case of corrosion (3-8), freeze-thaw damage (9-13), alkali-silica reaction (14,15). Standards such as ASTM C1760 (16), AASHTO TP119 (17) and AASHTO T 358 (18) have made the electrical resistivity of concrete a highly useful tool for industry. Formation factor (F), which is another electrical property, can provide additional benefits over electrical resistivity with respect to prediction of transport properties such as water absorption (19-21), chloride ingress (22-27), or permeability (28) of hardened concrete. Formation factor is determined from the ratio of bulk (concrete, mortar or paste) resistivity ( $\rho_b$ ) and pore solution resistivity ( $\rho_{ps}$ ), and is also

inversely related to the product of porosity ( $\varphi$ ) and pore connectivity factor ( $\beta$ ) such that:

$$F = \frac{\rho_b}{\rho_{ps}} = \frac{1}{\varphi\beta} \quad (3.1)$$

Specifications such as AASHTO R 101 (previously known as PP 84 (29)) specifies minimum formation factor (electrical resistivity) for hardened concrete to limit chloride ingress in concrete.

While the electrical resistivity and formation factor of hardened concrete have been used to assess its transport properties, in recent years, a number of studies (13,30-33) have also examined the use of electrical properties of fresh concrete as a potential quality assurance and quality control (QA/QC) tool. For example, the resistivity of fresh paste has been studied as a potential indicator of water-to-cementitious material ratio (w/cm) and supplementary cementitious material (SCM) content (31,33-35). Additionally, variations in electrical responses due to added water or admixture volumes have also been investigated in fresh mixtures (30,32,36). As a result, there are ongoing efforts to develop fast, effective, and practical field measurement techniques for the determination of the bulk and pore solution resistivity of fresh mixtures (37-44).

Most studies on the electrical properties of fresh mixtures are focused on paste because of its simplicity. In fresh concrete, the electrical resistivity is best described by using the modified parallel law (45):

$$\frac{1}{\rho_c} = \frac{1}{\rho_{ps}} \phi_{ps} \beta_{ps} + \frac{1}{\rho_{cm}} \phi_{cm} \beta_{cm} + \frac{1}{\rho_{agg}} \phi_{agg} \beta_{agg} + \frac{1}{\rho_{air}} \phi_{air} \beta_{air} \quad (3.2)$$

where  $\rho_c$  is the resistivity of the concrete,  $\rho_{(p)}$  is the resistivity,  $\phi_{(p)}$  is the volume fraction, and  $\beta_{(p)}$  is the connectivity parameter of each phase ( $p$ ). As shown in Equation 3.2, each phase of a concrete (i.e., pore solution, cementitious materials, aggregate, and air) impacts the electrical resistivity of the system based on their volume fraction. Phases other than pore solution have significantly high resistivity, orders of magnitude

larger than that of pore solution. For example, concrete aggregates typically have a resistance in the order of  $10^4$ - $10^8$  ohm.cm (46), and therefore, aggregates are typically assumed to be electrically insulating (37,46). Similarly, the vapor phase and cementitious binder have typical resistivities of  $10^{19}$  ohm.cm and  $10^7$  ohm.cm, respectively (47). Therefore, it can be assumed that the contribution of these phases to the resistivity of the system is minimal, and the pore solution is the main influence as shown in Equation 3.3.

$$\frac{\rho_{ps}}{\rho_{cm}} \approx \frac{\rho_{ps}}{\rho_{agg}} \approx \frac{\rho_{ps}}{\rho_{air}} \approx 0 \quad (3.3)$$

Due to the high resistivity of the other phases of a fresh concrete, studies often simplify the system and study just the pore solution of cement paste (Equation 3.4).

$$\frac{1}{\rho_c} = \frac{1}{\rho_{ps}} \phi_{ps} \beta_{ps} \quad (3.4)$$

This is the main reason behind why many studies choose pastes over mortar or concrete for investigating the electrical properties of fresh mixtures. This assumption, however, ignores potential impacts that aggregates may have on a fresh concrete system. It is well established that aggregates may dilute the pore solution system due to their water content (48,49), and some evidence suggests they may also adsorb specific ionic species from the pore solution. Both processes can influence the pore solution resistivity, hence, cause erroneous measurements.

Castro et al. and Barrett et al. (48,49) showed that some aggregates with high porosity may influence the bulk resistivity of a concrete system. Spragg et al. illustrated this correction was smaller for more conventional aggregates (50). The assumption that all aggregates are inert and won't adsorb any ions from the surrounding pore solution may not be true. Some aggregates might gain surface charge depending upon the pH of the surrounding solution and the mineralogy of the aggregate and might adsorb ions from the pore solution (51).

In past studies, the influence of aggregates on the resistivity of concrete (based on the assumption of non-conductive aggregate) has been investigated, specifically for the interfacial transition zone (ITZ) due to its potential to increase the resistivity of mortar or concrete (46,52-54). Volume fractions of aggregate in concrete and its impact on resistivity have also been studied, and relationships have been found such as the effective medium model that describe the increase in bulk resistivity with increased aggregate content (55-58). The gradation of aggregates has not been found to significantly impact the resistivity of concrete systems (59). The previous studies (55-58) mainly focused on the effect of different aggregates and aggregate contents on bulk resistivity of hardened mortar or concrete. However, limited work (60) has been done on comparing paste and mortar or concrete pore solution in terms of their chemistry and resistivity and the role of aggregates in it, especially in fresh mortar or concrete systems. In addition, several previous studies did not account for the effect of dilution from the moisture content of aggregates on the pore solution chemistry and resistivity. Therefore, a need exists to determine the role of aggregates in comparing paste and mortar pore solutions composition and resistivity. This study investigates the effect of different fine aggregates on the pore solution resistivity of fresh mortars specifically relating to aggregate porosity and potential surface adsorption of ions from pore solutions. This study aims to propose a practical method to identify aggregates that alter fresh mortar pore solution resistivity. In addition, this study aims to propose resistivity correction equations to account for the dilution from the water absorption of aggregates and surface adsorption of ions

### **Research Significance**

The electrical properties of fresh concrete have been discussed for use in QA/QC methods for concrete delivered to construction sites. The current assumption is often that the aggregates are inert and do not impact the electrical resistivity of pore solution in concrete. This study shows that this not necessarily accurate and that aggregates can adsorb some of the ions in the pore solution to increase its resistivity considerably. A methodology is proposed to identify the problematic aggregates and correct for the ion

concentration of pore solution. The proposed approach will help improve the developed QA/QC protocols that are based on electrical properties of fresh concrete

### 3.2 Materials

Multiple (16) fine aggregates that meet ASTM C33 were studied (61). The fine aggregates tested in this study are summarized in Table 3.1.

*Table 3.1 – Summary of fine aggregates properties used in this study*

Origin of Fine Aggregate	Sample ID	Fineness Modulus (FM)	Absorption Capacity (%)	Specific Gravity (SSD)	Estimated Surface Area per m <sup>3</sup> Aggregate (x 10 <sup>6</sup> m <sup>2</sup> )
Western Oregon	A-1	2.96	3.6	2.59	4.84
Southern Oregon	A-2	2.78	3.8	2.57	4.83
Florida	A-3	2.76	0.6	2.64	4.35
Central California	A-4	3.31	1.1	2.65	3.67
Eastern California	A-5	3.51	0.8	2.55	4.77
Idaho	A-6	2.62	2.5	2.59	5.07
South Dakota	A-7	3.09	1.4	2.61	4.11
Minnesota	A-8	2.75	1.0	2.65	4.71
Indiana	A-9	2.41	1.3	2.66	6.90
Kansas	A-10	2.78	0.6	2.63	4.53
North Carolina	A-11	2.83	0.5	2.64	4.28
Louisiana (LWA)	LWA-1	4.50	26.8	1.64	1.46
Southern California (LWA)	LWA-2	4.12	19.1	1.66	2.43
Missouri (LWA)	LWA-3	3.21	24.9	1.87	6.93
New York (LWA)	LWA-4	3.68	25.2	1.73	4.24
Texas (LWA)	LWA-5	3.26	24.6	1.84	7.19

For the mortar experiments, an ASTM C150 Type I ordinary portland cement (OPC) was used in this study (62); Table 3.2 lists chemical composition of this OPC. The specific gravity of this cement was 3.15, and the Blaine fineness was 420 m<sup>2</sup>/kg. The water used in all mixtures was ASTM D1193 Type II deionized (DI) water.

*Table 3.2 - Chemical composition of OPC*

Cement Oxides and LOI	OPC
	Percent by mass (%)
Silicon Dioxide (SiO <sub>2</sub> )	19.9
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	4.6
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.2
Calcium Oxide (CaO)	62.0
Magnesium Oxide (MgO)	3.8
Sulfur Trioxide (SO <sub>3</sub> )	2.8
Alkalis (Na <sub>2</sub> O+0.658*K <sub>2</sub> O)	0.57
Loss on Ignition (LOI)	1.6
<hr/>	
Bogue phase composition	Percent by mass (%)
Tricalcium Silicate (C <sub>3</sub> S)	57.0
Dicalcium Silicate (C <sub>2</sub> S)	14.0
Tricalcium Aluminate (C <sub>3</sub> A)	7.0
Tetracalcium Aluminoferrite (C <sub>4</sub> AF)	10.0

### 3.3 Methods

#### 3.3.1 Aggregate Simulated Pore Solution Tests

Three simulated pore solutions were prepared for this study. Table 3.3 summarizes the molar concentrations of calcium hydroxide (Ca(OH)<sub>2</sub>), sodium hydroxide (NaOH), and potassium hydroxide (KOH) used in each simulated pore solution. The purity of chemicals used was 95%, 98%, and 85%, respectively. The solutions were prepared using deionized (DI) water.

*Table 3.3 – Composition, pH, and resistivity of simulated pore solution composition.*

Label	Ca(OH) <sub>2</sub>	NaOH	KOH	pH	Resistivity (ohm.cm)
SPS-1	0.05 M	0.09 M	0.09 M	13.11	26.3
*SPS-2	0.10 M	0.19 M	0.19 M	13.29	13.4
SPS-3	0.10 M	0.29 M	0.29 M	13.37	9.6

\*SPS-2 was chosen as the standard solution for this study

20 cm<sup>3</sup> of each of the 16 aggregates were exposed to the standard solution, and resulting solution was tested for resistivity and chemical composition using XRF. Each fine aggregate was brought to SSD conditions according to ASTM C128 (63). Samples were double bagged and stored in a sealed container to limit evaporation of moisture from aggregates. Two samples weighing 300 ± 10 g of each prepared SSD aggregate were dried at 110°C for 24 hours to determine moisture content as tested.

Approximately 20 cm<sup>3</sup> of fine aggregate at SSD condition was measured into sealed 50 mL centrifuge tubes for testing. Two samples of each aggregate were tested and compared for consistency. Approximately 15 mL of SPS-2 (Table 3.3) was added to each centrifuge tube containing the sample, and tubes were shaken by hand for one minute to ensure all aggregate particles were exposed to the simulated pore solution. Samples were then tested at 30 minutes and 24 hours since initial fine aggregate contact with the solution.

To extract the pore solution, the test specimens in 50 ml centrifuge tubes were inserted into a centrifuge and spun at 4000 RPM for 2 minutes. The solution was then decanted from the top of the centrifuge tubes and placed into smaller 10 mL centrifuge tubes for the resistivity and XRF measurement.

An experiment was designed to study the impact of surface area. A-1 was sieved with #4, #8, #16, #30, #50, and #100 sieves (including a pan). Each gradation was soaked for 24 hours and brought to SSD according to ASTM C128 procedure (63). 20 cm<sup>3</sup> of each gradation was tested with 15 mL of the standard solution. The same absorption



and specific gravity were assumed for every gradation. To estimate the surface area of each gradation, the particles were assumed to be spherical and have a normal distribution of particle size on every sieve. The average radius was used to solve for the number of particles in each sieve gradation using Equation 3.5.

$$n = \frac{V}{\frac{4}{3}\pi r_a^3} \quad (3.5)$$

$V$  is the total volume of the particles ( $20 \text{ cm}^3$ ) in each gradation, and  $r_a$  is the average radius of the particles. The number of particles ( $n$ ) was then used in Equation 3.6 to estimate the total surface area of each gradation tested:

$$A = n(4\pi r_a^2) \quad (3.6)$$

where  $A$  is the total surface area of the particles.

Additionally, the effect of pore solution concentration on the adsorption of ions was tested on A-1. SPS-1, SPS-2, and SPS-3 (Table 3.3) were used in the test. The same specified 15 mL volume quantity of the solution was used with  $20 \text{ cm}^3$  of aggregate at SSD condition. The aggregate was also tested with modified SPS-2 solution with no calcium in the solution to investigate the effect of calcium and any pozzolanic reaction. Additionally, 1 M NaCl and DI water were tested.

### 3.3.2 Mortar Tests

For the mortars, each batch was prepared to have a w/cm of 0.45. Approximately  $247.0 \text{ cm}^3$  of fine aggregate was used for each mortar mixture. This volume was chosen as it is a typical volume ratio of fine aggregates in a concrete mixture. The mortars were mixed for approximately 30 minutes from initial contact with water, and the bulk resistivity was measured using a Giatec RCON™ meter connected to two embedded electrodes in a 7.6 (diameter) x 15.2 cm (length) concrete cylinder filled with fresh mortar. The geometry factor of the assembly was found using Equation 3.7:

$$G_f = \frac{R_{ST}}{\rho_{ST}} \quad (3.7)$$

where  $G_f$  is the geometry factor,  $R_{ST}$  is the resistance of standard solution (SPS-2), and  $\rho_{ST}$  is the resistivity of standard solution. The geometry factor of this assembly was  $41.6 \text{ m}^{-1}$ . SPS-1 and SPS-2 were used to determine the variability of the determined geometry factor, which was found to be  $0.95 \text{ m}^{-1}$ .

Once the resistivity of the bulk materials was measured, the pore solution resistivity was found by using a centrifuge to extract the pore solution from the mortar (44). This pore solution was decanted and poured into 10 mL centrifuge tubes for the resistivity and XRF measurements.

### 3.3.3 The Correction of Solution Resistivity for Dilution by Water

The water contained in the pores of an aggregate at SSD will come to equilibrium with the pore solution in a concrete and dilute the ionic concentration of the pore solution system (50). To determine the corrected concentration and resistivity of the simulated pore solution, resistivity-ion concentration relationships from Snyder et al. were used (64). The relationships between ions and the resistivity of the solution are represented by Equation 3.8:

$$\frac{1}{\rho_{ps}} = \sum_i C_i z_i \lambda_i \quad (3.8)$$

where  $\rho_{ps}$  is the resistivity of the pore solution,  $C_i$  represents the molar concentration of each ion  $i$ ,  $z_i$  is the number of valence electrons for each ion, and  $\lambda_i$  is the equivalent conductivity of each ion. The equivalent conductivity is simplified by Equation 3.9, which is accurate within 10% for pore solutions (64):

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i I_M^{1/2}} \quad (3.9)$$

where  $\lambda_i^\circ$  represents the equivalent conductivity of the ionic species at infinite dilution, and  $G_i$  is the conductivity coefficient, and  $I_M$  is the ionic strength of the solution. The values of  $\lambda_i^\circ$  and  $G_i$  can be found in Table 3.4 (64).

Table 3.4 – The equivalent conductivity at infinite dilution ( $\lambda^\circ$ ) and conductivity coefficient ( $G$ ) at 25 °C

Ionic Species	$z\lambda^\circ$ (cm <sup>2</sup> S/mol)	$G$ (mol/L) <sup>-1/2</sup>
OH <sup>-</sup>	198.0	0.353
K <sup>+</sup>	73.5	0.548
Na <sup>+</sup>	50.1	0.733
Cl <sup>-</sup>	76.4	0.548
Ca <sup>2+</sup>	59.0	0.771
SO <sub>4</sub> <sup>2-</sup>	79.0	0.877

The avionic strength,  $I_M$  can be calculated with Equation 10 (64):

$$I_M = \frac{1}{2} \sum_i z_i^2 C_i \quad (3.10)$$

To create a function of these variables that relate the change in conductivity of the pore solution in terms of water added to the system by aggregate water content, a dilution term can be introduced, as shown in Equation 11 (44), which quantifies the change in ion concentration due to the addition of DI water to the system:

$$C_{i,dil} = \frac{C_i}{1 + \frac{V_{Aw}}{V_{OS}}} \quad (3.11)$$

where  $C_{i,dil}$  represents the new ionic concentration after the dilution due to the fine aggregate water content,  $V_{Aw}$  represents the volume of added water due to the fine aggregate water content, and  $V_{OS}$  represents the original volume of simulated pore solution, which throughout testing was kept constant at 15 mL. The resulting function for the resistivity  $\rho_{dil}$ , can be obtained by merging Equations 3.8-3.11 and is shown below:

$$\frac{1}{\rho_{dil}} = \sum_i \left[ \frac{C_i z_i}{1 + \frac{V_{Aw}}{V_{OS}}} \right] \left[ \frac{\lambda_i^\circ}{1 + G_i \sqrt{\frac{1}{2} * \frac{C_K + C_{Na} + C_{OH} + C_{Ca}}{1 + \frac{V_{Aw}}{V_{OS}}}}} \right] \quad (3.12)$$

To obtain the dilute resistivity, the concentrations of ions in the simulated pore solutions can be substituted in Equation 3.12, where  $V_{Aw}$  is calculated by multiplying the mass of fine aggregate in each sample by the water content as tested. The resulting resistivities are reported as the predicted resistivity of the simulated pore solution.

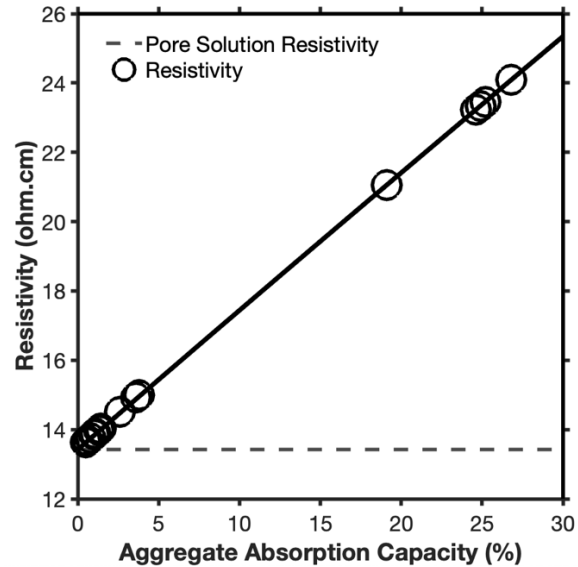
### 3.3.4 Resistivity and XRF Measurement

The resistivity of each solution was measured with a 3-pole platinum VWR conductivity electrode for a symphony series benchtop meter. The meter used in this study is a B40PCID symphony meter. Before every experiment in this study, the conductivity electrode was calibrated before measurements with a single 25 mS/cm (40 ohm.cm) buffer solution as per the manufacturer recommendation. A benchtop energy dispersive (X-ray fluorescence) XRF spectrometer was used to analyze the solutions in this study. A description of the calibration technique used for this particular device can be found in literature (65). Solutions were filtered using a 45-micron filter prior to XRF testing.

## 3.4 *Results and Discussion*

### 3.4.1 The Effect of Moisture in Aggregate (Dilution)

Moisture in aggregate pores dilute the ion concentration of the pore solution proportional to the amount of water they carry, which is a function of absorption capacity. Equation 3.12 calculates the resistivity of the pore solution due to this added water. Figure 3.1 illustrates the resistivity computed from Equation 3.12 as a function of the absorption capacity of the SSD aggregates.



*Figure 3.1 – Predicted resistivity of SPS-2 solution after testing against 16 SSD aggregates with different absorption capacities. Mass of all aggregate samples are 50 g.*

As shown in Figure 3.1, depending on the volume of aggregate, the absorption capacity can affect the resistivity of a pore solution significantly if the water in the pores is not considered. For example, an aggregate with an absorption of just 0.9% in a concrete mixture with a w/cm of 0.35 and 70% aggregate by volume will impact the pore solution resistivity by 10%. Similarly, a mixture of the same characteristics containing an aggregate with 2.5% absorption will impact resistivity by 25%. These changes to resistivity can be even larger when lightweight aggregates are used. Lightweight aggregates can have absorption capacities of 15% or greater. A lightweight aggregate with an absorption capacity of 20% will impact the resistivity by 137%. A correction for the water content due to the moisture in the aggregate must be taken into consideration when examining early age pore solutions. Henceforth, this effect will be referred as “dilution” in the paper.

### 3.4.2 The Effect of Ionic Adsorption on Aggregates (Adsorption)

The aggregate tests in simulated pore solution were designed to investigate if fine aggregates have the potential to adsorb ions from the solution to reduce the ionic concentrations and increase electrical resistivity. Figure 3.2 shows the measured resistivities of the standard simulated pore solution (SPS-2) against the predicted resistivity of the solution calculated using Equation 3.12.

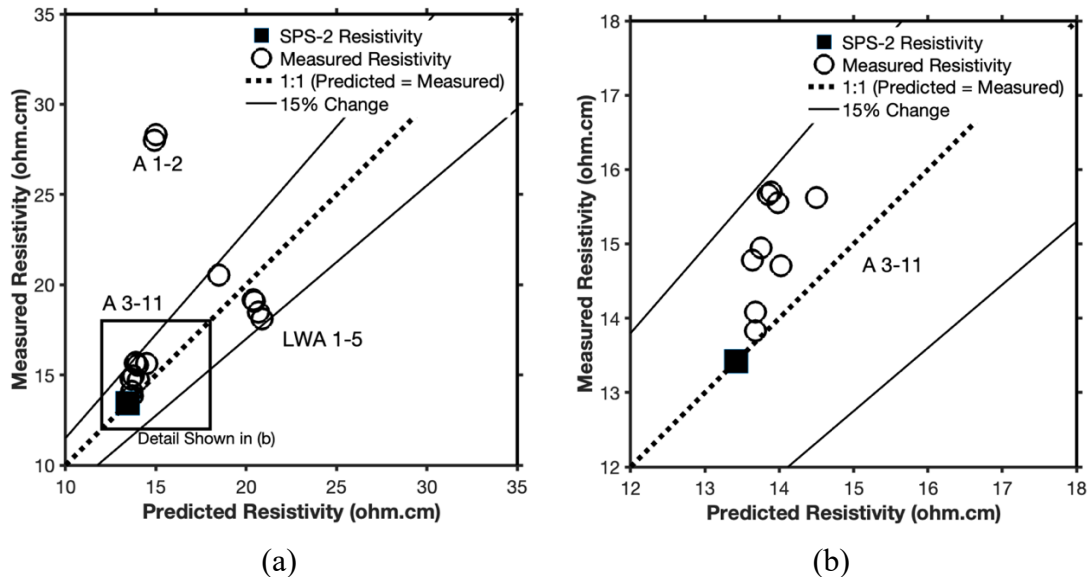


Figure 3.2 – (a) Fine aggregate simulated pore solution test results. (b) Detail of aggregates A-3 to A-11. A maximum difference between two measurements of the sample was found to be 0.52 ohm.cm; therefore, average values are reported.

Aggregates falling close or on the 1:1 line in Figure 3.2 have a change in pore solution resistivity that is primarily governed by the dilution due to the original water in the aggregate of the tested aggregates, as described in the previous section. Data points below the line are most likely aggregates with absorbed water that have not yet reached equilibrium with the simulated pore solution. Data points above the 1:1 line correspond to the cases for which the pore solution resistivity changes more than what is possible with just the effect of dilution due to moisture from aggregate. It is hypothesized that this observed difference is due to the adsorption effect of some aggregates, as also observed by Adams and Ideker (66). Ions may adsorb to the surface of some aggregates, thus decreasing the concentrations of ions in the simulated pore solution.

LWAs in Figure 3.2 changed the resistivity of the simulated pore solution 35-53%. This change in resistivity was governed by dilution due to the water from the aggregate. The high porosity of lightweight aggregates meant that the absorbed water diluted the system, increasing the resistivity of the simulated pore solution. A-3 to A-11 changed the resistivity of the simulated pore solution 3-17%. This change in resistivity was attributed to both dilution from aggregate water and adsorption effects. The resistivity of every one of these fine aggregates was above the 1:1 line, indicating that the concentration of ions in the pore solution was decreasing due to another mechanism outside of dilution. Aggregates A-1 and A-2 changed the resistivity of the simulated pore solution by 109% and 111%. These two aggregates increased the solution resistivity much more than predicted. This larger change in ion concentration is attributed to the adsorption of ions on the surface of aggregates. Note that to ensure that this adsorption was not a residual effect due to fine particles (e.g., clay, silt, etc.), A-1 samples were rinsed according to AASHTO T11 procedure (67). The resistivity results for rinsed A-1 samples were within 1.1% of the corresponding un-rinsed sample. Particles smaller than 75  $\mu\text{m}$  have an insignificant impact on the change in simulated pore solution resistivity. Table 3.5 shows the XRF results of the pore solution.

*Table 3.5 – Change in concentration of  $\text{Na}^+$  and  $\text{K}^+$  in SPS-2 after 30 minutes of exposure to 16 aggregates. Percent decrease in concentration is displayed adjacent to each concentration.*

Sample ID	$C_{\text{Na}^+}$ (mmol/L)	$C_{\text{K}^+}$ (mmol/L)
SPS-2	143.7	144.8
A-1	93.7 (53%)	35.6 (307%)
A-2	87.1 (65%)	56.3 (157%)
A-3	147.8 (-3%)	145.9 (-1%)
A-4	129.5 (11%)	114.8 (26%)
A-5	140.3 (2%)	128 (13%)
A-6	134.5 (7%)	117.7 (23%)
A-7	135.4 (6%)	116.4 (24%)
A-8	134 (7%)	120.3 (20%)
A-9	130.2 (10%)	125.1 (16%)

A-10	147.5 (-3%)	129.5 (12%)
A-11	138 (4%)	131.4 (10%)
LWA-1	103.7 (39%)	97.8 (48%)
LWA-2	112.0 (28%)	106.9 (35%)
LWA-3	118.9 (21%)	106.1 (36%)
LWA-4	108.4 (33%)	102.9 (41%)
LWA-5	107.7 (33%)	104.4 (39%)

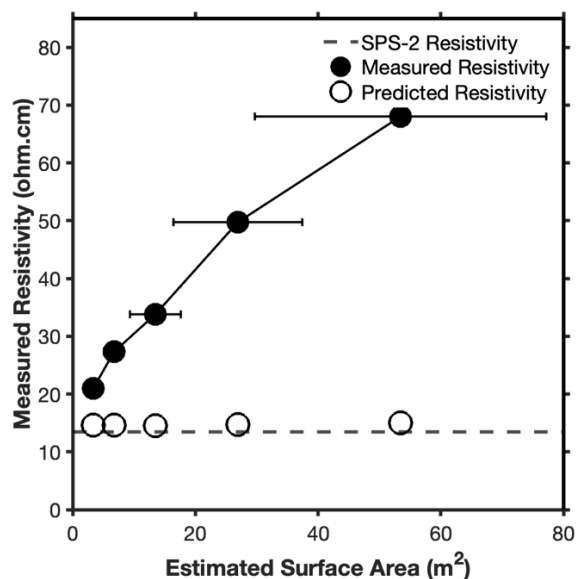
If dilution of the pore solution due to aggregate water content was the leading cause of reduction in resistivity, the percent decrease in  $\text{Na}^+$  and  $\text{K}^+$  concentration for each aggregate would be equal. Rather, experimental measurements showed that  $\text{K}^+$  ions were disproportionately reduced in the pore solution systems, on average 128% more than  $\text{Na}^+$  ions (in the standard solution). A-1 and A-2 stood out in XRF results, both reducing the concentration of ions in the pore solution by an average of 55% and 50%. It is likely that these two aggregates are adsorbing  $\text{Na}^+$  and  $\text{K}^+$  ions.

While other aggregates did not see a reduction in ion concentrations as dramatic as A-1 and A-2, they still disproportionately reduced the concentration of  $\text{K}^+$  ions in the system, suggesting that many aggregates may experience a small amount of adsorption. A-3 was the most inert aggregate in testing and was the only aggregate that did not follow this trend.

### 3.4.3 Effect of Aggregate Surface Area on Dilution and Adsorption

Figure 3.3 shows the change in the resistivity of standard simulated pore solution (SPS-2) due to a change in the estimated surface area of A-1. As the surface area of the particles exposed to SPS-2 increased, the resistivity of the pore solution increased.





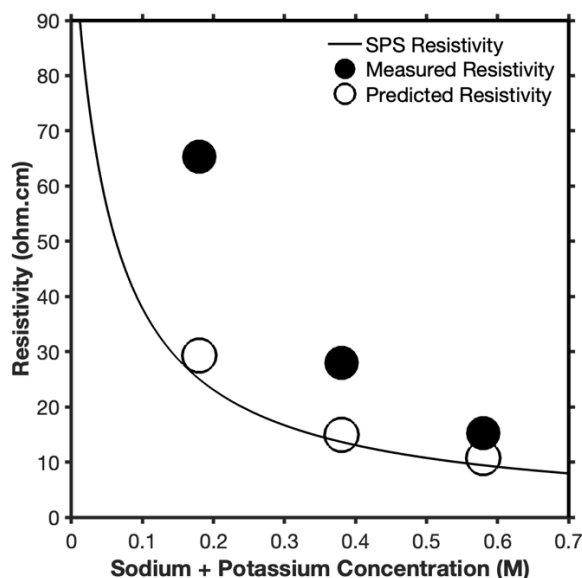
*Figure 3.3 – Measured resistivity of simulated pore solution exposed to different gradations of A-1. An estimated surface area greater than 54 m<sup>2</sup> yielded a constant change in simulated pore solution resistivity. The maximum difference between two measurements of the sample was found to be 0.46 ohm.cm; therefore, the average values are reported.*

The surface area of aggregate plays a critical role in the observed change of electrical resistivity (due to changes in ionic concentration), supporting the hypothesis that ions may be adsorbed on aggregate surfaces. When the surface area of 20 cm<sup>3</sup> of A-1 was 3.4 m<sup>2</sup>, the resistivity of the pore solution increased by 56%. When the same volume had a surface area of 53.5 m<sup>2</sup>, the resistivity increased by 147%. Aggregate particles passing the #100 sieve increased the simulated pore solution resistivity by 146%, indicating that there is a limit to adsorption of ions on smaller particles. Additionally, the adsorption of ions is not a phenomenon of a particular sized particle. The high adsorption of ions may be related to the overall mineralogy of an aggregate.

#### 3.4.4 Effect of Solution Concentration on Adsorption

The potential adsorption effect in fine aggregate was measured for A-1 using three simulated pore solutions of increasing ion concentrations (SPS-1, SPS-2, and SPS-3). Figure 3.4 shows the change in measured resistivity as a function of the initial

concentration of simulated pore solution. Hollow data points represent the predicted resistivity of the pore solution due to dilution only (without the effect of adsorption).



*Figure 3.4 – Fine aggregate influence on solution resistivity as a function of changing simulated pore solution ion concentration. Simulated pore solutions without calcium yielded statistically similar results to pore solutions with calcium. The maximum difference between two measurements of the sample was found to be 0.48 ohm.cm; therefore, average values are reported.*

The initial concentration of the solution affects the change in resistivity of the solution exposed to the aggregate. The change in the solution resistivity (difference between the predicted and measured resistivities) was not uniform for all the concentrations of the simulated pore solutions. SPS-1, SPS-2, and SPS-3 changed the resistivity of the solutions by 149%, 109%, and 58%. XRF was performed on each solution to examine the concentration of  $\text{Na}^+$  and  $\text{K}^+$  ions in the simulated pore solution before and after exposure to aggregate (Table 3.6).

*Table 3.6 – XRF results of the three simulated pore solutions before and after exposure for 30 minutes to A-1. Percentage decrease in concentration is displayed adjacent to the concentrations.*

Sample ID	$C_{Na^+}$ (mmol/L)	$C_{K^+}$ (mmol/L)
SPS-1	63.0	71.5
SPS-2	143.7	144.8
SPS-3	234.4	229.9
A-1 w/SPS-1	32.7 (48%)	12.1 (83%)
A-1 w/SPS-2	93.7 (35%)	35.6 (75%)
A-1 w/SPS-3	178.8 (24%)	102.3 (56%)

As the concentration of  $Na^+$  and  $K^+$  ions in the solution increased, more ions adsorbed to the surface of aggregates. This increase of adsorption, however, was not directly proportional to the increase in SPS ion concentration. It is hypothesized that aggregate surfaces may have a limit to the number of ions they are able to adsorb on their surfaces that is dependent upon the initial ion concentration of the solution. While surface area plays a key role in the amount of adsorption that can take place, another key factor may be the mineralogy of an aggregate. Therefore, ion adsorption curves are hypothesized to be specific to every aggregate.

Figure 3.5a and 3.5b show the change in  $Na^+$  and  $K^+$  ion concentrations after SPS-1, SPS-2 and SPS-3 are exposed to A-1 for 30 minutes. Best fit functions specific to A-1 were created to describe the rate of adsorption for an increase in the initial concentration of each ion. The best fit function to correlate  $Na^+$  ion adsorption with initial concentration was a power function (Equation 3.13), and the best fit function for  $K^+$  ions was a second-degree polynomial (Equation 3.14).

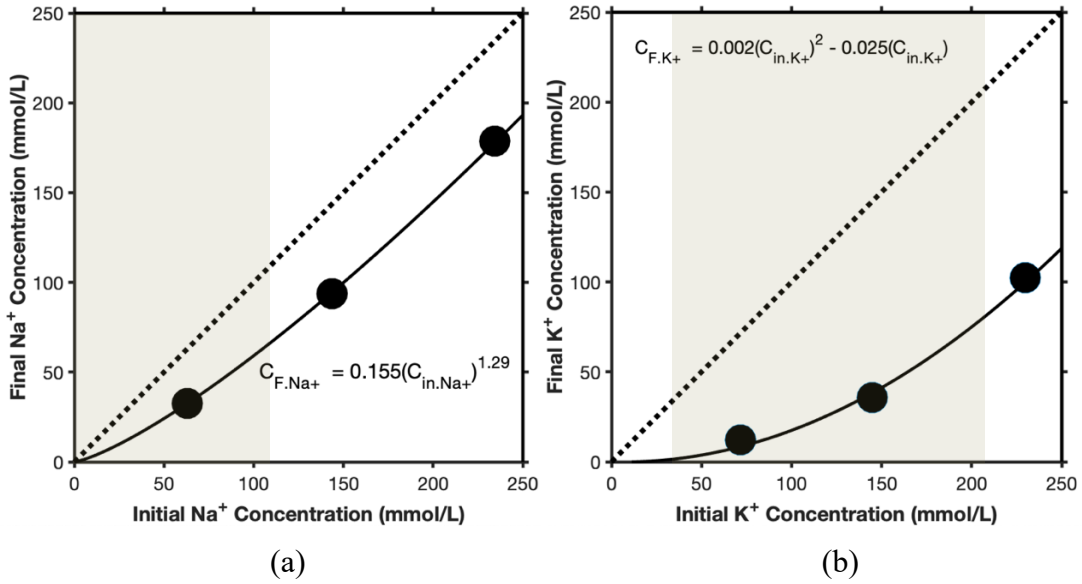


Figure 3.5 – (a) Change in concentration of  $\text{Na}^+$  ions for SPS-1, SPS-2, and SPS-3, with a power fit ( $R^2 = 0.99$ ) and (b) change in concentration of  $\text{K}^+$  ions in SPS-1, SPS-2, and SPS-3 with a second-degree polynomial fit ( $R^2 = 0.99$ ) after being adjusted for aggregate water contribution. Shaded regions represent the typical range of ion concentrations found in fresh concrete pore solutions.

$$C_{F.Na+} = 0.155(C_{in.Na+})^{1.29} \quad (3.13)$$

$$C_{F.K+} = 0.002(C_{in.K+})^2 - 0.025(C_{in.K+}) \quad (3.14)$$

$C_{in.i}$  represents the initial concentration of ion  $i$  in the simulated pore solution, and  $C_{F.i}$  represents the final concentration of ion  $i$  in the solution. These equations will give the amount of ion adsorption by A-1 for an initial concentration of  $\text{K}^+$  or  $\text{Na}^+$  ions. Further discussion of how these equations can be applied for adsorption corrections in mortars is discussed in section 3.4.6.

The authors believe that relationships describing the change in ion adsorption due to the initial concentration of ions could be described similarly to chloride binding isotherms (68-70). This hypothesis will require further analysis and testing of other aggregates other than A-1 at these varying concentrations to understand further.

The reduction in alkali concentrations and increase in resistivity of the solutions could be a result of chemical reactions including pozzolanic or alkali-silica reactions (ASR). To further check this, an identical SPS-2 was prepared without the addition of  $\text{Ca}(\text{OH})_2$  and exposed to the aggregate. It was observed that the presence of calcium had no significant effect on the change in solution resistivity (<11%), indicating that the reduction in ion concentrations is not necessarily due to chemical reactions such as pozzolanic or ASR (14).

A-1 was also exposed to solutions such as 1M NaCl and DI water that have pH around 7. No significant change (8.8% and <1%) in resistivity was observed. Therefore, the possible mechanism could be surface adsorption of cations due to gain in negative charge of minerals on the surface of aggregates, however further studies are needed to confirm this.

#### 3.4.5 Effects of Dilution and Adsorption in Mortar Samples

Aggregates A-1 through A-11 were tested in mortars at equal volumes and measured for pore solution and bulk resistivity. It was observed that the dilution and adsorption effects in mortar were magnified due to a smaller original volume of pore solution in the system when compared to aggregate tests. Apart from A-3, every aggregate increased the pore solution resistivity by more than 10%. Table 3.7 shows the change in  $\text{Na}^+$  and  $\text{K}^+$  concentrations in the pore solutions of the mortars.

*Table 3.7 – Resistivity and change in  $\text{Na}^+$  and  $\text{K}^+$  concentration in mortar pore solution after 30 minutes of mixing. Percent decrease in resistivity and concentration is displayed adjacent to values.*

Sample ID	$(\rho_{ps})$ (ohm.cm)	$C_{\text{Na}^+}$ (mmol/L)	$C_{\text{K}^+}$ (mmol/L)
Cement Paste	25	15.2	155.5
A-1	61.3 (145%)	11.3 (26%)	29.3 (81%)
A-2	58.9 (136%)	9.9 (35%)	47.7 (69%)
A-3	25.9 (4%)	24 (-58%)	146 (6%)
A-4	32.3 (29%)	14.5 (5%)	110.6 (29%)

A-5	33.2 (33%)	20.1 (-32%)	120.1 (23%)
A-6	32.1 (28%)	14.8 (3%)	115.2 (26%)
A-7	34.5 (38%)	18 (-18%)	116.8 (25%)
A-8	34.7 (39%)	16.5 (-9%)	122 (22%)
A-9	32.6 (30%)	15 (1%)	118.9 (24%)
A-10	31.6 (26%)	15.6 (-3%)	130.6 (16%)
A-11	29.1 (16%)	25.8 (-70%)	138.8 (11%)

Mortars experienced greater changes in pore solution resistivity and ion concentrations. This is mainly due to an increased surface area of aggregates per volume of pore solution. Both dilution and adsorption of ions change the concentration of ions by a greater amount. Samples A-1 and A-2 reduced the resistivity by 145% and 136%. Aggregates A-3 to A-11 reduced the resistivity between 4% and 38%. Overall,  $K^+$  ions were adsorbed at a larger rate than  $Na^+$  ions, however this could mainly be due to the original  $Na^+$  concentration being significantly lower than  $K^+$  ion concentration in the cement paste pore solution.

#### 3.4.6 Correcting Mortar Pore Solution Resistivity for Dilution and Adsorption

The change in ion concentration for a mortar can be predicted based on previous SPS aggregate test results by using a modified version of Equation 3.11. Two steps must be taken to make this correction. First, an aggregate-specific adsorption coefficient for each ion ( $Ad_i$ ) must be found that describes the adsorption of each ion  $i$  for a given initial ion concentration. Second, a new equation must replace Equation 3.11 that solves for the new ion concentration of the pore solution by relating both the aggregate adsorption and dilution due to the water content to the volume of aggregate in the mortar. The adsorption coefficient can be found by using Equation 3.15:

$$Ad_i = \frac{C_{F,i}(V_{OS} + V_{Aw}) - C_{in,i}(V_{OS} + V_{Aw})}{V_{agg.SPS}} \quad (3.15)$$

Where  $C_{in,i}$  is the initial concentration of ion  $i$  in the simulated pore solution, and  $C_{F,i}$  is the final concentration of ion  $i$  after 30 minutes of exposure to the tested volume of

aggregate in SPS ( $V_{agg.SPS}$ ). The aggregate-specific adsorption coefficient for a particular ion ( $Ad_i$ ) is in units of moles per meter cubed ( $\text{mol/m}^3$ ).

Equation 3.16 replaces Equation 3.11 and calculates the new ion concentration due to the dilution and adsorption of the aggregate ( $C_{i.dil+Ad}$ ).

$$C_{i.dil+Ad} = \frac{C_i(V_{OS}) - Ad_i(V_{Agg.M})}{(V_{OS} + V_{Aw})} \quad (3.16)$$

The volume of aggregate in the mortar ( $V_{Agg.M}$ ) is multiplied by the coefficient  $Ad_i$  to account for the residual ionic reduction at the cement paste ion concentration  $C_i$ . Equation 3.14 also incorporates the dilution of the pore solution due to the water content of aggregate ( $V_{Aw}$ ).

To demonstrate these corrections being used, this method was used for the A-1 aggregate. Calculated change in concentration of  $\text{Na}^+$  and  $\text{K}^+$  using Equation 3.16 was compared to the measured change in  $\text{Na}^+$  and  $\text{K}^+$  concentration from the mortar experiment. The cement paste pore solution in this study had an initial  $\text{Na}^+$  and  $\text{K}^+$  ion concentration of 15.2 and 155.5 mmol/L.  $Ad_i$  was calculated using the varied SPS ion concentration results discussed in section 3.4.4. The calculated change in  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations using Equation 3.16 was found to be 9.52 and 129.1 mmol/L, which is within 44% and 2.3% of what was measured in A-1 mortar XRF results. Worth noting is that the initial  $\text{Na}^+$  concentration of the cement paste pore solution was much less than that of the SPS solutions tested, so the calculated change in mortar  $\text{Na}^+$  concentration has a greater percent difference. While this is just a single example, further experimentation will be required to confirm this method works for other aggregates.

The resulting ion concentrations from this method can be used in Equation 3.12 to back-calculate for the resulting resistivity due to this change. Additional  $Ad_i$  coefficients for

ions such as  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  would need to be found for A-1 to complete this back-calculation. Further experimentation is required to complete this prediction.

### 3.4.7 Comparison of Fresh Concrete Parameters

All mortars were prepared using identical mixture proportions, with the only variable being the aggregate type (A-1 to A-11). Parameters such as the pore solution resistivity ( $\rho_{PS}$ ), bulk resistivity ( $\rho_b$ ), porosity ( $\phi$ ), connectivity parameter ( $\beta$ ), and F were compared to examine the impact of dilution from water content of aggregates and adsorption on these measurements. The porosity ( $\phi$ ) was calculated for all mortars using Equation 3.17 (45):

$$\phi = (\phi_{paste}) \left( \frac{\frac{w}{cm}}{\frac{w}{cm} + \frac{1}{SG_C}} \right) + (\phi_{agg})(ABS\%) \quad (3.17)$$

where  $SG_C$  is the specific gravity of the cement paste and ABS% is the absorption capacity of the aggregate tested. Corresponding connectivity parameter ( $\beta$ ) values were calculated using the relationship in Equation 3.18 (45):

$$\frac{\rho_{bm}}{\rho_{PSm}} = \frac{1}{\phi\beta} \quad (3.18)$$

where  $\rho_{bm}$  and  $\rho_{PSm}$  represent the bulk resistivity of the mortar and the pore solution resistivity of the mortar. As the volume ratio of fine aggregate to cement paste was held constant in this study, the maxwell effective medium model (10,46) (Equation 3.19) was used to find the predicted bulk resistivity of the mortars:

$$\frac{\sigma_m}{\sigma_p} = \frac{2\phi_p}{3 - \phi_p} \quad (3.19)$$



where  $\sigma_m$  is the bulk conductivity of the mortar, and  $\sigma_p$  is the bulk conductivity of the cement paste. The predicted bulk resistivity of the mortars was found to be 158.5 ohm.cm. Table 3.8 shows these various parameters for the mortars tested.

*Table 3.8 – Summary of Mortar measurements and calculated Porosity, Connectivity, and formation factor values of the systems. Percent increase in measured mortar pore solution and bulk resistivity from predicted is displayed next to the resistivity measurements (Predicted bulk resistivity of all mortars was 158.5 ohm.cm).*

Mortar Sample ID	Pore solution resistivity ( $\rho_{ps}$ ) (ohm.cm)	Bulk resistivity ( $\rho_b$ ) (ohm.cm)	Porosity ( $\phi$ )	Connectivity parameter ( $\beta$ )	Formation factor (F)
Cement Paste	25	60.7	0.59	0.70	2.43
A-1	61.3 (145%)	339.4 (114%)	0.30	0.60	5.54
A-2	58.9 (136%)	267.5 (69%)	0.30	0.73	4.54
A-3	25.9 (4%)	148.1 (-7%)	0.29	0.61	5.72
A-4	32.3 (29%)	178.6 (13%)	0.29	0.63	5.53
A-5	33.2 (33%)	160.9 (2%)	0.29	0.72	4.85
A-6	32.1 (28%)	183.9 (16%)	0.30	0.59	5.73
A-7	34.5 (38%)	168.3 (7%)	0.29	0.58	6.07
A-8	34.7 (39%)	167.5 (6%)	0.29	0.73	4.71
A-9	32.6 (30%)	153.3 (-3%)	0.29	0.72	4.82
A-10	31.6 (26%)	155.8 (-2%)	0.29	0.71	4.93
A-11	29.1 (16%)	176.3 (11%)	0.29	0.71	4.87

Although the volume of aggregates was kept constant for all studies, the pore solution and bulk resistivity varied significantly from theoretical predicted values. The pore solution resistivity was especially affected across all mortars. A-1 and A-2 aggregates increased the pore solution resistivity by 145% and 136%. All other aggregates increased the pore solution resistivity by an average of 27%. Not all aggregates that saw an increase in pore solution resistivity saw an accompanying increase in the bulk resistivity of the mortar. This could be explained by the varying gradations of sands A-1 through A-11. The tortuosity of each mortar system is different for each aggregate due to the different gradations present in each tested aggregate. The connectivity factor

of each mortar system varies in the range of 0.58-0.73 with an average value of 0.67 and standard deviation of 0.06 (Table 3.8).

Although the resistivity measurements ranged from 25.9-61.3 ohm.cm, the formation factor results negated much of this change. The formation factor varied between 4.54 – 6.07 for all experiments. When examining fresh concrete using electrical resistivity, the formation factor may be a better parameter that is less sensitive to changes in the resistivity because of adsorption. For example, aggregate samples A-1 and A-3 were the aggregates with the highest and lowest pore solution resistivities (61.3 and 25.9 ohm.cm). Their formation factors, however, were within just 0.18 of each other (5.54 and 5.72).

### **3.5 Conclusions**

It is often assumed that aggregates are inert and do not impact the electrical resistivity of fresh mortar and concrete. This study identifies two ways that aggregate may alter pore solution resistivity in mortar or concrete. Two corrections are discussed 1) ionic dilution and 2) ionic adsorption. Ionic dilution is related to aggregate porosity and accounts for the dilution of ions in the pore solution as the solution increases to include the absorbed water. Ionic adsorption is associated with the interaction of the ionic species with the surface of aggregates, effectively removing them from the conductive solution. Ionic adsorption resulted in a change of up to 116%. The reduction of  $K^+$  ions for the aggregate studied was more significant than  $Na^+$  ions. The ionic adsorption was measured to increase with the surface area of the aggregate nearly proportionally.

ASTM 128 was used to determine aggregate porosity (absorption capacity) for use in the correction. An experimental method was developed to evaluate ionic adsorption; however, it may need further development before it can be standardized. Correction terms were introduced to the concentration calculation to account for dilution and ionic adsorption. These ion concentrations can be used to back-calculate the resulting resistivity of a pore solution in mortar.

The bulk resistivity of a series of mortars made using various aggregates was measured. The porosity of the mortars was computed, and the pore solution was extracted and measured. The pore connectivity and formation factor were calculated. The results indicate that the resistivity between the aggregate had a coefficient of variation of 31.7%, while the formation factor had a coefficient of variation of 9.9%.

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## 4 CONCLUSIONS

Fresh concrete resistivity may have many promising applications for improving concrete QA/QC programs. The objective of this thesis was to 1.) investigate new techniques to make the field measurements of fresh pore solution resistivity from cementitious materials more practical for industry and 2.) correct the pore solution resistivity for factors such as dilution due to aggregate water content and adsorption. The following conclusions were drawn from the two chapters of the thesis.

### *4.1 Conclusions from Chapter 2*

Chapter 2 investigated new methods to extract and measure the pore solution of fresh cementitious mixtures. A pore solution extraction method and measurement method were tested and statistically compared to more common laboratory techniques. For instances where not enough pore solution can be collected for tests, a procedure was proposed to dilute and predict the original pore solution resistivity. Additionally, this chapter statistically compared the influence of time from initial mixing on resistivity measurements. It was found that:

- A centrifuge extraction method was developed that saves time and requires less equipment for users over previous pore solution extraction methods. Pore solution extracted using the centrifuge technique was found to have no statistically significant impact on resistivity measurements when compared to other laboratory extraction methods such as the vacuum method or nitrogen pressure method.
- The use of a resistivity/conductivity probe method to measure the pore solution resistivity saves time for recording pore solution resistivity measurements and corrections after measurement for factors like assembly geometry and temperature were done through the benchtop meter software. Variability of this method was found to be within 0.2 ohm.cm of the cell method of resistivity measurement (typical pore solution resistivity measurement variability is  $\pm 2$

ohm.cm) The resistivity readings of the probe were found to be statistically similar to other resistivity measurement methods.

- There is no significant difference in resistivity measurements taken between the range of 30 to 90 minutes from initial mixing. These results indicate that chemistry of cement paste pore solution does not evolve enough in the first 90 minutes to effect resistivity measurements. Field measurements can be performed in this window of time without a statistically significant change to the pore solution resistivity, confirming what other studies have observed (30,31).
- For instances in the field where not enough pore solution can be obtained (such as high aggregate volumes or low w/cm), a method can be used to dilute the pore solution, measure its resistivity, and back-calculate to predict the original pore solution resistivity of a cement paste or concrete. This method was tested and found to predict the original pore solution resistivity within 13 ohm.cm for the two-point dilution model, which is within 4.7% of the actual result.

#### ***4.2 Conclusions from Chapter 3***

This chapter aimed to investigate two potential influences that aggregate may have on fresh mortar and concrete mixtures: 1.) the dilution of pore solution due to the water content of aggregates and 2.) the potential adsorption of ionic species on the surface of aggregates. A test method was developed to test 16 fine aggregates from various regions in the United States and their influence on simulated pore solutions. Experiments were performed to investigate factors such as aggregate surface area and chemical composition and their impacts on ion concentration and resistivity. Additionally, mortars were prepared with the aggregates to investigate their influence on the pore solution of a mortar. Resistivity and XRF results were analyzed to investigate ions that had an affinity for adsorption, and to create relationships for correcting these changes to pore solution chemistry. It was found that:

- The dilution due to water content plays a role in pore solution resistivity increase (64).
- In some cases, the effects of adsorption increase the resistivity of the pore solution system. Some aggregates increased the simulated pore solution resistivity up to 114%. All aggregates consistently adsorbed  $K^+$  ions more than  $Na^+$  ions.
- The amount of adsorption that can occur is speculated to be related to the mineralogy of an aggregate, the surface area of an aggregate, and the original concentration of the pore solution. Thus, all aggregates experience different adsorption behaviors.
- With mortars, 10 of 11 aggregates changed the pore solution resistivity by more than 10%. In the case of two aggregates, the resistivity changed by 145% and 136%. Mortar bulk resistivity was also impacted by the pore solution resistivity change, and in the case of the two most influential aggregates, the bulk resistivity was increased by 114% and 69%.
- The adsorption of an ion by an aggregate can be predicted through the determination of an aggregate-specific ion adsorption factor. This factor can be found by testing aggregates in varying simulated pore solution concentrations and examining the number of ions that are adsorbed.
- Formation factor may be a better fresh concrete measurement parameter. Although the resistivity measurements ranged from 25.9-61.3 ohm.cm, the formation factor varied between 4.54 – 6.07 for all experiments.

#### ***4.3 Recommendations for Future Work***

The following is a list of research related to this thesis topic that requires further investigation:

- Early age resistivity measurements have been proven useful in some studies for determining parameters such as the w/cm in fresh concrete. The resistivity field

measurement techniques in this thesis may be useful for determining some QA/QC parameters for standard concrete mixtures in practice.

- In this thesis, it was assumed that the reduction of ions in pore solution was the result of ion adsorption on the surfaces of aggregates. Further studies are required to confirm adsorption is the mechanism taking place on aggregate surfaces. Furthermore, the mineralogy that causes this reduction of ions to take place is unknown.
- Other aspects of concrete may influence the resistivity of a fresh concrete system that may not have been previously examined, such as admixtures like accelerators, retarders, and corrosion inhibitors. While a number of these variables have been studied in past research, a review of these studies and identification of variables that have not been investigated is recommended for future work.

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