AN ABSTRACT OF THE THESIS OF

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Title: <u>The Evaluation of Cementitious Pore Solution Composition and Electrical</u> <u>Resistivity Using X-ray Fluorescence (XRF)</u>

Abstract approved:

W. Jason Weiss

Interest in performance specifications has been growing in the civil and construction industry in the past decade. One major focus area has been on understanding how to prolong the service life of concrete structures, since repair and rehabilitation of existing infrastructure have cost many trillions of dollars. Deterioration mechanisms such as corrosion can shorten the service life of a structure and are typically determined by the moisture and ionic species ingress into the concrete, or, in other words, the transport properties of the concrete.

Ionic transport in concrete can be described using the formation factor, which is defined as the ratio of the resistivities of the concrete and the pore solution. Therefore, there is significant value in rapid and simple methods to measure these electrical properties. Measuring the resistivity of concrete, or bulk resistivity, is relatively straightforward; however, measuring the pore solution resistivity is more complex since extracting pore solution from hardened concrete is rather challenging.

The pore solution resistivity value may be assumed from literature, directly measured using a resistivity meter, or computed from the pore solution composition using different chemical analysis methods. The objective of this thesis is to investigate the use of X-ray fluorescence (XRF) as a chemical analysis method to obtain the chemical composition of the pore solution which enables the calculation of pore solution resistivity.

The first part of this study focuses determining the feasibility of using XRF to assess the chemical composition of the main ionic species in simulated pore solutions and to calculate the pore solution resistivity from the chemical composition. Two analysis methods were explored: the solution method and the fused bead method. The measured ionic concentrations were compared to theoretical concentrations; the calculated resistivities were compared to measured resistivities using a resistivity meter as a direct measurement. The results from this study showed that XRF can accurately detect the ionic composition of simulated pore solutions and can be used to accurately calculate the pore solution resistivity using both methods of analysis.

The second part of this study focuses on measuring the ionic concentrations and calculating the resistivity of expressed pore solutions. The influence of test parameters such as sample size and storage time on the composition and resistivity was also studied. The calculated resistivities were compared to measured resistivities using a resistivity meter as a direct measurement. Chemical composition and resistivity determined using XRF were also compared with an online pore solution conductivity calculator developed at the National Institute of Science and Technology (NIST). The results from this study showed that the calculated resistivities from XRF match the measured resistivities from the resistivity meter. Therefore, it can be concluded that XRF can be used to accurately calculate the electrical resistivity of pore solutions. Chemical compositions determined from the XRF matched the ones determined from the NIST calculator after 24 hours of expressed age (but not earlier), since the NIST calculator neglects sulfate and calcium, which are present in significant amounts in pore solutions before 24 hours.

In conclusions, the results from this thesis indicate that XRF is a potential alternative to time consuming methods which are currently used to determine the pore solution composition that can then be used to predict resistivity. This method could potentially bring benefits in terms of time and cost reductions, since XRF is a device commonly used in the cement industry.

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The Evaluation of Cementitious Pore Solution Composition and Electrical Resistivity Using X-ray Fluorescence (XRF)

by Marisol Tsui Chang

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APPROVED:

Major Professor, representing Civil Engineering

Head of the School of Civil and Construction Engineering

Dean of the Graduate School

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.

Marisol Tsui Chang, Author

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Dr. W. Jason Weiss (advisor), Dr. Prannoy Suraneni (post-doctoral researcher), Dr. O. Burkan Isgor (professor), and Dr. David Trejo (professor) were involved in the writing of Chapter 2.

Dr. W. Jason Weiss (advisor), Dr. Prannoy Suraneni (post-doctoral researcher), and Luca Montanari (graduate researcher) were involved in writing Chapter 3.

Nathalene Then, Naomi Salgado, and James Sweeney (undergraduate laboratory assistants) helped performed several of the experiments reported in Chapter 2 and Chapter 3,

TABLE OF CONTENTS

1.	Introducti	on	1
	1.1 Resea	rch Objectives	4
	1.2 Thesis	Organization	5
2.	Using X-	ray fluorescence to assess the chemical composition and resis	tivity of
	simulated	cementitious pore solutions	7
	2.1 Abstra	ıct	7
	2.2 Introd	uction	7
	2.3 Mater	ials and Methods	10
	2.3.1	Materials	10
	2.4 Exper	imental Methods	11
	2.4.1	XRF Calibration	11
	2.4.2	Solution Sample Preparation and Analysis	14
	2.4.3	Solution Bead Sample Preparation and Analysis	14
	2.4.4	Resistivity Calculations	15
	2.4.5	Measuring Resistivity	16
	2.5 Exper	imental Results	17
	2.5.1	Ionic Concentrations	17
	2.5.2	Electrical Resistivity	19
	2.5.3	Applications of XRF to study Cementitious Pore Solutions	22
	2.6 Concl	usions	23
	2.7 Ackno	owledgements	24

TABLE OF CONTENTS (CONTINUED)

	3.2.1	XRF Background	
	3.3 Mater	ials	
	3.3.1	Materials	
	3.3.2	Mixture design and mixing	
	3.4 Exper	imental Methods	
	3.4.1	Pore Solution Expression	
	3.4.2	Resistivity Measurement	32
	3.4.3	XRF Measurement	
	3.4.4	Solution Sample Preparation	
	3.4.5	Calculating Resistivity from XRF	
	3.4.6	Effect of Sample Size	35
	3.4.7	Effect of Storage Time	
	3.4.8	NIST Calculator comparison	
	3.5 Exper	imental Results	
	3.5.1	Ionic Concentration vs. Sample Size Tested	
	3.5.2	Ionic Concentration vs. Storage Time	
	3.5.3	Ionic Concentration and Electrical Resistivity	40
	3.5.4	NIST Calculator Comparison	44
	3.6 Concl	usions	48
	3.7 Ackno	owledgements	49
4.	Conclusio	ons	50
	4.1 Concl	usions from Chapter 2	50
	4.2 Concl	usions from Chapter 3	51
	4.3 Furthe	er Research	
5.	Bibliogra	phy	

TABLE OF CONTENTS (CONTINUED)

Page 1

6.	Appendices	61
	6.1 Appendix 1	61
	6.2 Appendix 2	71

LIST OF FIGURES

<u>Figure</u>	Page
1	(a) Closed and (b) Open energy dispersive XRF bench-top system 12
2	Representative energy spectrum for an application standard for sodium and potassium
3	Step-by-step assembly of plastic containers with polypropylene film for solution XRF testing
4	(a) Top and (b) side of a representative fused solution bead 15
5	Measured (a) sodium and (b) potassium ionic concentrations of simulated pore solutions using XRF solutions and beads compared to theoretical ionic concentrations. The dashed line represents a 1:1 correlation
6	Calculated resistivity based on ionic conductivities compared to measured resistivity with a resistivity meter. The dashed line represents a 1:1 correlation
7	(a) Mechanical pressure expression system and (b) system schematic used for the pore solution expression
8	Resistivity cell set up (a) unassembled and (b) assembled to test the pore solution resistivity with the resistance meter
9	Ionic concentration versus sample size tested for all ions at 1 day. The dashed lines are the average concentrations for each ion
10	Ionic concentration of the main ions with respect to time for a representative sample at an expressed age of 1 d. The dashed lines are the average concentrations for each ion
11	Ionic concentrations from chemical analysis using XRF for (a) Na^+ , K^+ and OH^- and (b) SO_4^{2-} and Ca^{2+} at various ages
12	Calculated resistivities using XRF versus measured resistivities using a resistivity meter. The dashed line represents a 1:1 correlation
13	Figure 13: Evolution of the pore solution resistivity (a) at different ages and (b) at different degrees of hydration (DOH)

LIST OF FIGURES (CONTINUED)

<u>Figure</u>	Page
14	Ionic concentration of (a) Na^+ , (b) K^+ , and (c) OH^- from XRF compared to estimated concentrations from the NIST calculator
15	Calculated resistivity from XRF and estimated resistivity from the NIST calculator compared to the measured (true) resistivity from the meter. The dashes represent a 1:1 line
16	Schematic of the resistivity cell components
17	Resistivity cell individual components 64
18	Assembled resistivity cell
19	Injection of solution in the assembled resistivity cell
20	Assembled resistivity cell connected to the probes using alligator clips for resistivity measurement
21	Assembling procedure for XRF solution cups

LIST OF TABLES

Table	Page
2.1	Concentrations of Na ⁺ and K ⁺ in simulated pore solutions 11
2.2	Fitted line regressions of sodium and potassium using XRF solution and bead
2.3	Percent error of ionic concentration for XRF solution and bead with respect to theoretical ionic concentrations
2.4	Measured and calculated resistivity values
2.5	Percent error of calculated resistivity measurements for XRF solution and bead with respect to the measured resistivity values
3.1	Oxide contents of the cement and fly ash from XRF
3.2	Fitted linear regressions for the calculated resistivity with respect to the measured resistivity for each sample size tested using XRF at various ages, where y is the calculated resistivity from XRF concentrations and x is the measured resistivity using the resistivity meter
6.2.1	Detailed steps for fusion of fused bead sample
6.2.2	Ionic species present in pore solution and included in this document
6.2.3	Conductivity coefficients for each ionic species

1 Introduction

In the past decade, the civil and construction industry has focused on understanding how concrete structures perform as they age in different environments and the various mechanisms that contribute to concrete deterioration. These deterioration mechanisms can lead to trillions of dollars of cost in infrastructure repair and rehabilitation. Some deterioration mechanisms that can shorten the life of a reinforced concrete structure include: corrosion, alkali-aggregate reaction, sulfate attack, and freeze-thaw.

Many of these mechanisms are strongly affected by the fluid transport properties of a concrete, or, in other words the movement of moisture and ionic species into concrete when exposed to different environments [1–4]. Previously, the use of electrical measurements to evaluate the transport properties of concrete have been explored in some detail; specifically, the use of uniaxial resistivity to rapidly measure the electrical resistivity of concrete [5]. However, electrical resistivity of concrete is not a fundamental measure of its microstructure.

Formation factor, F, is a material property that is a fundamental measure of the concrete microstructure. It can be related to transport properties and durability of concrete [6], [7]. The formation factor is inversely related to the product of porosity, ϕ , and pore connectivity, β , It can also be defined as the ratio of the bulk electrical resistivity, ρ_b , and the pore solution resistivity, ρ_o , as shown in Equation 1.1 [8]:

$$F = \frac{1}{\phi\beta} = \frac{\rho_b}{\rho_o}$$
 Equation 1.1

While measuring the concrete bulk resistivity is relatively straightforward [5], measuring pore solution resistivity is more intricate since extracting pore solution, especially from hardened concrete, is quite challenging.

The following sections present a brief background on the different methods used to determine the electrical resistivity of pore solution, which is then used to calculate the formation factor.

The pore solution resistivity is primarily dependent on the ionic composition and strength of the pore solution [9,10]. The main ionic species in cementitious pore solutions are sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻), and sulfate (SO₄²⁻) for plain ordinary Portland cement systems [11]. The concentrations of these ions are highly dependent on the cement chemistry, the curing conditions, the water to cement ratio (w/c), and the degree of hydration [11–13].

It is also important to note that the composition of cementitious pore solutions is also important to understand key mechanisms of ionic transport [6,14], concrete durability issues [15–20], and cement hydration [21,22]. Specifically, pore solution composition can be used as an input for thermodynamic modeling [23–25], to study mechanisms that affect concrete durability such as alkali-silica reaction and corrosion [9,26], and to obtain insights on the interactions between the liquid and the formation of solid phases occurring during hydration kinetics [27].

The electrical resistivity of a pore solution can be indirectly calculated by using a model developed by Snyder et al. [10] that estimates the pore solution conductivity from the concentration of ionic species in the pore solution. This model, further explained in Chapter 2 and Chapter 3, allows for the determination of the electrical resistivity of pore solution in a simple and straightforward manner that can potentially be programed in a Microsoft Excel sheet or software application.

From this model [10], an online calculator was developed by Bentz at the National Institute of Standards and Technology (NIST) that can be used to determine the pore solution resistivity from the mixture proportions and the alkali content of the cementitious materials [28]. Similar to the aforementioned model, this calculator is relatively simple and can easily be used for any mixture design and cement mill sheet. However, the application has some limitations for its use. The online calculator is further discussed in Chapter 3.

Extracted pore solutions have been studied to determine their resistivity by direct and indirect analysis [29]. Direct analysis consists of using a resistivity or conductivity meter to measure the resistivity. Indirect analyses consist of using chemical analysis of the extracted pore solutions to obtain the ionic concentration of the different species which then enables to use of the above-mentioned model to calculate the electrical resistivity of pore solution. Pore solution expression methods and related experimental parameters are further discussed in Chapter 3.

Pore solution resistivity can be tested using a resistivity meter [5]. This method typically uses a resistivity cell that consists of a small polycarbonate tube with two detachable metallic (platinum, copper, stainless steel) end plates [5,10]. The solution is injected inside the tube using a syringe and the resistance is then measured with a commercially available impedance/resistance meter and corrected using a geometry factor based on the geometry of the resistivity cell [5]. This method is further described in Chapter 2 and Chapter 3.

Indirect methods to calculate the pore solution resistivity from Snyder's model described previously involve obtaining the chemical composition of pore solution, specifically the ionic concentration of the main ions: sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻), and sulfate (SO₄²⁻). Some methods that have been used to determine the chemical composition of pore solution include:

- Inductively coupled plasma (ICP-MS/OES) [30]
- Ion chromatography (IC) [31]
- Atomic absorption spectroscopy (AAS) [32]

This thesis introduces the use of X-ray fluorescence (XRF) as an addition to the list of chemical analysis methods to determine the chemical composition of cementitious pore solutions. XRF is a non-destructive technique that detects the chemical composition of different materials [33]. XRF can be used to obtain both qualitative and quantitative compositional results for solid, liquid, and powdered samples, as well as bead samples prepared from powders and solutions. Details of how the XRF works are further described in Chapter 2 and Chapter 3.

XRF can be considered as a suitable alternative to the previously mentioned chemical analysis methods, as XRF is commonly used in the cement industry. Cement companies frequently use XRF to determine the chemical composition and for quality control and quality assurance of cement batches.

1.1 Research Objectives

The main objectives of this thesis are to:

- Develop a new method to measure the chemical composition of cementitious pore solution through a study of simulated and expressed cementitious pore solutions.
- To explore two different analysis methods using XRF: the fused bead method and the solution method.
- To determine experimental parameters, such as sample size, storage time, and experiment time, for both analysis methods and to compare the pros and cons of both methods.
- To compare the chemical composition and calculated electrical resistivity of cementitious pore solutions using XRF to estimated values from the NIST pore solution conductivity calculator.
- To develop two standard operating procedures to be included in a provisional document submitted to the American Association of State Highway and Transportation Officials, AASHTO-PP84, to be balloted in 2018.

1.2 Thesis Organization

This thesis consists of four chapters and two appendices.

The first chapter is a literature review of the use of electrical properties, specifically as they pertain to the calculation of formation factor, to study transport properties of concrete. In addition, the state-of-the-art on methods to determine the chemical composition of cementitious pore solutions is also discussed. This chapter also states the objectives for this thesis. Finally, this chapter serves to present the organization of the chapters in this thesis.

The second chapter of this thesis presents a published journal publication titled: "Using X-ray fluorescence to assess the chemical composition and resistivity of simulated cementitious pore solutions", co-authored by Dr. Prannoy Suraneni, Dr. O. Burkan Isgor, Dr. David Trejo, and Dr. W. Jason Weiss. This paper was published in the International Journal of Advances in Engineering and Applied Mathematics, Volume 3, pages. 1-8. The main objective of this publication is to study the feasibility of using XRF to study the chemical composition and predict resistivity of simulated pore solutions.

The third chapter presents the use of XRF to study the chemical composition and predict resistivity of expressed cementitious pore solutions. This chapter also presents a comparison of composition and resistivity between the XRF results and estimated values from the NIST calculator. In this chapter, the resistivity results are also compared to direct resistivity measurements with a resistivity meter. This chapter is in preparation to be submitted to a journal.

The fourth and last chapter summarizes the main findings from the previous chapters and presents the future steps for this research study. The first appendix consists of the standard operating procedure for the direct measurement of pore solution resistivity using a resistivity meter and resistivity cell.

The second appendix consists of the standard operating procedure for the use of X-ray fluorescence to calculate the pore solution resistivity from the measured chemical composition of cementitious pore solutions using the solution and fused bead method.

2 Using X-ray fluorescence to assess the chemical composition and resistivity of simulated cementitious pore solutions

2.1 Abstract

Ionic transport in concrete can be described using the formation factor, which is the ratio of the resistivity of the concrete and the pore solution resistivity. The pore solution resistivity may be assumed, directly measured, or computed from the pore solution composition. This paper describes an experimental investigation aimed at determining the feasibility of using X-ray fluorescence (XRF) to obtain the alkali concentrations of the pore solution which enable the calculation of pore solution resistivity. In order to do this, simulated pore solutions containing known amounts of sodium and potassium were prepared and analyzed using XRF. XRF was performed on two sample types: 1) the simulated solutions and 2) beads where the water from the solution is evaporated and the remaining material is fused using a fluxing agent. The compositions obtained experimentally from XRF are compared to known compositions to demonstrate the accuracy of the technique. In addition, the measured simulated pore solution resistivity was compared to the simulated pore solution resistivity calculated from XRF measurements. The results indicate that the composition had an average error of 0.50%while the estimated simulated pore solution resistivity had an average error of 10.95%. The results of this study indicate that XRF has the potential to be an alternative to the time consuming methods currently used to measure the composition of the pore solution.

2.2 Introduction

The properties of the pore solution of hydrating cementitious materials can provide insights into hydration behavior and ionic transport through the cementitious materials [11,24,29]. Some important properties of cementitious pore solutions are its ionic strength, pH, electrical resistivity, and their anionic and cationic composition [11].

The pore solution resistivity strongly influences transport of deleterious ions (such as chloride) through concrete [9]. Transport properties of concrete are controlled by its microstructure which can be described using the formation factor [6]. The formation factor, F, is inversely related to the product of pore volume and pore connectivity. It can also be defined as the ratio of the bulk electrical resistivity, ρ_b , and the pore solution resistivity, ρ_o , as shown in Equation 2.1 [4–8]:

$$F = \frac{\rho_b}{\rho_o}$$
 Equation 2.1

where:

 $\rho_b = \text{concrete bulk electrical resistivity in Ohm-m}$ $\rho_o = \text{pore solution electrical resistivity in Ohm-m}$ $\phi = \text{porosity}$ $\beta = \text{connectivity}$

Studies have shown that formation factor can be related to ionic diffusion coefficients, water absorption, and other transport properties for concrete and other porous media [4,6,9,34]. While measuring the bulk resistivity is relatively straightforward [35,36], measuring pore solution resistivity is more intricate since extracting pore solution, especially from hardened concrete, is somewhat challenging [9].

The pore solution resistivity is primarily related to the ionic composition of the pore solution. In cementitious systems made from ordinary Portland cements, in the absence of supplementary cementitious materials and chemical admixtures, the primary ionic species in the pore solution (concentrations larger than 0.02 M [30]) are sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻), and sulfate (SO₄²⁻). The concentrations of these ions depend on the cement chemistry, degree of hydration, and the water-to-cement ratio [11]. After approximately 1 day of hydration, typically, only Na⁺, K⁺, and OH⁻ are present in concentrations larger than 0.01 M [37], therefore, after

1 day, the pore solution resistivity is controlled by the concentrations of Na^+ , K^+ , and OH^- ions [38].

Research has been devoted to analytical and experimental analysis of cementitious pore solutions. The alkali content of the cementitious material has been used to predict the ionic concentrations of the resulting pore solution [12]. Pore solution resistivity can be calculated when the alkali contents of the pore solution are known [10]. An online calculator to determine pore solution resistivity from mixture proportions and cement alkali content is also available [39]. Extracted pore solution can also be studied to determine its resistivity using a resistivity meter [40,41].

Since the pore solution resistivity is heavily influenced by the alkali contents of the pore solution, the alkali contents can be used to indirectly calculate pore solution resistivity. Several methods could conceivably be used to determine alkali contents in a pore solution. Inductively coupled plasma mass spectrometry (ICP-MS) uses mass spectrometry to separate the ions from the ionization of a sample with inductively coupled plasma [30,42]. Ion chromatography (IC) is a technique that separates ionic species depending on the size and quantifies the concentration of each ion using a detector that measures the change in conductivity [43,31]. Atomic absorption spectroscopy (AAS) is another technique that uses the absorption of photons of light to measure the concentration of gas-phased ions [32].

This work evaluates whether energy dispersive X-ray fluorescence (XRF) spectrometry may be used to measure the alkali composition of the pore solution. In XRF testing, a sample is excited using a primary X-ray source. As a result of this, the primary X-ray displaces an electron from the K energy level. The atom then becomes unstable, which leads to an electron from the L energy level replacing the missing electron. The emitted energy from this replacement is known as the fluorescent or secondary X-ray and is detected in the XRF [44]. Each element is distinguished by its characteristic secondary X-ray energy, and therefore, XRF can be used to determine elemental composition of any material in a non-destructive manner [44]. XRF can be used to obtain both qualitative and quantitative compositional results for solid, liquid, and powdered samples, as well as bead samples prepared from powders and solutions [44].

The cement industry extensively utilizes XRF for quality control during the cement production process. Primary uses of the XRF include the analysis of the raw materials (limestone, clay) as well as the feed stream materials (gypsum, clinker). It is also used for quality control of cement [45]. In the laboratory, XRF is performed for determining oxide contents of cements and supplementary cementitious materials [45] and for determining chloride contents [46]. Although XRF has been performed on solutions in other studies [47], this is the first study performed using XRF on cementitious solutions, to the best of the authors' knowledge. If XRF can be shown to accurately measure pore solution composition, it would enable cement manufacturers to use a tool already at their disposal to provide more information about the cement for a wide variety of applications.

This study examines the use of XRF to study simulated pore solutions. Solutions of sodium hydroxide (NaOH) and potassium hydroxide (KOH) are prepared and analyzed using XRF. Ionic concentrations obtained from XRF performed on solutions and on beads prepared from solutions are compared with theoretical values. Resistivities calculated from ionic concentrations are compared with measured resistivity and theoretical resistivity.

2.3 Materials and Methods

2.3.1 Materials

Solutions were made by dissolving varying amounts of sodium hydroxide (>95% pure) and potassium hydroxide (>85% pure) pellets in deionized water. Since the objective is to measure pore solution composition, these solutions simulate a typical range of concentrations and pH for pore solutions from literature [11]; additionally these

solutions are comprised of about 90% by mass sodium and potassium, which compares well with cementitious pore solutions [11]. The calculated concentrations of sodium and potassium for the studied simulated pore solutions are shown in Table 2.1.

Solution (M _{NaOH} + M _{KOH})	[Na+] (mol/L)	[K+] (mol/L)
1.00 + 0.00	1.031	0.000
0.00 + 1.00	0.000	0.901
1.00 + 1.00	1.069	0.925
0.25 + 0.75	0.259	0.676
0.75 + 0.25	0.776	0.224
0.50 + 0.50	0.513	0.458
0.25 + 0.00	0.259	0.000
0.50 + 0.00	0.517	0.000

Table 2.1: Concentrations of Na⁺ and K⁺ in simulated pore solutions

2.4 Experimental Methods

2.4.1 XRF Calibration

A PANalytical Epsilon 3^{XLE} bench-top energy dispersive X-Ray fluorescence (XRF) spectrometer and software is used to analyze the composition of the solutions studied. The XRF was demonstrated to comply with ASTM C114 standards for chemical analysis of hydraulic cement [48] upon installation for bead samples. Figure 1 shows an image of the XRF machine.



Figure 1: (a) Closed and (b) Open energy dispersive XRF bench-top system

For each sample type (solution or bead), a calibration was performed with known standards (in this case, using varying concentrations of >99% pure sodium chloride (NaCl) and potassium chloride (KCl)) to accurately quantify the elements studied. The calibration is performed by measuring high purity samples with known concentrations and establishing a relationship between the measured intensities and concentrations.

In the XRF, different groups of elements are analyzed with varying condition sets such as the energy and current of the X-ray tube, testing time, and the resolution of the detector. The condition set for each element depends on their atomic weights. Elements with a lower atomic weight require longer times to excite their electrons and therefore require longer test times. For example, sodium, a lighter element, is excited with a measuring time of 300 seconds at 5 kV, 765 μ A; and potassium, a heavier element, is excited with a measuring time of 60 seconds at 12 kV, 584 μ A.

Each calibration standard has its own elemental energy spectrum, where intensity in units of counts per second of each element's fluorescent (or secondary) X-rays are plotted with respect to the emitted energies. Qualitative analysis shows each peak as the presence of a specific element, depending on the energy associated with the peak. Quantitative analysis uses the intensity or the net counts to quantify the concentration over a specific energy range. Figure 2 shows a representative energy spectrum for sodium and potassium. The spectrum of each calibration standard is carefully fitted to minimize error that can occur when there are overlapping energy peaks between Kalpha and K-beta peaks¹. The calibration standards are then combined into a regression line that fits the corrected intensities measured with the known concentrations of each standard. The XRF then uses this fitted regression line to match the measured intensities of an unknown sample with its respective concentration.



Figure 2: Representative energy spectrum for an application standard for sodium and potassium

This paper discusses two methods to use XRF for the analysis of the simulated pore solutions. The first method analyses solutions, whereas the second method analyses solutions fused into beads.

¹ K-alpha is the emission line due to an electron transition from the L-shell to the K-shell; considered the strongest energy spectral line. K-beta is the emission line due to an electron transition from the M-shell to the K-shell.

2.4.2 Solution Sample Preparation and Analysis

Samples of solution were measured directly in a plastic container with a 4-micron thick polypropylene film base as shown in Figure 3. The 4-micron thick polypropylene film was chosen as it has good resistance against degradation at high pH values, which are typically encountered in cementitious pore solutions. The plastic containers consist of two concentric plastic cylinders, where the smaller cylinder is placed inside the larger one after placing a polypropylene film between both cylinders. The assembled plastic containers have an outer diameter of 35 mm. Figure 3 shows a step-by-step process of the assembly of the containers. After assembling the containers, solutions are placed in the containers and left on a dry paper towel for 2 minutes to ensure that the film has no leaks due the high pH of the samples that could potentially damage the XRF. The samples are then analyzed with the XRF solution application.



Figure 3: Step-by-step assembly of plastic containers with polypropylene film for solution XRF testing

2.4.3 Solution Bead Sample Preparation and Analysis

The preparation of the sample beads consists of combining 1 g of solution with 5 g of flux (consisting of 49.75% lithium metaborate, 49.75% lithium tetraborate, and 0.50% lithium iodide) in a platinum flat bottom crucible. The fluxing agent was selected to minimize potential peak overlap with elements of interest. After combining the solution with the fluxing agent, the sample is dried at 105° C for 90 minutes in a laboratory oven (to evaporate the water) and then fused at a temperature of 1050° C in a LeNeo Fluxer fusion device with a predetermined fusing program for 15 minutes. Figure 4 shows a

representative solution fused bead with a diameter of 30 mm. The sample is then analyzed with the XRF solution bead application.



Figure 4: (a) top and (b) side of a representative fused solution bead

2.4.4 Resistivity Calculations

The electrical resistivity for each simulated pore solutions was calculated using the model developed by Snyder et al. [10], that estimates the pore solution conductivity from the concentration of ionic species in pore solution. This method, shown in Equation 2.2, estimates the electrolyte conductivity, σ_{calc} , of pore solution as the weighted sum of the individual equivalent conductivities, λ_i , of each ionic species present. To find the equivalent conductivities of each species, the model takes into account the equivalent conductivity coefficient, G_i , from the literature. This model is reported to be accurate within 8% of the predicted conductivity for ionic strengths as high as 2 mol/L and for potassium to sodium molar ratios from 1:1 to 4:1 [10]. The pore solution electrical resistivity can be then directly calculated by taking the inverse of the electrolyte conductivity.

$$\sigma_{calc} = \sum_{i} z_i c_i \lambda_i$$
 Equation 2.2a

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i I_M^{1/2}}$$
 Equation 2.2b

where:

 σ_{calc} = electrolyte conductivity of a single ionic species in S/m

 $\lambda_i = equivalent$ conductivity of a single ionic species in $cm^2 \; S/mol$

 z_i = valence concentration of a single ionic species

- $c_i = molar$ concentration of a single ionic species in mol/L
- λ_i° = equivalent conductivity of an ionic species at infinite dilution in cm^2 S/mol
- G_i = empirical conductivity coefficient of a single ionic species in (mol/L)^{-1/2}

 I_M = ionic strength (molar basis) in mol/L

i = a single ionic species

2.4.5 Measuring Resistivity

The simulated pore solution resistivity was tested using a method for directly testing resistivity using a resistivity meter [49]. This method uses a resistivity cell that consists of a 25.4 mm long, 9.525 mm in diameter polycarbonate tube with two detachable stainless steel end plates. The solution is injected inside the tube using a syringe to make sure the tube has no air bubbles. The resistance is then measured at a frequency between 1 and 10 kHz. To calculate the resistivity, the resistance is multiplied by a geometry factor based on the geometry of the resistivity cell. Experimental measurements on the simulated solutions were tested at a frequency of 7 kHz. From the resistivity meter, the resistance value in Ohms was obtained for each simulated pore solution. This resistance value was corrected by a geometry factor of 0.002805 m, based on the cross-sectional area (71.26 mm²) divided by the length (25.4 mm) of the resistivity cell tube.

2.5 Experimental Results

2.5.1 Ionic Concentrations

The XRF testing yields results in parts per million, therefore theoretical densities [50] were used to calculate the concentration of each ionic species in moles per liter. Figure 5a shows a comparison of the concentrations obtained from the solution and bead analysis with theoretical concentrations for sodium. Sodium concentrations measured using XRF show a strong correlation with the theoretical sodium concentrations (a nearly 1:1 relation with high correlation ($R^2 > 0.99$) for both methods). The potassium concentrations (Figure 5b) measured with both XRF solution and beads also show a strong correlation to the theoretical potassium concentrations with a nearly 1:1 relation with high correlation ($R^2 > 0.99$) for both methods. Table 2.2 shows the linear regressions for XRF solution and bead from the sodium and potassium concentration gives values slightly higher than the theoretical values, whereas XRF results from beads gives values slightly lower than the theoretical values.

Table 2.2: Fitted line regressions of sodium and potassium using XRF solution and

	XRF S	olution	XRF	Bead
[Na+]	y = 1.005x	$R^2 = 1.00$	y = 0.966x	$R^2 = 1.00$
[K+]	y = 1.002x	$R^2 = 1.00$	y = 0.977x	$R^2 = 1.00$

bead



Figure 5: Measured (a) sodium and (b) potassium ionic concentrations of simulated pore solutions using XRF solutions and beads compared to theoretical ionic concentrations. The dashed line represents a 1:1 correlation.

Table 2.3 shows the percent errors between the ionic concentration values obtained with both XRF solution and bead compared to the theoretical ionic concentrations. The error averages 0.50% and the highest error is 1.11%. For both sodium and potassium, the error increases as the sodium or potassium amount in the solution increases. Along with the results previously shown Figure 5, these numbers show that both methods can be used to accurately measure ionic concentrations of sodium and potassium in simulated pore solutions.

Solution	Percent E	Crror (%)	Percent E	Crror (%)
$(\mathbf{M}_{N_{2}}\mathbf{O}\mathbf{H} + \mathbf{M}_{K}\mathbf{O}\mathbf{H})$	XRF Solution	Concentration	XRF Bead C	oncentration
	[Na+]	[K +]	[Na+]	[K+]
1.00 + 0.00	1.02	0.00	1.01	0.00
0.00 + 1.00	0.02	0.91	0.03	0.88
1.00 + 1.00	1.11	0.92	1.01	0.90
0.25 + 0.75	0.25	0.68	0.25	0.66
0.75 + 0.25	0.79	0.22	0.76	0.21
0.50 + 0.50	0.50	0.46	0.50	0.45
0.25 + 0.00	0.25	0.00	0.25	0.00
0.50 + 0.00	0.48	0.00	0.51	0.00

Table 2.3: Percent error of ionic concentration for XRF solution and bead with respect to theoretical ionic concentrations

2.5.2 Electrical Resistivity

The results from the resistivity measurements and the calculated resistivity from the XRF solutions and bead methods, and resistivity values found in literature are presented in Table 2.4.

Solution (М _{NaOH} + Мкон)	Measured Resistivity (Ohm-mm)	XRF Solution Resistivity (Ohm-mm)	XRF Bead Resistivity (Ohm-mm)	Resistivity from Literature [51], [52] (Ohm-mm)
1.00 + 0.00	59.52	58.10	58.49	55.94
0.00 + 1.00	55.12	57.51	57.94	52.53
1.00 + 1.00	29.38	31.92	33.57	N/A
0.25 + 0.75	50.42	58.70	59.82	N/A
0.75 + 0.25	50.49	57.04	59.35	N/A
0.50 + 0.50	49.81	58.52	59.00	N/A
0.25 + 0.00	192.59	206.80	202.33	193.02
0.50 + 0.00	98.12	113.58	107.01	100.90

Table 2.4: Measured and calculated resistivity values

The percent error between the XRF solution and bead resistivity with respect to the measured resistivity for the sample set is shown in Table 2.5. The error values range from 2.39% to 18.64%, and are on average 10.95%. While experimental errors in the resistivity measurements and the XRF measurements may contribute to these values, it is also noted that computing electrical resistivity from the ionic concentration approximates an empirical conductivity coefficient, which can lead to additional error. It is also likely that the impurities in the sodium hydroxide (> 95% pure) and potassium hydroxide (> 85% pure) could contribute to the error, and studies with purer materials are currently underway. It should be noted that the measured resistivities and resistivities calculated from XRF are consistently greater than the measured resistivity values.

Solution	Percent Error (%)	Percent Error (%)
$(\mathbf{M}_{\mathbf{NaOH}} + \mathbf{M}_{\mathbf{KOH}})$	XRF Solution Resistivity	XRF Bead Resistivity
1.00 + 0.00	2.39	1.73
0.00 + 1.00	-4.32	-5.12
1.00 + 1.00	-8.63	-14.28
0.25 + 0.75	-16.43	-18.64
0.75 + 0.25	-12.97	-17.53
0.50 + 0.50	-17.49	-18.45
0.25 + 0.00	-7.38	-5.06
0.50 + 0.00	-15.76	-9.07

 Table 2.5: Percent error of calculated resistivity measurements for XRF solution and bead with respect to the measured resistivity values

The calculated and measured resistivity values for the simulated pore solutions are plotted in Figure 6; results show an almost 1:1 relation with high correlation ($R^2 > 0.98$) for both methods. This relationship reinforces the validity of the XRF for use in measuring electrical resistivity of pore solutions.


Figure 6: Calculated resistivity based on ionic conductivities compared to measured resistivity with a resistivity meter. The dashed line represents a 1:1 correlation.

The calculated resistivities were also compared with measured and calculated resistivities from the study in which the used model was proposed [10]. This was done two samples $(1.0 \text{ M}_{\text{NaOH}} + 1.0 \text{ M}_{\text{KOH}}, 0.5 \text{ M}_{\text{NaOH}} + 0.5 \text{ M}_{\text{KOH}})$ since both studies tested the same samples. The error from this comparison matched the 8% error reported in the earlier study [10].

2.5.3 Application of XRF to study Cementitious Pore Solutions

From the results presented earlier, it has been shown that XRF can be used to determine elemental concentrations (sodium and potassium) and electrical resistivity in simulated pore solutions for solutions and beads. We are currently working on extending these results to extracted cementitious pore solutions, to study if the XRF can be used to determine elemental concentrations and electrical resistivity of extracted pore solutions. It should be noted that both XRF solution and bead techniques can be used to analyze early age pore solutions due to the relatively large amount of solution that is

usually extracted. However, for later ages, the amount of solution obtained is very small [29], therefore, only the XRF bead technique can be used to analyze later age pore solutions. Moreover, the XRF bead technique allows the fused bead sample to be maintained for a longer period of time for later testing, if required.

Since XRF is commonly used in cement companies, the authors envision that the XRF technique presented in this study could potentially be implemented in cement companies to obtain the time dependent pore solution ionic composition of a cement batch; information that could then be included in the mill sheet to calculate the formation factor of a cementitious mixture at a given water-to-cement ratio and degree of hydration (or age) for potential use in specifications like that of AASHTO PP-84 [53].

Although in this study only sodium and potassium concentrations have been determined, the XRF can be used to determine nearly any elemental concentrations in the pore solution. This suggests the use of XRF for applications such as:

- the determination of chloride in pore solutions, which can be used to quantify free chloride [54] and for studies of the formation of calcium oxychloride [55];
- the determination of calcium and aluminum in pore solutions, which affect the dissolution kinetics of cementitious phases [21,22,56];
- the determination of the effect of chemical admixtures [30,38], and supplementary cementitious materials [24,57] on pore solution composition.

2.6 Conclusions

This paper has shown that X-ray fluorescence (XRF) can be used to experimentally determine sodium and potassium concentrations in simulated pore solutions. The testing was performed on solutions as well as samples where solution was fused into beads. The use of glass beads enables a smaller volume of pore solution to be tested. In addition, the beads enable the samples to be maintained for an extended period of

time for multiple testing as desired. Experimental measurements demonstrated that XRF was capable of determining the concentration with a 0.50% error for the solutions and the beads. Resistivity calculated from the ionic concentrations of sodium and potassium has an average error of 10.95%.

2.7 Acknowledgements

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3 Determination of chemical composition and electrical resistivity of expressed cementitious pore solutions using X-ray Fluoresence

3.1 Abstract

Ionic transport in concrete can be described by the formation factor, which is defined as the ratio of the resistivity of the concrete and the resistivity of the pore solution. The calculation of formation factor, requires a knowledge of pore solution resistivity. The goal of the study is to explore the use of X-ray fluorescence (XRF) to determine pore solution composition. The pore solution composition is then used to calculate the pore solution resistivity. Resistivity measurements are compared with the resistivity that is computed based on the chemical composition results from the XRF. The influence of test parameters on the XRF results is explored. The results indicate that XRF can be used to accurately calculate the resistivity of pore solution from the composition detected by the XRF. Overall, XRF is a potentially attractive method when compared to current methods to determine the pore solution composition due the availability of XRF in the industry and the reductions in testing time and cost.

3.2 Introduction

The chemical composition of the liquid phase in concrete, or pore solution, strongly influences key mechanisms of ionic transport [6,14], concrete durability [15–18,20], and cement hydration [22,58]. Specifically, pore solution analysis is often used to obtain information about hydration kinetics [58], formation of the hydrated solid phases [27], calibration inputs for thermodynamic models [23,24], and to describe deleterious mechanisms that reduce the durability of concrete [15–18,20,26]. Concrete durability related issues such as alkali-silica reaction (ASR) [15,16], and corrosion [17,18,20] are examples of deleterious mechanisms that are correlated to the pore solution composition.

The chemical composition of the pore solution can be used to determine the pore solution resistivity. The pore solution resistivity can then be used to calculate the formation factor (*F*). The formation factor describes the concrete microstructure and transport of ions through the concrete (for example, chloride ingress, which lead to corrosion). The formation factor has been previously related to ionic diffusion coefficients [6,9,59], water absorption [60], permeability [61], and other transport properties [2,14,41,62] that determine the durability of a concrete system. The formation factor (*F*) is defined as the ratio between the concrete bulk electrical resistivity (ρ_b) and the pore solution electrical resistivity (ρ_o) and the inverse of the porosity (ϕ) and the connectivity (β) of the microstructure, as shown in Equation 3.1 [4, 8,63–66]:

$$F = \frac{1}{\phi\beta} = \frac{\rho_b}{\rho_o}$$
 Equation 3.1

where:

 $\rho_b = \text{concrete bulk electrical resistivity in Ohm-m}$ $\rho_o = \text{pore solution electrical resistivity in Ohm-m}$ $\phi = \text{porosity}$ $\beta = \text{connectivity}$

The primary pore solution properties of interest are its ionic strength, pH, electrical resistivity, and the ionic composition [4,6,9,34]. The pore solution composition for an ordinary Portland cement paste primarily consists of sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻), and sulfate (SO₄²⁻) ions at concentrations higher than 0.02 M [30]. The concentrations of these ions in pore solution primarily depend on the cement or cementitious materials chemistry, degree of hydration and degree of reactivity, curing conditions, and the water-to-cement ratio [11]. Typically, after approximately 1 day of hydration, the most significant ions present in concentrations larger than 0.1 M in the pore solution are Na⁺, K⁺, and OH⁻ [37]. Therefore, after 1 day, the pore solution resistivity is predominantly controlled by the concentrations of Na⁺, K⁺, and OH⁻ ions [37,38].

Methods have been developed to directly and indirectly determine the pore solution composition and resistivity [9,10,28,30,67,68]. An online calculator was developed by Bentz at the National Institute of Science and Technology (NIST) which enables the pore solution resistivity to be computed based on only the mixture design and mill certificate of the cementitious materials used [28]. Direct measurements of chemical composition are typically performed using inductively coupled plasma spectroscopy (ICP) [30,42], ion chromatography (IC) [31], titration [68], and atomic absorption spectroscopy (AAS) [32]. These types of measurements are time consuming and each ionic species is usually tested separately; therefore, a combination of test methods and samples is needed to obtain a complete characterization of the main ionic species in pore solution.

A previous study examined the use of energy dispersive X-ray fluorescence (XRF) to determine the ionic composition and resistivity of solutions made from dissolving sodium hydroxide (NaOH) and potassium hydroxide (KOH) in deionized water at varying concentration levels [69]. The concentrations of the sodium (Na⁺) and potassium (K⁺) ions could be accurately determined using XRF. The concentration of the hydroxide (OH⁻) ions was then calculated based on principles of electrical charge balance. The electrical resistivity was then calculated using the model by Snyder et al. [10] and compared to resistivities measured using a resistivity meter. It was concluded that both ionic composition and resistivity of the simulated pore solutions were accurately obtained using the XRF with an average error of 0.50 % for the ionic composition results and an average error of 10.95 % for the resistivity.

This study specifically aims to further examine the use of XRF to study the chemical composition and resistivity of early age expressed pore solutions. Pore solutions were expressed from a plain cement paste at several ages up to 7 days. The influence of sample size and pore solution storage duration on the XRF results was also evaluated in order to experimentally determine optimum testing parameters to be used. The ionic

composition and resistivity values obtained using the various methods are compared to each other.

3.2.1 XRF Background

XRF is based on the principle of exciting a sample using a primary X-ray source. The primary X-ray beam displaces an electron from the lowest energy electron level or K energy level of an atom. The atom then becomes unstable and as a result, an electron from a higher energy electron level (or L energy level) replaces the missing electron. The emitted energy from this replacement is known as the fluorescent or secondary X-ray and this secondary X-ray is consequently detected in the XRF [44]. Each element has its own characteristic secondary X-ray energy, which can then be used to identify the elemental composition of any material in a non-destructive manner. This method can be used to obtain both qualitative and quantitative analysis for solid, powdered, liquid, and fused samples [44].

Currently, the cement industry uses XRF extensively for quality control and quality assurance throughout the cement manufacturing process. XRF is primarily used to analyze the chemical composition of the raw materials (limestone, clay), the feed stream materials (clinker, gypsum), and the final product (Portland cement) [45,70]. While a previous study examined the feasibility of using XRF for simulated cementitious pore solutions [69], this study focuses on analyzing the chemical composition and electrical resistivity of expressed cementitious pore solutions. This method would enable cement manufactures to use a tool already at their disposal to provide more information about the cement and its properties for a wide variety of applications.

Since the XRF testing equipment is available at many cement manufacturing companies and research laboratories, the use of XRF to study pore solution could provide accurate information about the chemical composition and resistivity for multiple applications for a lower cost and shorter testing time than other methods. For

example, when comparing preparation and testing time between a commonly used method such as ICP, testing time is reduced from 50 minutes per sample for ICP to 8 minutes per sample for XRF. This method could extend the applications for XRF and could potentially be implemented in industry fairly quickly.

3.3 Materials

3.3.1 Materials

An ordinary Type I/II cement was used to prepare cement pastes in this study. The cement had a Blaine fineness of 380 m²/kg and a specific gravity of 3.15. The potential phase composition from the mill sheet is 60.1 % C₃S, 10.1 % C₂S, 8.2 % C₃A, 8.2 % C₄AF (using cement chemistry notation, C = CaO, $S = SiO_2$, $A = Al_2O_3$, and $F = Fe_2O_3$). The oxide contents of the cement is shown in Table 3.1.

Material	Cement	
Oxide	Mass %	
Na ₂ O	0.26	
MgO	3.39	
Al_2O_3	4.77	
SiO ₂	19.11	
SO ₃	3.21	
Cl	0.03	
K ₂ O	0.78	
CaO	62.62	
Fe ₂ O ₃	2.88	

Table 3.1: Oxide contents of the cement from XRF

3.3.2 Mixture design and mixing

The expressed pore solutions were studied for a mixture with water to cement ratio (w/c) of 0.36 at several different ages (degrees of hydration). The mixtures consisted of a plain cement system (OPC) prepared using 200.0 g of water and 555.6 g of cement. Mixing was performed following ASTM C305-14. The paste samples were mixed and cast in 50.8 mm x 101.6 mm plastic cylinders. These samples were sealed and placed in an environmental chamber with a set relative humidity and a temperature of 50 ± 2 % and $23 \pm 1^{\circ}$ C. Pore solutions were extracted from all mixtures at different ages to study the evolution of the pore solution through time. The following ages were chosen for this study: 10 min, 1 h, 3 h, 5 h, 7 h, 12 h, 1 d, 3 d, 5 d, and 7 d.

After the paste samples were cast, at the time of expression, the samples were crushed and their pore solution was then expressed using a mechanical or gas pressure device. All of the pore solutions expressed from the OPC system were immediately analyzed by XRF using samples of differing sample size (sample mass: 1 g, 2 g, total g), in order to determine the influence of the sample size on the results. The resistivity of the solution samples was also directly measured using a resistivity meter in combination with a resistivity cell. The influence of the storage time after expression on the composition and resistivity of the pore solutions was also studied on three samples (ages: 1 h, 1 d, 7 d). Measurements were performed at 6 h, 1 d, and 7 d from the time of expression. After determining the optimum sample size and time for testing, all other samples were tested using a sample size equal to the total sample mass, which was recorded and typically ranged from 2.5 g to 4 g, immediately after expression. Finally, the resistivity values obtained from the XRF and from the resistivity meter were compared to calculated values using the NIST calculator for pore solution resistivity.

3.4 Experimental Methods

3.4.1 Pore Solution Expression

Pore solutions at ages of 30 min, 1 h and 3 h were expressed from the paste specimens using a Millipore pressurized filtration system. The system used a cellulose membrane filter with a 0.45 µm average pore size to prevent any contamination from unreacted cement grains. The pressure was set using nitrogen gas with a maximum pressure of 225 kPa. Pore solutions expressed at ages later than 3 hours were expressed from paste specimens using a highly pressurized mechanical pore press device shown in Figure 7 originally designed by Longuet et al. [71] and modified by Barneyback and Diamond [29].



Figure 7: (a) Mechanical pressure expression system and (b) system schematic used for the pore solution expression

At the time of expression, paste samples were demolded and crushed in a plastic bag to minimize moisture loss. The crushing continued until the fragments were no larger than 9 mm in diameter. The crushed specimen was then placed inside the pore press device, where the pore solution was expressed by applying a mechanical load with a compression testing machine (load_{max} = 890 kN; load rate = 2.2 - 2.9 kN/s). The expressed pore solutions were collected in 6 mL plastic vials and transferred into 6 mL

syringes for the resistivity and XRF measurements. Once the measurements were performed, the samples were moved back inside the syringes and stored inside an environmental chamber at 5 ± 1 °C. The syringes provide a sealed storage condition to minimize contact with air and reduce the potential for carbonation and evaporation [72].

3.4.2 Resistivity Measurement

The expressed pore solution resistivities were tested by directly measuring the resistance of the sample using a Giatec RCON2 concrete bulk resistivity meter [73]. The resistance of the pore solution samples is measured by using a resistivity cell that consists of a 25.4 mm long, 9.525 mm diameter polycarbonate tube with two detachable brass end plates shown in Figure 8. The solution was injected inside the tube through on of the two 3.18 mm in diameter circular ports using a syringe. To ensure that there were no air bubbles within the tube, the resistivity cell was periodically tilted to direct the air bubble in the tube to one of the ports. The resistance value was then measured (Ohms). The frequency of 7 kHz was chosen in order to minimize the phase angle or imaginary component of the impedance [41].



Figure 8: Resistivity cell set up (a) unassembled and (b) assembled to test the pore solution resistivity with the resistance meter

To calculate the resistivity, the resistance was then multiplied by a geometry factor based on the resistivity cell geometry. For this particular resistivity cell, the measured resistance values were corrected by a geometry factor of 2.805 mm, which was calculated from the cross-sectional area (71.26 mm²) divided by the length (25.4 mm) of the resistivity cell tube. Additionally, all resistivity of all samples were corrected from their measured temperatures to a reference temperature of 25 °C [74]. The Arrhenius equation was used to make this correction with a measured activation energy (E_{a-cond}) value of 11.5 kJ/mol, which is consistent with activation energy values from literature for fluids [75]. The measured activation energy was calculated by testing one representative sample (1 d) at different temperatures, ranging from 19 °C to 26 °C.

3.4.3 XRF Measurement

A PANalytical Epsilon 3XLE bench-top energy dispersive XRF spectrometer and software were used in this study to analyze the chemical composition of the expressed cementitious pore solutions. The expressed pore solutions were analyzed using a pre-calibrated testing application that specifically detects the main ions desired for this study and that can be detected using XRF: sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), and sulfide (S²⁻). It is assumed that the sulfide ions correspond to the sulfate (SO4²⁻) in the system; therefore, a simple stoichiometry calculation yields the concentration of the sulfate. A charge balance calculation yields the concentration of the hydroxide ions (OH⁻) in the system.

Calibration was performed with known standards (using varying concentrations of >99% pure sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl₂) and aluminium sulfate (Al₂(SO₄)₃)) to accurately quantify the elements studied. The calibration was performed by measuring these samples with known concentrations and establishing a relationship between the measured intensities and concentrations. A detailed description of the calibration and measurement is described elsewhere [69].

3.4.4 Solution Sample Preparation

The expressed pore solutions were measured directly in a plastic container with a 4micron thick polypropylene film base. The 4-micron thick polypropylene film was selected instead of a mylar film as it has good resistance against degradation at high pH values, which are typically encountered in cementitious pore solutions [11]. The assembled plastic containers have an outer diameter of 35 mm. After assembling the containers, solutions are placed in the containers and left on a dry paper towel for two minutes to ensure that the film has no leaks that could potentially damage the XRF. The samples are then moved inside the XRF and analyzed.

3.4.5 Calculating Resistivity from XRF

The electrical resistivity for each expressed pore solution was calculated using the model developed by Snyder et al. [10]. This model estimates the pore solution conductivity using the concentration of the primary ionic species in pore solution (Na⁺, K⁺, OH⁻, Ca²⁺, SO₄², and Cl⁻), as shown in Equations 3.2 and 3.3. This model was found to be accurate within 8% of the predicted conductivity for ionic strengths as high as 2 mol/L and for potassium to sodium molar ratios from 1:1 to 4:1 [10]. The electrical resistivity can be then directly calculated by taking the inverse of the conductivity.

$$\sigma_{calc} = \sum_{i} z_i c_i \lambda_i$$
 Equations 3.2

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i I_M^{1/2}}$$
 Equations 3.3

where:

$$\begin{split} \sigma_{calc} &= \text{electrolyte conductivity of a single ionic species in S/m} \\ \lambda_i &= \text{equivalent conductivity of a single ionic species in cm}^2 \text{ S/mol} \\ z_i &= \text{valence concentration of a single ionic species} \\ c_i &= \text{molar concentration of a single ionic species in mol/L} \end{split}$$

 λ_i° = equivalent conductivity of an ionic species at infinite dilution in cm² S/mol G_i = empirical conductivity coefficient of a single ionic species in (mol/L)^{-1/2} I_M = ionic strength (molar basis) in mol/L

i = a single ionic species

3.4.6 Effect of Sample Size

As a paste or concrete sample hydrates, the volume of pore solution yielded from the expression decreases. Therefore, the size of the sample of pore solution that can be tested accurately in the XRF was studied. All samples were tested using the XRF at 1 g, 2 g, and the total expressed mass. The earlier the sample age, the higher the amount of pore solution is expressed and tested. However, after 1 day of hydration and assuming no supplementary cementitious materials (or chemical admixtures) were added, the typical amount of pore solution expressed for a sample cured in sealed conditions is 2 g or less.

3.4.7 Effect of Storage Time

Previous studies have shown that expressed pore solutions must be kept in conditions that prevent carbonation, dilution, or evaporation, which can subsequently change the composition and integrity of the sample [72]. Most studies suggest that samples are immediately tested to minimize any changes in the composition of the samples [24]. Therefore, the influence of the storage conditions on samples was studied. Samples were stored in sealed syringes to prevent any air contact and in an environmental chamber at 5 ± 1 °C. Three samples from the plain cement system (OPC 1 h, 1 d, 7 d) were chosen to be re-measured after 6 h, 1 d, and 7 d of being expressed to determine the influence of storage time on the composition and resistivity.

3.4.8 NIST Calculator Comparison

Bentz at NIST developed an online calculator [10,39] that can calculate the conductivity (inverse of resistivity) of pore solutions from the mixture proportions and chemical composition of the cementitious materials used [28]. This model makes an assumption that 75 % of the alkali oxides in the cementitious material (cement, silica fume, slag, and fly ash) are released at any given degree of hydration into the pore solution and that only the alkalis paired with hydroxide (OH⁻) significantly influence the resistivity of the pore solution [39]. The calculator uses these estimated concentrations of sodium (Na⁺), potassium (K⁺) and hydroxide (OH⁻) to calculate the conductivity (inverse of resistivity) of the pore solution using Equations 3.2 and 3.3 [10].

The pore solution resistivity calculated from the calculator was compared to the measured resistivity values from the meter and calculated resistivity values from the XRF. The mixture proportions and cement chemistry, specifically the alkali content from XRF, were input in the calculator. For each age, a specific degree of hydration was calculated from previous models, initially developed by Parrot and Killoh [76] and further developed by Lothenbach [77,78]. The input parameters for this model are the w/c ratio, cement compound composition, and the Blaine fineness of the cement, which were found in the cement mill certification report. The percent hydrated phases and the degree of hydration are calculated with respect to the age.

3.5 Experimental Results

3.5.1 Ionic Concentration vs. Sample Size Tested

Figure 9 shows the representative behavior of the ionic concentration for one age (1 d) with respect to the sample size (mass) tested. The dashed lines represent the average concentration value for each ion. It is observed that the sample size does not

significantly affect the concentration for all ions, where the average coefficient of variation (COV) of Na⁺, K⁺, OH⁻, Ca²⁺, SO4²⁻ was of 2.74 %, 0.35 %, 1.43 %, 17.19 %, and 0.58 % respectively. The relatively high coefficient of variation for the Ca²⁺ concentration is likely due to the small concentrations (< 0.03 mol/L) detected for this ionic species. Moreover, it was also observed from the data that the COV of Ca²⁺ increased with age, as the concentration of Ca²⁺ is further reduced. As these concentrations are quite low, the Ca²⁺ does not contribute significantly to the electrical resistivity of pore solution compared to other ions in solution. Therefore, since the COV for all ions excluding Ca²⁺ are all considerably small, the authors suggest that a minimum mass of 1 g for testing in the XRF can be used. This allows for small samples to be tested without the need to dilute the sample, which may lead to greater error in the analysis.



Figure 9: Ionic concentration versus sample size tested for all ions at 1 day. The dashed lines are the average concentrations for each ion.

The resistivity values calculated from the XRF for all sample sizes tested were compared with the measured values with a resistivity meter. A summary of the linear regressions for each sample size set and their respective percentage errors is shown in Table 3.2. The average percentage error decreases as the mass of the sample tested increases. However, the errors for 1 g and 2 g are below 8 % and suggest that while using a greater sample mass is beneficial, testing a sample size as low as 1 g would still yield accurate results.

Table 3.2: Fitted linear regressions for the calculated resistivity with respect to the measured resistivity for each sample size tested using XRF at various ages, where y is the calculated resistivity from XRF concentrations and x is the measured resistivity using the resistivity meter.

Sample Mass (g)	Fitted Regression Line	R-squared	Percent Error (%)
1	y = 1.071x	$R^2 = 0.974$	7.38
2	y = 1.069x	$R^2 = 0.977$	7.19
total	y = 1.021x	$R^2 = 0.997$	2.92

The main challenge observed by the authors when analyzing a sample with a mass of 1 g was that the sample had to be carefully dispersed at the bottom of the container for the XRF due to the limited amount of solution with respect to the surface area of the container. Therefore, for practical purposes, the authors recommend to use a minimum mass of 2 g to ensure that the pore solution is thoroughly distributed at the bottom of the container.

3.5.2 Ionic concentration vs. Storage Time

The ionic concentrations of three samples selected (OPC expressed at ages: 1 h, 1 d, 7 d) were measured at four various times after the sample was expressed. The results for one representative sample (1 d) are shown in Figure 10, where the dashed lines represent the average concentration of each ion.



Figure 10: Ionic concentration of the main ions with respect to time for a representative sample at an expressed age of 1 d. The dashed lines are the average concentrations for each ion.

No significant change was observed in the measured ionic concentration of the samples when analyzing the sample at time of expression and at 6 h, 1 d, and 7 d after the time of expression. The COV of Na⁺, K⁺, OH⁻, Ca²⁺, and SO4²⁻ were 2.21 %, 0.50 %, 2.26 %, 17.83 %, and 1.75 %, where again, excluding Ca²⁺ ions, the COV are considerably small. As explained earlier, the Ca²⁺ ion concentration does not contribute significantly to the electrical resistivity of pore solution compared to other ions in solution. This means that there is no significant change in the ionic concentration and resulting pore solution resistivity with respect to testing time under the storage conditions presented herein, where the pore solution is stored in sealed syringes with no air bubbles at 5 ± 1 °C, which allows for a sample to be re-tested and preserved after expression.

3.5.3 Ionic Concentration and Electrical Resistivity

Since the two main experimental parameters were defined, the ionic concentration and electrical resistivities were analyzed using a sample size of the total sample mass tested immediately after expression. The total sample mass was recorded and typically ranged from 2.5 g to 4 g.

The evolution of the ionic concentration of the ions of interest is show in Figure 11. The evolution of the ionic species broadly follows classical cement hydration kinetics curves [27,37]. The rapid dissolution of the main ions into the pore solution is shown from the relatively high concentrations of Na⁺, K⁺, OH⁻, Ca²⁺, and SO4²⁻ at 10 minutes [24,27,30,77]. Ionic concentrations are roughly constant from an age of 30 minutes until 3 hours, which may be considered to be the induction period. Hydration starts to accelerate after approximately 3 hours and around this time, the ionic concentrations change. The Na⁺ and K⁺ ionic concentrations increase due to the release of alkalis from the clinker [27,77]. The concentration of SO_4^{2-} ions decreases rapidly at around 8 to 10 hours. The depletion of the sulfates can be attributed to the reaction between the sulfate ions and the aluminate phases to form AFm and AFt phases, which occurs during the acceleration period [27]. The formation of CH and C-S-H causes the Ca^{2+} to decrease. And lastly, the OH⁻ concentration increases to conserve charge balance within the pore solution as the concentrations of SO₄²⁻ decreases and the concentrations of Na⁺ and K⁺ increase. The general trends and concentration ranges shown from analyzing the pore solution concentration using XRF are as expected from literature [11,24,38], where Na^+ , K^+ , and OH^- ionic concentrations steadily increase with time, whereas the Ca^{2+} and SO_4^{2-} ionic concentrations decrease with time.



Figure 11: Ionic concentrations from chemical analysis using XRF for (a) Na^+ , K^+ and OH^- and (b) SO_4^{2-} and Ca^{2+} at various ages

The measured resistivity values were compared to the calculated resistivities from the XRF samples. The results are shown in Figure 12. The comparison showed that the measured and calculated resistivities have a 1:1 linear relationship and high correlation ($R^2 = 0.997$). The percent error was also calculated with respect to the measured resistivity values. The average error of this data set was 2.92 %. This shows that XRF can be used to accurately determine the electrical resistivity of pore solution while also providing significant information about the ionic composition of pore solution.



Figure 12: Calculated resistivities using XRF versus measured resistivities using a resistivity meter. The dashed line represents a 1:1 correlation.

The evolution of the pore solution resistivity with age and with degree of hydration was examined and is shown in Figure 13. The pore solution resistivity starts from a relatively high value and then decreases over time, as seen in literature previously [41]. However, not many studies have examined the pore solution resistivity after 48 hours. It can be seen that after 48 hours, the pore solution resistivity reaches a relatively constant value in between 0.06 Ohm-m and 0.07 Ohm-m, which is consistent with the



behavior of the ionic concentrations reaching a constant value after 48 hours and up to 7 days (DOH > 59%), where the coefficient of variation (COV) is of 1.69 %.

Figure 13: Evolution of the pore solution resistivity (a) at different ages and (b) at different degrees of hydration (DOH)

A previous study suggested to use of 0.1 Ohm-m as an assumed pore solution resistivity for mature samples based on samples from different cement sources and cement blends [5]. However, the use of 0.1 Ohm-m as an assumed value is only an approximate value. A literature review on the concentrations for each ionic species was used to calculate a range of constant resistivities after 24 hours [24,25]. These calculated resistivities from the literature showed that the constant resistivity value after 24 hours can vary from 0.06 Ohm-m to 0.21 Ohm-m and is based on the cement chemistry (specifically the alkali content), water to cement ratio, curing conditions, and the addition of supplementary cementitious materials [9,24,25,37]. From this, it can be presumed that a single pore solution resistivity value can be used, as long as it is representative of the cementitious system.

3.5.4 NIST Calculator Comparison

The NIST calculator yields the ionic concentration of the main ions in pore solution (Na⁺, K⁺, and OH⁻ only) and conductivity (inverse of resistivity) (in S/m) after 1 d. A comparison between the ionic concentrations as calculated with the NIST calculator and the ones experimentally measured with XRF are shown in Figure 14. From this figure, it can be observed that both the Na⁺ and K⁺ ions are broadly similar, with an average error of -9.57 % for Na⁺ and 11.49 % for the K⁺. However, the NIST calculator overestimates the OH⁻ ion concentration with an average error of -25.02 % for samples with an age smaller than 12 h. This can be attributed to the fact that a significant amount of SO₄²⁻ ions are present in the solution up until 12-24 hours of age [11], which is not considered in the calculator. Therefore, a charge balance calculation based on the Na⁺ and K⁺ ionic concentration is not always appropriate for early age pore solution (12-24 h typically).





Figure 14: Ionic concentration of (a) Na⁺, (b) K⁺, and (c) OH⁻ from XRF compared to estimated concentrations from the NIST calculator.

A miscalculation of the OH^- ions and its subsequent effect on the resistivity can also be observed when comparing the resistivity values calculated from the XRF and estimated using the NIST calculator with respect to the measured (or true) resistivity values shown in Figure 15, keeping in mind that higher resistivity values correspond to samples at earlier ages (up to 7 h).



Figure 15: Calculated resistivity from XRF and estimated resistivity from the NIST calculator compared to the measured (true) resistivity from the meter. The dashes represent a 1:1 line.

The NIST calculator underestimates the resistivity of the pore solutions with an age before 12 hours by 20-70 %. This underestimation was also shown in a previous study, where the margin of error of 30 % was observed [41]. The average error between the calculated resistivity using XRF and estimated using the NIST calculator was 20.66 %. Hence, the authors believe that to validate the use of XRF compared to the NIST calculator, only the ionic concentration of Na⁺, K⁺, and OH⁻ after 24 hours should be taken into account.

For a data set containing only the results from the samples after 1 d, the average error between the XRF results and the NIST calculator results for the ionic concentrations of Na⁺ was -12.01 %, K⁺ was 10.89 %, OH⁻ was -4.21 %, and resistivity was 0.93 %. The errors decrease significantly for the OH⁻ ions and for resistivity when analyzing only the data after 24 hours, and remain relatively similar for Na⁺ and K⁺. Therefore, it is

suggested that the NIST calculator can be misleading at ages earlier than 24 h, as the estimated resistivity does not match the measured resistivity due to an overestimation of OH⁻ ions and the omitted effects of other ions in pore solution.

3.6 Conclusions

This paper explored the use of XRF to determine the chemical composition and electrical resistivity of expressed pore solutions. The influence of sample size and storage time of the solutions on the XRF results was studied. The sample size had little effect on the variation of ionic concentration and resistivity, as long as the bottom of the sample container was completely exposed to solution. In general, a minimum of 2 g of solution for testing is recommended for the sample geometry in this paper. It was also concluded that the storage conditions for pore solutions described previously guarantees that the pore solution will not change significantly for up to 7 d, allowing the solutions to be re-tested with no significant changes to the results.

A strong 1:1 correlation exists between the measured resistivities and calculated resistivities using XRF for expressed cementitious pore solutions, where results matched with a 1:1 relationship and high correlation with an R-squared value of 0.997 and an average percent error of 2.92 %. This shows that XRF can be used to accurately determine the electrical resistivity of pore solution, while also providing useful information about its ionic composition.

The expected ionic composition trends for the cementitious systems match results shown in literature. Therefore, it was concluded that using this tool can be used to study the pore solution chemical composition. The results from the NIST calculator for pore solution composition and conductivity (inverse of resistivity) were compared to the results from XRF. From this comparison, it can be concluded that XRF can accurately determine the electrical resistivity and ionic concentration of Na⁺, K⁺, and OH⁻. However, it was only applicable to samples expressed after 24 hours due to the significant presence of SO_4^{2-} in the pore solution at earlier ages, which are not considered in the online calculator.

Overall, this method could potentially enable cement manufactures to use a tool already at their disposal to provide more information about the cementitious pore solution and its properties, such as the chemical composition and resistivity, for numerous applications and at a lower cost and testing time than conventional methods.

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4 Conclusion

This thesis explored the use of X-ray fluorescence (XRF) to determine the chemical composition of simulated and expressed pore solutions. The electrical resistivity of the simulated and expressed pore solutions were calculated from the ionic concentrations detected by the XRF and compared to direct measurements using a resistivity meter. Each individual chapter studied different sample sets and different aspects of the method. Therefore, for the individual chapters, the following conclusions were drawn:

4.1 Conclusions from Chapter 2

This chapter explored the feasibility of using XRF to study the composition and resistivity of simulated pore solutions made from sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions at different concentrations. Samples were studied using two different sample geometries in the XRF – solution method and fused bead method. The main conclusions from this study were:

- The ionic concentrations of sodium and potassium detected by the XRF showed a strong 1:1 correlation ($R^2 > 0.99$) with the theoretical concentrations of the sodium and potassium ions of the simulated pore solutions.
- XRF can be used to experimentally determine the concentrations of the main cations in pore solution, sodium (Na⁺) and potassium (K⁺), where an average error of 0.50% was reported for both the solution method and the fused bead method.
- The calculated resistivities from the XRF ionic concentrations showed a strong 1:1 correlation ($R^2 > 0.98$) with the measured resistivities from the resistivity meter of the simulated pore solutions.

• The ionic concentrations of the simulated pore solutions detected by the XRF can be used to calculate the pore solution electrical resistivity, with an average error less than 11 % for both the solution method and the fused bead method.

4.2 Conclusions from Chapter 3

This chapter aimed to study the chemical composition and electrical resistivity of expressed cementitious pore solutions for an ordinary Portland cement system and the effects of sample size and storage time on the ionic concentrations detected by XRF. This chapter also compared the composition and resistivity between the XRF results and estimated values from the NIST calculator. The main conclusions from this study were:

- The calculated resistivities from the XRF ionic concentrations match the measured resistivities from the resistivity meter of the expressed pore solutions, where the average error was of 2.92 %.
- The expected ionic composition trends for the cementitious systems are conceptually comparable to results shown in literature. An increase in the alkali (Na⁺, K⁺, OH⁻) concentrations and decrease in the Ca²⁺ and SO₄²⁻ concentrations are shown, which are consistent with pore solution evolution trends reported in previous studies. Therefore, XRF can be potentially used to study the pore solution chemical composition.
- For the solution method:
 - The sample sizes studied had no significant influence on the ionic concentration detected by the XRF. However, a minimum sample size of 2 g of solution is recommended to test in order to fully expose the bottom face of the container to solution and to maintain a constant interaction depth.

- The storage time had no significant influence on the ionic concentration detected by the XRF. Using the storage conditions previously presented, pore solutions can be tested immediately after expression but can also be re-tested after 7 days with no significant changes to the ionic concentration results.
- The optimal storage solution for cementitious pore solutions consist of transferring the pore solution right after expression into sealed syringes (with no air bubbles) in a 5 °C \pm 1 °C chamber.
- XRF can accurately determine the electrical resistivity and ionic concentration of sodium (Na⁺), potassium (K⁺), and hydroxide (OH⁻) when compared to estimated resistivities from the NIST calculator for samples after 24 hours of expressed age.
- The NIST calculator overestimates the resistivity at early ages (up to 24 hours of expressed age) due to the significant presence of SO₄²⁻ in the pore solution, which are neglected in the online calculator.

Overall, this study shows that using XRF for expressed pore solution could potentially enable cement manufactures to use a tool already at their disposal to provide more information the chemical composition and resistivity of cementitious pore solutions for numerous applications and at a lower cost and testing time than conventional methods.

4.3 Further Research

• The expressed pore solution ionic concentrations detected by the XRF must undergo further comparison with a previously validated method to detect the concentrations such as ICP.

- This method could also be validated using thermodynamic modelling software like GEMS, which have been used before to model cement hydration and pore solution evolution over time.
- This study could potentially be expanded to other mixes with binary and ternary systems of OPC and different SCMs to study the effects of SCM addition on the electrical resistivity of pore solution.
- This method could be potentially used to:
 - Examine the role of the alkalinity of pore solution for alkali-silica reaction studies;
 - detect chloride concentrations for chloride binding and corrosion studies;
 - \circ study the composition of chemical admixtures and additives in concrete.

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6.1 Appendix 1

Standard Method of Test for Quantifying Electrical Resistivity of Cementitious Pore Solution

1. SCOPE

- 1.1 This test method covers the procedure for quantitative determination of the electrical resistivity of cementitious pore solution.
- 1.2 The values stated in SI units are to be regarded as the standard.
- 1.3 This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. REFERENCED DOCUMENTS

- 2.1 AASHTO Standard:
- 2.1.1 *TP-119-15*, Electrical Resistivity of a concrete cylinder Tested in a Uniaxial Resistance Test
- 2.1.2 *T* 358-17, Surface Resistivity Indication of Concrete's Ability to Resist Chloride Ion Penetration
- 2.1.3 XX-XX (Task 1.2c), Temperature Corrections for Resistivity Measurements using Activation Energy of Conduction

3. TERMINOLOGY

- 3.1 Pore solution: the liquid phase in concrete consisting of an aqueous solution containing several ionic species
- 3.2 Electrical resistivity: an intrinsic property that quantifies how strongly a material resists the flow of an electric current.

3.3 Formation factor: an empirical quantitative relationship between porosity, electrical resistivity, and saturation solution of a porous media based on Archie's law.

4. SUMMARY OF TEST METHOD

- 4.1 This test method covers the procedure for quantitative determination of the electrical resistivity of a solution (like a cementitious pore solution) using a resistivity meter and a cell.
- 4.2 The method consists of setting up a resistivity cell designed to test the resistance/impedance of a cementitious pore solution using a commercially available impedance meter or electrical resistivity meter. The resistivity is calculated from either the resistance and a geometry factor or the impedance, the phase angle, and a geometry factor based on the resistivity cell used.
- 4.3 The resistivity meter will yield either a resistance or an impedance value, *Z*, in Ohms, and/or a phase angle, φ , in degrees.
- 4.4 The temperature, *T*, of the pore solution is also recorded with a needle thermocouple to correct for temperature effects using a method in shown in AASHTO XX-XX (Task 1.2c).

5. SIGNIFICANCE AND USE

- 5.1 This test method is used for determining the electrical resistivity of extracted cementitious pore solutions. This can be used for example to calculate the formation factor of a concrete.
- 5.2 This technique serves as a simple, fast, and practical way to measure the electrical resistivity of pore solution using the same device that measures the bulk electrical resistivity of concrete (ASTM TP 119-15, T 358-17).

6. INTERFERENCES

6.1 Temperature conditions may interfere with the stability of the measurement. If the temperature of the sample changes more than 2% over a 3 second period, an inaccurate reading of the sample may occur. Make sure to report a resistance

measurement when the temperature is not changing as previously detailed. Overall, the measured values in this procedure must be corrected for temperature using a temperature correction procedure outline in AASHTO XX-XX (Task 1.2c).

7. APPARATUS

- 7.1 *Syringe and needle* 5mL disposable syringe and 1.6 mm x 25 mm (16Gx1'') attachable needle to inject the pore solution into the resistivity cell.
- 7.2 Resistivity cell— set up (an example is shown in Figure 16-17) consisting of a polycarbonate tube and two (2) stainless steel (316 stainless steel) end plates. The tube has a length of 25.40 mm (1.00''), an inner diameter of 9.53 mm (3/8''), an outer diameter of 12.70 mm (1/2''), and two (2) holes on the length of the tube with a diameter of 3.18 mm (1/8''). The two (2) stainless steel plates have circular milled out sections with a diameter of 12.70 mm (1/2'') of 3.18 mm to 6.35 mm depth (1/8'' to 1/4'' depth) to attach the tube and a screw (socket head cap screw, M4 X 20 mm) of the same stainless steel (316 stainless steel) fastened in each plate.



Polycarbonate Tube



Figure 16: Schematic of the resistivity cell components



Figure 17: Resistivity cell individual components

7.3 *Concrete Bulk Resistivity Meter*— AC measurement impedance meter with a frequency range of 1 Hz to 30 KHz to measure the electrical resistance of the pore solution with a precision of 0.01 Ohm.

Note 1— If the resistivity meter used does not provide resistance, use an appropriate conversion to report a resistance value for this procedure in Ohm.

- 7.4 *Alligator clips* to attach to the resistivity meter probes onto the electrical resistivity cell, compatible with the size of the probes of the resistivity meter used.
- 7.5 *Needle Thermocouple* to measure the temperature of the pore solution at the time of the electrical resistivity measurement (± 0.1 °C). The diameter of the thermocouple needle must be smaller than 3.175 mm (1/8").
- 7.6 *Steel wool* to clean the resistivity cell end plates.

8. SAMPLE PREPARATION

- 8.1 *Pore solution* A cementitious solution sample expressed from hardened paste.
- 8.2 Transfer the solution to the syringe, preventing the ingress of solid particles and the exposure to the environment.

9. TESTING PROCEDURE

- 9.1 The pore solution should be tested during the first three hours after expression. If this is not possible, the pore solution can be stored in its sealed solution syringe in a 5 °C \pm 1 °C chamber to avoid carbonation of the solution and can be tested within 7 days.
- 9.2 Resistivity Cell
- 9.2.1 Ensure that the resistivity cell (the end plates and tube) are clean and dry. The resistivity cell must be cleaned before every measurement using cotton swabs, paper towels and DI water. If on the end plates there are visible corrosion products (rust), use steel wool and DI water to scrub the end plates and remove the rust. Make sure to dry the end plates after cleaning and before using.
- 9.2.2 Connect the stainless steel end plates to the ends of the polycarbonate tube, ensuring that the plates are tight against the tube and parallel to each other. The

plates must be tight enough against the tube so that the assembled cell does not leak any pore solution fluid. The assembled cell is shown in Figure 18.

Note **2**— The assembled cell should not leak any pore solution fluid. In prior experience, the partially milled hole is usually tight enough to prevent the loss of solution. If more protection against leaking solution is needed, a bar clamp could be used to clamp both plates tightly. A thread seal tape could also be used on the edges of the polycarbonate tube where it contacts the steel electrode. In no case should the tape cover the cross-sectional contact area of solution and stainless steel electrode.



Figure 18: Assembled resistivity cell

9.3 Pore Solution Injection

9.3.1 Use the syringe and needle to inject the pore solution into the resistivity cell from one of the two 3.175 mm (1/8") holes from the length of the tube, avoiding the formation of air bubbles within the tube or on the surface of the electrode. The injection process is shown in Figure 19. A minimum amount of pore solution required for testing is of 1.81 mL.

Note 3— The removal of air bubbles might require emptying and refilling the cell or by slightly tilting the cell to direct the air bubble towards one of the 3.18 mm (1/8") holes



Figure 19: Injection of solution in the assembled resistivity cell

9.4 Resistivity Measurement

- 9.4.1 Connect the alligator clips to the end probes and turn on the device. The probes, clips, and resistivity cell are shown in Figure 20.
- 9.4.2 Apply a frequency to the resistivity cell that yields the smallest phase angle, φ . Alternatively, a frequency sweep, that measures the impedance and phase angle at multiple frequencies, can be conducted.
- 9.4.3 Once both the impedance and phase angle values (or resistance values) are stable and do not change more than 5% over a 3 second period, record the impedance, Z, reading to the nearest 0.1 Ohm, and the phase angle, ϕ reading to the nearest 1 °, if provided by the impedance meter (or the resistance value reading to the nearest 0.1 Ohm).

Note 4— Frequency for measurements should be chosen based on the phase angle. A typical acceptable phase angle should read between 0 o and 5 o . If phase angle is not shown by the device, use a frequency in between 10 and 30 kHz.

Note 5— If the measurement is not stable, it is recommended to check that: there is no presence of rust on the end plates, there is a good connection between the plates and the polycarbonate tube (with no leaks), the temperature of the solution is not changing more than 2% over a 3 second period, the polycarbonate tube is completely filled with solution and no air bubbles are present, and that there is a good connection between the probes and the alligator clips, as well as between the alligator clips and the end plates.



Figure 20: Assembled resistivity cell connected to the probes using alligator clips for resistivity measurement

9.5 Temperature Measurement

- 9.5.1 After the resistance measurement, use a needle thermocouple to measure the temperature, T, to the nearest 0.1 °C of the pore solution while the sample is still inside the cell. The needle tip must be inserted all the way down the tube. *Note* 6— A temperature correction calculation can be calculated using AASHTO XX-XX (Task 1.2c).
- 9.6 Cleaning— After the resistivity measurement, the solution shall be removed and all the parts of the cell shall be thoroughly washed with deionized water. The components shall be thoroughly dried, either with the help of compressed air or isopropanol.

10. CALCULATION AND INTERPRETATION OF RESULTS

10.1Electrical resistivity— The electrical resistivity of the pore solution is calculated based on Equation 1. The measurement of the impedance, Z, is corrected by the measured phase angle, φ , and geometry factor, k, of the resistivity cell. The geometry factor is based on the geometry of the resistivity cell used and can be calculated using Equation 2.

Note 7— If the device used to measure resistance does not provide a phase angle, φ , assume a phase angle of 0 ° and a resistance equal to impedance.

$$\rho_o = Z * \cos \varphi * k \tag{1}$$

Where:

 ρ_o = electrical resistivity of pore solution in Ohm-m

Z = electrical impedance in Ohm

 φ = phase angle in degrees

k = geometry factor in m

$$k = \frac{A}{L} \tag{2}$$

Where:

k = geometry factor in m

- A = inner cross sectional area of the cell tube in m²
- L =length of the cell tube in m
- 10.2*Example Calculation* After running the resistivity measurement, the device will read an impedance value, *Z*, of 25.1 Ohm and a phase angle, φ , of 1 °. The temperature, *T*, of 24.5 °*C* is also measured with a thermocouple.
- 10.2.1 Use Equations 2 to calculate the geometry factor, k

$$A = \left(\frac{d}{2}\right)^2 \pi = \left(\frac{9.525 * 10^{-3} \text{ m } (3/8 \text{ in})}{2}\right)^2 \pi = 7.125 * 10^{-5} m^2 (0.110 \text{ in}^2)$$
$$L = 0.0254 \text{ m } (1 \text{ in})$$
$$k = \frac{A}{L} = \frac{7.125 * 10^{-5} m^2 (0.110 \text{ in}^2)}{0.0254 \text{ m } (1 \text{ in})} = 2.805 * 10^{-3} \text{ m } (0.11 \text{ in})$$

10.2.2 Use Equations 1 to calculate the resistivity, ρ_o

$$\rho_o = Z * \cos \varphi * k = 25.1 \ Ohm * \cos(1^\circ) * 2.805 * 10^{-3} \ m \ (0.11 \ in)$$
$$= 0.07 \ Ohm * m \ (2.76 \ Ohm * in)$$

$$\rho_o = 0.07 \ Ohm * m \ (2.76 \ Ohm * in)$$

 $T = 24.5 \ ^{\circ}C$

11. REPORT

11.1*Report the following, if known*:

- 11.1.1 *The measured electrical resistivity of the sample*: in Ohm-m to the nearest 0.01 Ohm-m.
- 11.1.2 The measured temperature of the sample: in °C to the nearest 0.1 °C.

12. PRECISION AND BIAS

12.1*Precision*:

- 12.1.1 *Single-Operator Precision* No data is currently available on the single operator precision.
- 12.1.2 *Multilaboratory Precision*—No data is currently available on experimental variation between multiple laboratories.

12.2*Calibration*:

- 12.2.1 A calibration of the resistivity cell using a 1.0 m KCl solution at a reference temperature of 25 °C in accordance with Reference 14.1 is prepared in order to verify the cell constant, k.
- 12.2.2 According to Reference 14.1, the measured conductivity of a 1.0 m KCl solution at a reference temperature of 25 °C is of 10.8620 S/m, which corresponds to a resistivity of 0.092 Ohm-m.

13. KEYWORDS

13.1Pore solution, electrical resistivity, formation factor.

14. REFERENCES

- 14.1National Institute of Standards and Technology. Standard Reference Materials: Primary Standards and Standard Reference Materials for Electrolytic conductivity. Special Publication 260-142, National Institute of Standards and Technology, Gaithersburg, MA, 2004.
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Quantifying the Chemical Composition and Electrical Resistivity of Cementitious Pore Solution using X-Ray Fluorescence Spectroscopy

1. SCOPE

- 1.1 This test method covers the procedure for quantitative determination of the chemical composition of cementitious pore solution and calculation of electrical resistivity.
- 1.2 The values stated in SI units are to be regarded as the standard.
- 1.3 This standard does not purport to address the safety issues, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. REFERENCED DOCUMENTS

- 2.1 AASHTO Standard:
- 2.1.1 M 231, Weighing Devices Used in the Testing of Materials

2.2 ASTM Standards:

- 2.2.1 D1193, Standard Specification for Reagent Water
- 2.2.2 C114, Standard Test Methods for Chemical Analysis of Hydraulic Cement

2.3 Other Standard:

2.3.1 Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, Committee on Analytical Reagents of the American Chemical Society

3. TERMINOLOGY

3.1 *Pore solution:* the liquid phase in concrete consisting of an aqueous solution containing several ionic species

3.2 *Electrical resistivity:* an intrinsic property that quantifies how strongly a material resists the flow of an electric current.

4. SUMMARY OF TEST METHOD

- 4.1 This test method covers the use of X-ray fluorescence (XRF) for quantitative determination of the chemical composition of a solution (e.g., pore solution). The chemical composition can then be used to calculate the electrical resistivity.
- 4.2 Two (2) methods are presented for sample preparation and testing using XRF: the solution and fused bead methods. Each method requires the development of an individual application and calibration within the testing equipment. The solution method requires at least 2 g of sample to be tested, while the fused bead method requires only 1 g to be tested.
- 4.3 The XRF generates results (ionic concentration of all positively charged ions) in parts per million (ppm), where an assumed density of 1000 g/L will be used in order to convert the results to mole per liter (mol/L) for reporting. A model developed by Snyder et al. (Reference 14.1) uses the results in mole per liter (mol/L) and empirical values in order to calculate the electrical resistivity of a sample.

5. SIGNIFICANCE AND USE

- 5.1 This test method is used for determination of the chemical composition of extracted cementitious pore solutions. The chemical composition can be used to calculate the pore solution resistivity which is used for the calculation of the formation factor of a cement paste, mortar or concrete.
- 5.2 Since XRF is commonly used in the cement industry, this technique could potentially be implemented to obtain the degree of hydration dependent pore solution ionic composition of various cementitious mixtures.
- 5.3 Although this procedure focuses on only sodium (Na⁺) and potassium (K⁺), the XRF can be used to determine nearly any elemental concentrations in the pore solution including calcium (Ca²⁺) and sulfur (S²⁻ for sulfates (SO₄²⁻)).
 Note 1: The XRF application and calibration would need to be modified in order

to detect additional ionic species in pore solution for further applications.

6. INTERFERENCES

6.1 The test procedure was developed to be used on samples sealed prior to testing. It is known that samples in contact with curing water or other fluids can imbibe those fluids or leach ions from the pore solution which may alter the results.

7. APPARATUS

- 7.1 *Balance* analytical balance, Class A, conforming to the requirements of AASHTO M 231 to weigh the solution and flux in the crucible. The balance must have a precision of 0.1 mg.
- 7.2 *Micropipette* to add the liquid to flux for fused beads. The micropipette must have a precision of 0.1 μ L.
- 7.3 Drying oven— for sample preparation of liquid fused beads at a temperature of $105^{\circ} \text{ C} \pm 1^{\circ} \text{ C}$.
- 7.4 *Liquid Sample Cups for XRF* to assemble with film to test samples in XRF as solutions.
- 7.5 *Polypropylene films* to assemble with liquid sample cups for solution testing in XRF.
- 7.6 *Automatic Fusion Instrument* to prepare fused beads for sample testing. The fusion instrument must be able to fuse at a temperature of $1050^{\circ} \text{ C} \pm 1^{\circ} \text{ C}$.
- 7.7 *Flat bottom platinum crucible* to prepare fused beads for sample testing. The crucible must be compatible with the Automatic Fusion Instrument.
- 7.8 *Platinum mold* to prepare fused beads for sample testing. The mold must be compatible with the Automatic Fusion Instrument used in testing.
- 7.9 Energy Dispersive X-ray Fluorescence Spectrometer—In accordance with ASTM C114.

8. SAMPLE PREPARATION

8.1 *Reagents*—Reagent grade chemicals shall be used for calibration standard solutions. Unless otherwise indicated, all reagents shall conform to the

specifications of the Committee on Analytical Reagents of the American Chemical Society.

- 8.1.1 For this standard, reagent grade sodium chloride (NaCl) and potassium chloride (KCl) are used to prepare calibration standard solutions at different concentration levels.
- 8.1.2 At least three (3) different calibrations standards, excluding a pure DI water (blank) calibration sample, must be prepared in order to properly calibrate the XRF equipment to detect the concentration of the ions. The concentrations of the calibration standards must include a range of concentrations with a maximum concentration of 1 mol/L for both NaCl and KCl.
- 8.2 *Water*—Unless otherwise indicated, water used shall be Type II reagent water in accordance with ASTM D1193.
- 8.3 *Sample Geometry* —Two (2) methods can be used to detect the ionic composition of a pore solution sample: solution and fused bead. Either method can be used and the method used should be reported.

Note 2— The method of sample preparation is chosen depending on the available equipment, time permitted to perform the measurement, the amount of solution available to test, and whether the specimen is needed as a long term reference.

8.4 Calibration Standard Sample Preparation

8.4.1 Solution Preparation

Calibration samples of solution are to be measured directly in a plastic container with an outer diameter of 35 mm and a 4 μ m thick polypropylene film base. Note 3— The size of the sample may be varied depending on the equipment available.

8.4.1.1 The plastic containers consist of two concentric plastic cylinders with a polypropylene film base. The procedure of assembling the containers is shown in Figure 21.



Figure 21: Assembling procedure for XRF solution cups

8.4.1.2 Place the polypropylene film on the top of the larger diameter cylinder. Then, place the smaller cylinder inside the larger pushing down on the polypropylene film between both cylinders

Note 4—A polypropylene film is preferred to other materials tested in earlier studies due to its high resistance to high pH solutions (Reference 14.2).

8.4.1.3 After assembling the containers, place the calibration solution inside the container. Each calibration standard solution should contain least 6 g ± 0.001 g in order to yield accurate results.

Note 5—The actual sample requires a minimum solution mass of 2 g \pm 0.001 g.

- 8.4.1.4 After placing the solution in the containers, leave samples on a dry paper towel for 2 minutes to ensure that the film has no leaks due to the high pH of the samples that could potentially damage the XRF.
- 8.4.2 Fused Bead Preparation

- 8.4.2.1 Measure 5 g ± 0.001 g of flux (consisting of 49.75% lithium metaborate, 49.75% lithium tetraborate, and 0.50% lithium iodide) in a platinum flat bottom crucible.
- 8.4.2.2 Use the micropipette to add 1 g ± 0.001 g of a calibration standard solution to the flux in the platinum crucible.
- 8.4.2.3 After combining the solution with the fluxing agent, dry the sample at 105° C $\pm 1^{\circ}$ C for 90 minutes in a laboratory oven (to evaporate the water).
- 8.4.2.4 Fuse sample at a temperature of $1050^{\circ} \text{ C} \pm 1^{\circ} \text{ C}$ in a fusion device with the heat steps shown in Table 6.2.1.

Note 6— If the fusion device available does not provide a program with the heat steps shown in Table 6.2.1, use a program that complies with the heating steps shown. Make sure that a consistent fusion procedure is always followed for the sample calibration and sample preparation.

Step	Туре	Duration (min)	Heat (°C)	Rotating Speed (rpm)	Rotating Angle (°)	Fan (On/Off)
1	Heat	4:00	1050	0	0	Off
2	Heat	3:00	1050	5	15	Off
3	Heat	2:00	1050	30	40	Off
4	Heat	1:00	1050	0	0	Off
5	Heat	1:00	1050	25	45	Off
6	Pour	-	-	-	-	Off
7	Cool	1:15	_	_	_	On
8	Cool	3:30	_	-	_	On

Table 6.2.1: Detailed steps for fusion of fused bead sample

8.4.2.5 The fused bead will have a diameter of 30 mm.

8.5 Sample Preparation

8.5.1 Pore Solution Sample Preparation

- 8.5.1.1 Samples of solution are to be measured directly in a plastic container with an outer diameter of 35 mm and a 4 μm thick polypropylene film base.
- 8.5.1.2 The plastic containers consist of two concentric plastic cylinders with a polypropylene film base. The procedure of assembling the containers is shown in Figure 1.
- 8.5.1.3 Place the polypropylene film on the top of the larger diameter cylinder. Then, place the smaller cylinder inside the larger pushing down on the polypropylene film between both cylinders.

Note 7— A polypropylene film is preferred to other materials tested in earlier studies due to its high resistance to high pH solutions (Reference 14.2).

- 8.5.1.4 After assembling the containers, place the solution inside the container. Each sample pore solution tested will need at least 2 g ± 0.001 g in order to yield accurate results.
- 8.5.1.5 After placing the solution in the containers, leave samples on a dry paper towel for 2 minutes to ensure that the film has no leaks due to the high pH of the samples that could potentially damage the XRF.

8.5.2 Pore Solution Fused Bead Sample Preparation

- 8.5.2.1 Measure 5 g ± 0.001 g of flux (consisting of 49.75% lithium metaborate, 49.75% lithium tetraborate, and 0.50% lithium iodide) in a platinum flat bottom crucible.
- 8.5.2.2 Use the micropipette to add 1 g ± 0.001 g of solution to the flux in the platinum crucible.
- 8.5.2.3 After combining the solution with the fluxing agent, dry the sample at 105° C $\pm 1^{\circ}$ C for 90 minutes in a laboratory oven (to evaporate the water).
- 8.5.2.4 Fuse sample at a temperature of $1050^{\circ} \text{ C} \pm 1^{\circ} \text{ C}$ in a fusion device with the heat steps shown in Table 6.2.1.
- 8.5.2.5 The fused bead will have a diameter of 30 mm.

9. TESTING PROCEDURE

9.1 XRF application development

- 9.1.1 A specific application must be developed for each testing method (solution and fused bead) using the software associated with the XRF device used.
- 9.1.2 Each application will need to be calibrated with its respective calibration standards.

9.2 Solution Application

- 9.2.1 The software application must initially define the sample type as solution.
- 9.2.2 The elements quantified in this application are sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻). Regardless of which ionic species are needed to calculate the electrical resistivity of pore solution, all elements used for the calibration standards (sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻)) must be quantified into the application as a compound tested.
- 9.2.3 The condition sets for the sodium (Na⁺) and potassium (K⁺) are as follows. A condition set is the defined set of analysis parameters (such as measuring time, excitation energy and current, medium, and filter) for a specific group of elements.
- 9.2.4 The potassium (K⁺) will usually uses a condition set with a measuring time of 60 seconds at 12 kV and 584 μA.
- 9.2.5 The sodium (Na⁺) will be required to use a condition set with a measuring time of 300 seconds at 5 kV and 629 μ A.
- 9.2.6 The sodium condition set will also be required to have an analysis background fit for the results with an initial energy of 0.500 keV and an ending energy of 1.500 keV.
- 9.2.7 Balance is required with a balance channel of oxygen (labelled H₂O). A balance channel calculates the remaining compound in the material. The concentration of the balance channel compound is calculated as 100% minus the sum of all other compounds measured in the application. By defining a balance channel of oxygen (labelled H₂O), the application assumes that the sample is comprised of the compounds defined and measured with the XRF (i.e. sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻)) and the remaining compound is H₂O.

9.2.8 Verify that the application yields accurate results by testing known solutions of sodium hydroxide (NaOH) and potassium hydroxide (KOH) at different concentration levels within the calibration range. The application yields accurate results if the error is within 5 %.

9.3 Solution Application Calibration

- 9.3.1 Measure the solution calibration standards to calibrate for each ionic species contained in the solution standards.
- 9.3.2 After the standards are measured, use a matrix correction model (linear, alphas, FP) that will yield the minimum relative RMS (%) for each calibration to create the best linear fit for the calibration of each ionic species.
- 9.3.3 Each ionic species may have a different matrix correction model that yields its minimum relative RMS. Recalculate the calibration until the minimum relative RMS is obtained. All relative RMS values for all ionic species must be less than 2 %.

9.4 Fused Bead Application

- 9.4.1 The software application must initially define the sample type as fused bead.
- 9.4.2 The elements quantified in this application are sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻).

Note 8 — Regardless of which ionic species are needed to calculate the electrical resistivity of pore solution, all elements used for the calibration standards (sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻)) must be quantified into the application as a compound tested.

- 9.4.3 Create an application using the software default settings for each condition set. Make sure that the condition sets for the sodium (Na⁺) and potassium (K⁺) are as follows. A condition set is the defined set of analysis parameters (such as measuring time, excitation energy and current, medium, and filter) for a specific group of elements.
- 9.4.4 The potassium (K⁺) will usually uses a condition set with a measuring time of 60 seconds at 12 kV and 584 μA.

- 9.4.5 The sodium (Na⁺) will be required to use a condition set with a measuring time of 300 seconds at 5 kV and 765 μ A.
- 9.4.6 The sodium (Na⁺) condition set will also be required to have an analysis background fit for the results with an initial energy of 0.700 keV and an ending energy of 3.750 keV.
- 9.4.7 Balance the loss of ignition (L.O.I.). A balance with a L.O.I. assumes that the sample is comprised of the compounds defined and measured with the XRF (i.e. sodium (Na⁺), potassium (K⁺), and chlorine (Cl⁻)) and the remaining is attributed to a loss of ignition from the fusing process. The L.O.I. is calculated as 100% minus the sum of all other compounds measured in the application.
- 9.4.8 Verify that the application yields accurate results by testing known solutions of sodium hydroxide (NaOH) and potassium hydroxide (KOH) at different concentration levels within the calibration range. The application yields accurate results if the error is within 5 %.

9.5 Fused Bead Application Calibration

- 9.5.1 Measure the solution calibration standards to calibrate for each ionic species contained in the solution standards.
- 9.5.2 After the standards are measured, use a matrix correction model (linear, alphas, FP) that will yield the minimum relative RMS (%) for each calibration to create the best linear fit for the calibration of each ionic species.
- 9.5.3 Each ionic species may have a different matrix correction model that yields its minimum relative RMS. Recalculate the calibration until the minimum relative RMS is obtained. All relative RMS values for all ionic species must be less than 2%.

9.6 Sample measurement

- 9.6.1 Place samples in each sample holder.
- 9.6.2 Measure each sample according to its sample holder position and XRF application. Make sure that solution samples use a 35 mm sample holder outer ring and that fused beads use a 30 mm sample holder outer ring.

10. CALCULATION AND INTERPRETATION OF RESULTS

- 10.1 *Ionic Concentration*—The ionic concentration of a single ionic species, c_i , is tested in parts per million (ppm) using the XRF. The ions detected in the XRF are sodium (Na⁺) and potassium (K⁺). A charge balance calculation shown in Section 10.1.1 is needed to calculate the concentration of the hydroxides (OH⁻) from all other ionic species. After calculating the concentrations of the hydroxides (OH⁻), the ionic concentration of each ionic species is converted to mol/L in Section 10.1.2 for the purpose of reporting.
- 10.1.1 *Calculate hydroxide (OH⁻) from cations (Na⁺ and K⁺)* Use Equation 1 to calculate the concentration of hydroxide based on a charge balance calculation. The molecular weights of all ions are shown in Table 6.6.2.

$$c_{OH^{-}} = \frac{c_{Na^{+}} * M_{OH^{-}}}{M_{Na^{+}}} + \frac{c_{K^{+}} * M_{OH^{-}}}{M_{K^{+}}}$$
(1)

Where:

 c_{OH^-} = calculated ionic concentration of hydroxide in ppm

 M_{OH^-} = molecular weight of hydroxide in g/mol

 c_{Na^+} = measured ionic concentration of sodium ions from XRF in ppm

 M_{Na^+} = molecular weight of sodium in g/mol

 c_{K^+} = measured ionic concentration of potassium ions from XRF in ppm

 M_{K^+} = molecular weight of potassium in g/mol

10.1.2 Concentrations in mol per liter— For the purpose of reporting, the ionic concentration of each ionic species must be presented in mol per liter (mol/L). Equation 2 presents the conversion from parts per million (ppm) to mol per liter (mol/L). This equation can be applied for each ionic species. All the ionic species (*i*) discussed in this document with their respective molecular weights are shown in Table 6.2.2.

$$C_i = \frac{c_i * \rho}{M_i * 10^6} \tag{2}$$

Where:

- C_i = ionic concentration of a single ionic species in mol/L
- c_i = ionic concentration of a single ionic species in ppm obtained from XRF
- ρ = density of the solution in g/L
- M_i = molecular weight of a single ionic species in g/mol
- i = a single ionic species

Note 9— The density of pore solution can be assumed to be 1000 g/L, unless otherwise specified.

Ionic Species (<i>i</i>)	Molecular Weight (<i>M_i</i>) (g/mol)	
Sodium (Na ⁺)	22.9898	
Potassium (K ⁺)	39.0983	
Hydroxide (OH ⁻)	17.008	

Table 6.2.2: Ionic species present in pore solution and included in this document

10.2 *Electrical Resistivity*—The electrical resistivity, ρ_{calc} , is calculated by using the model developed by Snyder et al. in Reference 14.1, where the resistivity of pore solution (Equation 3) is estimated as the inverse of the weighted sum of the individual equivalent conductivities, λ_i , (Equation 4) of each ionic species present. To find the equivalent conductivities of each species, the model takes into account the equivalent conductivity of an ionic species at infinite dilution, λ_i° , the ionic strength (Equation 5), I_M , and an empirical conductivity coefficient for each ionic species, G_i , from the literature. Both λ_i° and G_i are shown in Table 6.2.3.

$$\rho_{calc} = \frac{1}{\sum_i z_i c_i \lambda_i} \tag{3}$$

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i l_M^{1/2}} \tag{4}$$

$$I_M = \frac{1}{2} \sum_i z^2 c_i \tag{5}$$

Where:

 ρ_{calc} = electrical resistivity of a single ionic species in Ohm-m

 λ_i = equivalent conductivity of a single ionic species in cm² S/mol

 z_i = valence concentration of a single ionic species

 c_i = molar concentration of a single ionic species in mol/L

 λ_i° = equivalent conductivity of ionic species at infinite dilution in cm² S/mol

 G_i = empirical conductivity coefficient of a single ionic species in (mol/L)^{-1/2}

 I_M = ionic strength (molar basis) in mol/L

i = a single ionic species

Ionic Species (<i>i</i>)	Valence (z _i)	Equivalent conductivity at infinite dilution (λ_i°) (cm ² S/mol)	Empirical conductivity coefficient (<i>G_i</i>) (mol/L) ^{-1/2}
Sodium (Na ⁺)	1	50.1	0.733
Potassium (K ⁺)	1	73.5	0.548
Hydroxide (OH-)	1	198	0.353

Table 6.2.3: Conductivity coefficients for each ionic species

10.3 *Example Calculation*— Consider the following results from the XRF analysis:

Ionic Species	Concentration	
(<i>i</i>)	(ppm)	
Sodium (Na ⁺)	5000	
Potassium (K ⁺)	20000	

10.4 Step 1: Using Equation 1, calculate the hydroxide concentration.

$$\begin{split} c_{OH^-} &= \frac{5000 \; ppm * 17.008 \; g/mol}{22.9898 \; g/mol} + \frac{20000 \; ppm * 17.008 \; g/mol}{39.0983 \; g/mol} \\ &= 12399.15 \; ppm \end{split}$$

10.5 **Step 2:** Using Equation 2, convert the ionic concentrations of all species from parts per million (ppm) to mol per liter (mol/L).

$$C_{Na^+} = \frac{5000 \ ppm * 1000 \ g/L}{22.9898 \ g/mol * 10^6} = 0.217 \ mol/L$$

$$C_{K^+} = \frac{20000 \ ppm * 1000 \ g/L}{39.0983 \ g/mol * 10^6} = 0.512 \ mol/L$$

$$C_{OH^-} = \frac{12399.15 \, ppm * 1000 \, g/L}{17.008 \, g/mol * 10^6} = 0.729 \, mol/L$$

10.6 **Step 3:** Using Equations 3-5, calculate the electrical resistivity from the ionic concentrations in mol/L.

$$I_M = \frac{1}{2} \left((1)^2 * 0.217 \frac{mol}{L} + (1)^2 * 0.512 \frac{mol}{L} + (1)^2 * 0.729 \frac{mol}{L} \right) = 0.729 \ mol/L$$

$$\lambda_{Na^{+}} = \frac{50.1 \, (mol/L)^{-1/2}}{1 + (0.733 \, (mol/L)^{-1/2} * \left(0.729 \frac{\text{mol}}{\text{L}}\right)^{\frac{1}{2}})} = 30.815 \, \text{cm}^2 \text{S/mol}$$

$$\lambda_{K^+} = \frac{73.5 \ (mol/L)^{-1/2}}{1 + (0.548 \ (mol/L)^{-1/2} * \left(0.729 \frac{\text{mol}}{\text{L}}\right)^{\frac{1}{2}})} = 50.072 \ \text{cm}^2\text{S/mol}$$

$$\lambda_{OH^{-}} = \frac{198 \ (mol/L)^{-1/2}}{1 + (0.353 \ (mol/L)^{-1/2} * \left(0.729 \frac{mol}{L}\right)^{\frac{1}{2}})} = 152.144 \ cm^{2} \text{S/mol}$$

$$\rho_{calc} = \frac{1}{\left[\left((1)^2 * 0.217 \frac{mol}{L} * 30.815 \frac{cm^2 S}{mol} \right) + \left((1)^2 * 0.512 \frac{mol}{L} * 50.072 \frac{cm^2 S}{mol} \right) + \left((-1)^2 * 0.729 \frac{mol}{L} * 152.144 \frac{cm^2 S}{mol} \right) \right]}$$

 $ho_{calc} = 0.07 \ Ohm \cdot m$ $C_{Na^+} = 0.22 \ mol/L$ $C_{K^+} = 0.51 \ mol/L$ $C_{OH^-} = 0.73 \ mol/L$

11. REPORT

- 11.1 Report the following, if known:
- 11.1.1 Type of sample tested: solution or fused bead
- 11.1.2 *Ionic concentration of the main ions detected by the XRF:* potassium (K⁺) and sodium (Na⁺) concentration in mol/L to the nearest 0.01 mol/L;
- 11.1.3 *The calculated electrical resistivity of the sample*: in Ohm-m to the nearest 0.01 Ohm-m.

12. PRECISION AND BIAS

- 12.1 Precision:
- 12.1.1 *Single-Operator Precision* No data is currently available on experimental variation between multiple laboratories.
- 12.1.2 *Multilaboratory Precision*—No data is currently available on experimental variation between multiple laboratories.

13. KEYWORDS

13.1 Pore solution; X-ray fluorescence, chemical composition, electrical resistivity, formation factor.

14. REFERENCES

14.1 Snyder, K.A., Feng, X., Keen, B. D., and Mason, T. O., "Estimating the electrical conductivity of cement paste pore solutions from OH-, K+ and Na+ concentrations," *Cement and Concrete Research*, Vol. 33, No. 6, 2003, p. 793–798. 14.2 Tsui-Chang, M., Suraneni, P., Isgor, O. B., Trejo, D., Weiss, W. J., "Using X-ray fluorescence to assess the chemical composition and resistivity of simulated cementitious pore solutions", *International Journal of Advances in Engineering Sciences and Applied Mathematics*, Vol 9, No. 3, 2017, p. 136-143.