# Analysis of the Physicochemical Interactions of Waste and Recycled Materials in Concrete

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## Abstract

This thesis broadly addresses the issue of materials sustainability in the production of Portland cement concrete. Two topics are presented, both aimed at achieving more sustainable concrete through the use of waste and recycled materials. The first topic involves utilizing reclaimed asphalt pavement (RAP) as an aggregate in structural concrete, and the second topic involves utilizing waste quarry fines as partial replacement of Portland cement in cementitious mixes.

Many efforts have been made in recent years to justify the use of RAP aggregates in concrete. All previous efforts appear to unanimously report a reduction in concrete mechanical performance with varying proportions of RAP usage. The poor performance of RAP aggregates in concrete is attributed mainly to a larger, more porous interfacial transition zone (ITZ) and to the cohesive failure of the asphalt. It is hypothesized that the detrimental impact on the ITZ is attributable to organic compounds leached from the asphalt in the high pH pore solution. This study proves the presence of organic compounds in the pore solution and demonstrates that there is an apparent retardation of cement hydration. This study attempted to pretreat the RAP in a sodium hydroxide (NaOH) solution to pre-leach the organic compounds. The pretreatment demonstrated that organic compounds were leached and that NaOH modified the asphalt surface chemistry. However, only a marginal improvement in compressive strength was observed by completing the pretreatment.

Replacement of Portland cement by filler materials is a practice aimed at reducing the carbon footprint of concrete, such as is common with Type IL Portland limestone cement. This study

investigates the impact of replacing cement with seven different quarry fines materials. The quarry fines were used to replace cement at 5% to 20% by volume in either cement paste or mortar samples that were then analyzed for various physicochemical properties. It was found that all the quarry fines had detrimental impact on the hydration kinetics of cement pastes. The inclusion of quarry fines was also found to cause varying degrees of reduction in mortar compressive strength. While further analyses of the quarry fines are required, quarry fines 2, 5 and 7 did display encouraging signs to suggest the potential for use as a filler material in blended cements.

# Analysis of the Physicochemical Interactions of Waste and Recycled Materials in Concrete

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## General Audience Abstract

This thesis broadly addresses the issue of sustainability in the cement and concrete industry. Sustainability is a significant problem for the cement and concrete industry due to the large amount of carbon emissions produced in the manufacturing process of Portland cement. One method to reduce the carbon footprint of concrete is to use recycled aggregates, and reclaimed asphalt pavement (RAP) is investigated in this thesis as a recycled aggregate option. Previous studies have shown that the use of RAP in concrete results in poor mechanical performance when compared to conventional concrete. In this thesis, the RAP was pretreated by soaking it in sodium hydroxide (NaOH) to see if any improvement is noted. It was determined that the pretreatment resulted in marginal improvements in concrete performance. Another method to reduce the carbon footprint of concrete is through the use of substitutions of Portland cement. In this thesis, quarry fines from around Virginia were investigated for potential as substitutive material. Quarry fines are a by-product from quarrying operations and are often considered a waste material because they have limited applications. This study analyzed the performance of cementitious materials prepared with various substitutive percentages of quarry fines and found that, in general, the inclusion of quarry fines resulted in a decrease of mechanical performance. In total, seven quarry fines were tested and only two showed potential for use as a substitution in Portland cement concrete. These two investigations are essential in reaching the goal of reducing the carbon footprint of the cement and concrete industry.

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## Attribution

This thesis is presented in the "Manuscript Format" as defined by the Virginia Tech Graduate School. In this format, it is necessary to provide an outline of the contents of the thesis and my specific contributions to each of the manuscripts included.

There are two manuscripts presented in this thesis:

1. **Effect of Leachate from Reclaimed Asphalt Pavement Aggregates on Cement Hydration.**

   This paper is currently in the final editing stages and has not been published yet. It is intended that it will be published into an academic journal in the coming months. I am listed as the second author of the paper, and the other authors are Amir Behravan (1st author), Thien Tran, Mehdi Ashraf-Khorasani, Xu Feng, and Alexander Brand (corresponding author). This paper was a collaborative effort, but the sections that I was primarily responsible for are listed below:

   - **2.4.1** and **2.5.1**: Total Organic Carbon (TOC) Analysis
   - **2.4.5** and **2.5.5**: Isothermal Calorimetry (IC)
   - **2.4.8** and **2.5.8**: Pore Solution Extraction and Analysis
   - **2.4.9** and **2.5.9**: Compressive Strength and Split Tensile Analysis
   - **2.4.10** and **2.5.10**: Contact Angle and Surface Free Energy

2. **Effect of Quarry Fine Substitution on Cement Hydration.**

   This research was conducted as an initial investigation of the quarry fine materials and the findings are intended to be used in conjunction with studies being carried out by other

graduate students. The methods, results, and findings presented in this thesis are entirely my work. While my work focusses on the hydration characteristics and physicochemical interactions between the quarry fine materials and the other phases within concrete, other researchers are investigating the durability characteristics and quantitative characterization of the materials. The intention is that all the findings will be compiled to give a comprehensive understanding of the quarry fine materials. Those findings may ultimately be published in an academic journal, but the status of that is not currently determined.

# 1. Introduction

## 1.1. Overview

The issue of sustainability in the concrete industry is complex and can seem overwhelming due to the immense size of the industry. A number of organizations have attempted to tackle the problem through strategic planning approaches. For example, in the United States, the Portland Cement Association (PCA) has developed a detailed roadmap to carbon neutrality [1]. Internationally, the Global Cement and Concrete Association (GCCA) has proposed a similar roadmap for the cement industry to achieve net zero carbon emissions by 2050 [2]. The roadmap clearly identifies a categorized list of areas where carbon reduction can be achieved, and the contents of this thesis fall under two of these categories: “Efficiency in concrete production” and “Savings in cement and binders”. “Efficiency in concrete production” refers primarily to the optimization of mix design and minimizing waste in the production of concrete [2]. The GCCA estimates that savings in this category will account for 11% of the ultimate reduction of carbon to zero by 2050. Chapter 2 of this thesis would fall under this category, as the utilization of reclaimed asphalt pavement would reduce the demand for virgin aggregate, resulting in a more sustainable mix design. The other major component of this thesis, presented in Chapter 3, falls under the category of “Savings in cement and binders” which is estimated to account for 9% of carbon savings [2]. This category includes substitution and alternatives to Portland cement clinker. In Chapter 3, quarry fines are investigated to determine if the material could be a suitable substitute for Portland cement, similar to the use of limestone in Type IL Portland limestone cements. While the GCCA roadmap is quite ambitious, it is only through the continued effort of researchers and industry stakeholders that advancements can be made towards achieving the goal of a more

sustainable concrete industry. The research conducted for this study is specifically aimed at contributing to the knowledge base and the widespread effort to achieve that goal.

## 1.2. Origin of Materials

All materials investigated in this thesis originate in Virginia, USA. The RAP aggregate was sampled from a stockpile at a quarry in Blacksburg, VA. It is assumed that the material is sourced from the reconstruction of roadways in the surrounding region. That material is currently being used as aggregate in the production of new asphalt concrete. The quarry fines were provided by quarries around the state of Virginia. While the exact locations and functions of the quarries are unknown to researchers, it is known that all quarry fines were by-products from quarries that are currently operational.

## 1.3. Organization of Thesis

Chapter 1 serves as the introduction to the thesis, covering the motivation for research and any background information.

Chapter 2 is a draft manuscript of a co-authored paper intended for submission and publication in an academic journal. The focus of this paper is the use of RAP aggregates as aggregate in structural concrete.

Chapter 3 is a preliminary investigation into the physicochemical properties of quarry fines. Once more information is known about these quarry fines, the results are intended for publication at a later date.

Chapter 4 constitutes the Conclusions and Recommendations for the thesis material. While each of Chapters 2 and 3 contain their own conclusions, Chapter 4 serves to summarize and expand on the conclusions and recommendations as they pertain to the general theme of the thesis.

# 2. Effect of Leachate from Reclaimed Asphalt Pavement Aggregates on Cement Hydration

## 2.1. Introduction and Literature Review

While the U.S. possesses a significant supply of crushed aggregate [3], it is apparent that certain regions have or will have limited access to quality aggregate [4]–[5]. This issue has also been recognized on a global scale [6]. For viable concrete infrastructure sustainability, it is very likely that recycled aggregates will require greater attention in the future [7]. While recycled concrete aggregate has received significant attention [8]–[10], reclaimed asphalt pavement (RAP) has received comparatively less research focus. RAP is produced by milling asphalt pavements during construction operations. A significant amount of RAP is used in the production of new asphalt pavements, but significant stockpiles remain. In 2019, around 97 million tons of RAP were produced in the U.S., while 89 million tons were used in new asphalt pavements [11]. The remainder is stockpiled, and the total stockpile in the U.S. is estimated at 138 million tons [11]. Storing RAP aggregates in stockpiles or disposing of them as waste in landfills has ecological and environmental impacts [12]. Using RAP in both Portland cement concretes, and asphalt mixtures will expedite the use of massive volumes of RAP stockpiles, which can help to solve the problems arising from RAP accumulation and stockpiles management. As a result, researchers in the U.S. and internationally have begun exploring the use of RAP as a partial to full replacement of aggregates in cementitious composites.

Many studies are available in the literature that have investigated the use of RAP in various Portland cement, concrete, or mortar mixes [13]–[54], roller compacted concrete mixes [55]–[70], pervious concrete mixes [71]–[73], self-compacting concrete mixes [74]–[78], dry lean concrete

and cement-treated base mixes [79]–[87], and geopolymer and alkali-activated concretes [88]–[93]. Most – if not all – of these studies have reported a reduction in concrete mechanical and durability performance when RAP aggregates are used. While a number of factors (e.g., gradation effects and fines content [15], [94], agglomerated RAP particles [15], [21], percent asphalt coating [94], percent asphalt content [15], degree of oxidation of the asphalt on the RAP [37]) have been reported to affect the mechanical or durability properties of concrete with RAP, data from microstructural and chemical bond analyses have indicated that the primary causes for the reduced performance are: 1) the formation of a larger, more porous interfacial transition zone (ITZ) around the RAP particles relative to virgin aggregates [36], [37], [95], and 2) the predominance of asphalt cohesion failures [37], [96].

While researchers have found strength improvement by abrasion and attrition of the RAP aggregate [27] and have demonstrated increased interfacial bonding energy after chemical treatment [37], it is clear that no one solution has yet demonstrated the ability to produce a concrete with RAP that has the equivalent mechanical performance to virgin aggregate concrete. While the use of supplementary cementitious materials (SCMs) can have a dramatic improvement on the ITZ properties and mechanical properties of concrete with virgin aggregates [97]–[100], the use of SCMs in concrete with RAP is not as effective, if at all. Brand and Roesler [36], [37] argued that, while silica fume did decrease the porosity in the ITZ around RAP aggregates, the predominance of an asphalt cohesion failure still resulted in a silica fume mixture with only slightly greater compressive strengths and dynamic moduli compared to a control cement mixture. Similarly, Huang et al. [21] showed almost no strength improvement with using silica fume for concretes with coarse or fine RAP. Brand and Roesler [36] also showed that fly ash and ground granulated blast furnace slag were unable to statistically increase the compressive or split tensile strengths of

a mortar with RAP. However, Singh et al. [34] and Debbarma et al. [65] showed that silica fume can increase the strength of concrete with RAP, while fly ash, bagasse ash, and sugarcane ash did not offer much (if any) improvement [34], [47], [65].

Although the focus of the majority of the investigations available in the literature is on identifying mechanical and durability properties of concrete mixes containing different proportions of RAP, the effectiveness of the proposed methods to mitigate the reduction in mechanical properties of the concrete does not answer the root question of if there is a chemical interaction that causes this decrease in performance. To answer why RAP increases the size and porosity of the ITZ, Brand and Roesler [35] postulated that the high pH pore solution from cement hydration solubilized organic compounds from the asphalt on the RAP and that these organic compounds were detrimental to cement hydration. Indeed, studies have shown that alkaline solutions will leach compounds from asphalt [101], [102]. Neutral pH solutions and water have also been shown to leach organic compounds from asphalt [12], [103]–[108]. While the compounds leached from asphalt have not necessarily been explicitly studied for their effect(s) on cement hydration, the literature clearly indicates that certain organic compounds and organic functional groups are detrimental to cement hydration [109]–[120]. Thus, the working hypothesis for this study is that organic compounds are leached from the RAP and that these compounds can negatively affect cement hydration. This study uses a suite of characterization techniques to quantify if organic leachate is present and if pretreatment can reduce the leachate content to improve the mechanical properties of concrete with RAP aggregates. This study advances the state-of-the-art by exploring the properties of RAP leachate in connection with cement hydration, which has previously not been studied in the literature.

## 2.2. Overview of Experiments

This research study was developed in two phases. The first phase examined the properties of organic leachates from RAP aggregates. The second phase intended to pre-leach the organic compounds as a potential method to improve properties of mortar with RAP.

In Phase I, RAP aggregates were soaked in two solutions: deionized water and 0.01 M NaOH solution. The water was selected as a baseline solvent with the NaOH solution serving as a high pH analogue for cement pore solution. The objective of this phase was to quantify and identify the properties of any leachate from the RAP. Fine RAP aggregates were soaked in the aforementioned solutions with the solid to liquid ratio of 1:1 for up to 55 days. The leachate was then studied using total organic carbon (TOC) analysis, Fourier transform infrared (FTIR) spectroscopy, gas chromatography (GC), and high-performance liquid chromatography (HPLC). The RAP aggregates after leaching were also examined using X-ray photoelectron spectroscopy (XPS), FTIR, and optical imaging. Finally, isothermal calorimetry was performed on cement paste mixtures that were cast with leachate solution to identify if the leachate affected hydration kinetics.

In Phase II, the RAP aggregates were pretreated by soaking in a 0.01 M NaOH solution in an attempt to pre-leach the organic compounds. The treated RAP aggregates were used in a Portland cement mortar and compared to mixtures with untreated RAP. The mortars were tested for compressive and split tensile strengths. In addition, pore solution extraction was used to collect pore solution for compositional analysis.

## 2.3. Materials

### *2.3.1. Cement*

For cement paste and mortar mixes, ASTM C150 Type I Portland cement was used.

*2.3.2. Virgin Fine Aggregates*

Natural sand consisting of primarily crushed silica ($SiO_2$) aggregates were used in Phase II to make cylindrical mortar specimens for compressive strength, tensile strength, and pore solution extraction. Mixtures with natural sand were used as the control to compare mixtures with RAP. Aggregates passing the #16 sieve (1.18 mm) and retained on the #50 sieve (300 μm) were used in this study. This limited range in gradation was implemented to reduce the effect of aggregate size, which is important in concrete with RAP aggregate [14,93] as well as important in the development of the ITZ in general [121]. The water absorption and bulk specific gravity of the natural sand were 1.5% and 2.65, respectively, per ASTM C128 [122].

*2.3.3. Fine RAP Aggregates*

RAP aggregates were obtained from a local stockpile without any knowledge of the source pavement. Sandstone composed of silica ($SiO_2$) was the core rock of RAP aggregates. The RAP aggregates consisted of a mixture of coarse aggregates (size $> 4.75$ mm) and fine aggregates (size $< 4.75$ mm). The fine RAP aggregates were separated from the stock, since they had a greater asphalt content per unit volume. The water absorption and bulk specific gravity of the fine RAP were 1.9% and 2.24, respectively, per ASTM C128 [122].

In Phase I, to control any gradation effects, two sizes of fine RAP were blended: 50% by weight consisted of particles passing the #4 sieve (4.75 mm) and retained on the #8 sieve (2.36 mm) and 50% by weight consisted of particles passing the #8 sieve (2.36 mm) and retained on the #16 sieve (1.18 mm). The reason for using two sizes of fine RAP was to remove dust and at the same time increase the surface area of the RAP exposed to the leachate solution.

In Phase II, the RAP aggregates with particle sizes passing the #16 sieve (1.18 mm) and retained on the #50 sieve (0.3 mm).

*2.3.4. Water and NaOH Solution*

Potable water per ASTM C1602 [123] at room temperature was used for the production of the mortar mixes in Phase II. Deionized water was used for leaching in Phase I and also for the cement paste samples used for isothermal calorimetry in Phase I.

The NaOH solution used in Phases I and II had a concentration of 0.01 M (pH ≈ 12). The NaOH solution was prepared using deionized water.

**2.4. Test Methods**

*2.4.1. Total Organic Carbon (TOC) Analysis*

TOC analysis is a measure of the potential range of dissolved organic carbon in liquids. A Shimadzu TOC-VCSN instrument was used, which utilizes a 680°C combustion catalytic oxidation method followed by non-dispersive infrared detection to quantify the TOC.

In Phase I, as a control, TOC analysis was performed on the deionized water and NaOH solutions before soaking the RAP aggregates. Subsequent TOC analyses were performed after 1 day, 5 days, 15 days, and 20 days of soaking. In Phase II, TOC analysis was performed on the pore solutions extracted from the mortar specimens cured for 3 days and 7 days.

All solutions were kept in glass jars during the leaching experiment and after pore solution extraction to prevent any contamination of the solution with potential organic leachate from containers (i.e., as would be a potential issue if plastic containers were used). All solutions were passed through a 0.22 μm filter prior to TOC analysis. Prior to analysis, samples were acidified

with hydrochloric acid to reach a pH < 4, as was necessary for the TOC analysis. The instrument was calibrated before each use with standardized TOC solutions of 100 mg/L in Phase I and 1000 mg/L in Phase II. The standard solutions' concentration in each phase was determined by preliminary testing and by measuring the approximate amounts of organic chemicals presented in the leachate solutions. Nanopure water was used as the reference (TOC = 0 mg/L) solution during the calibration and analysis.

*2.4.2. Fourier Transform Infrared (FTIR) Spectroscopy*

FTIR was employed in order to identify the functional groups of the organic compounds in the leachate and in the asphalt on the RAP. FTIR was performed using attenuated total reflection (FTIR-ATR) using a Nicolet iS50 instrument. Spectra were collected and averaged over 64 scans with a spectral resolution of 4 cm–1.

Given that water will oversaturate the FTIR spectrum and small peaks may be unobservable, the water was separated from the organics in the leachate during Phase I. To do this, leachate was collected from the NaOH solution after soaking the fine RAP for 55 days. A reference solution of NaOH without leachate was also prepared. 10 mL of each solution were mixed with 10 mL of dichloromethane in a separatory funnel for 10 minutes; this was repeated three times. Then all three samples were mixed, and the leachate was then concentrated to 1 mL using a Kuderna-Danish concentrator, after which the concentrated leachate was dried with anhydrous sodium sulfate. Some methanol residue was also present in the concentrated leachate from the process. To evaporate the methanol and only leave the organic compounds from the leachate, a heat gun was used to evaporate the droplet of leachate on the ATR diamond, which resulted in the solid residue of the concentrated leachate.

FTIR-ATR was also used during Phase I to examine the functional groups in the asphalt film on the fine RAP aggregates to observe any changes before and after soaking in solutions.

*2.4.3. Gas Chromatography (GC)*

GC is used for the analysis of volatile and semi-volatile organic compounds (VOCs, SVOCs). Usually, GC with a flame ionization detector (FID) is used to separate and detect the presence of organic compounds in aqueous samples after being extracted with a non-polar organic solvent (e.g., dichloromethane, hexane).

In Phase I, GC was used to detect the presence of any non-polar or low molecular weight organic compounds in the NaOH solution before and after soaking the fine RAP aggregates for 55 days. To complete qualitative analysis with GC/FID, samples were prepared by extracting with dichloromethane in a separatory funnel and a Kuderna-Danish concentrator as described in Section 2.4.4. GC/FID was used after drying the concentrated leachate with sodium sulfate. An Agilent 6850 GC/FID was used. Separations were obtained using a J&W Scientific DB-5 capillary column (30 m long, 250 µm inner diameter, and 0.25 µm film thickness). The settings used for GC/FID analysis are shown in Table 1.

***Table 1: Settings used for GC/FID analysis***

| | |
|---|---|
| Injection Port Temp. | 280°C |
| Purge Valve | 3 mL/min |
| Purge Time | 1 min |
| Total Flow | 13 mL/min |
| Constant Flow | 1.1 mL/min |
| Injection Volume | 1µL,split 1:10 |
| Column Oven Initial Temp. | 40°C |
| Column Oven Initial Time | 3 min |
| Column Oven Ramp Rate | 5°C/min to 165°C |
| Column Oven Final Temp. | 295°C |
| Column Oven Final Time | 4 min |
| MSD Transfer line Temp | 280˚C |

*2.4.4. High-Performance Liquid Chromatography (HPLC)*

HPLC is used for the analysis of non-volatile polar or non-polar compounds. Usually, HPLC uses ultraviolet (UV) spectroscopy or mass spectrometry (MS) as a detector. In order to detect a compound via a UV detector, the compound must contain a UV chromophore. However, for MS detection, the compound must be ionized either in positive or negative mode. To ionize the compounds, an electrospray ionization (ESI) source is commonly used. Phase I experiments utilized an ACQUITY UPLC I-Class System coupled to a Waters Xevo G2 Quadrupole Time-of-Flight (QTOF) MS detector via ESI interface. Chromatographic separations were achieved using an ACQUITY UPLC BEH C18 column (1.7 µm particle size, 2.1 cm length, 100 mm inner diameter). Separations were performed at 40°C. The mobile phase consisted of a mixture of acetonitrile, water, and formic acid at a flow rate of 0.5 ml min−1. Acetonitrile with 0.1% formic acid was used as "mobile phase B," and water with 0.1% formic acid was used as "mobile phase A." A 90/10 mixture of water/acetonitrile was utilized as the weak wash solvent and 50/50 water/acetonitrile was used as the strong wash solvent for rinsing the injection needle. Prior to running the elution, the column was equilibrated to 90/10. The elution gradient program was 90–10% A from 0 min to 6 min, 10% A from 6 min to 7.5 min, 10–90% A from 7.5 minmin to 8 min, and 90% A from 8 min to 9 min.

For Phase I, solid phase extraction (SPE) was used to concentrate the leachate from the NaOH solution with RAP after 55 days. A control NaOH solution without RAP was also prepared. A 3 mL Supelclean LC-18 SPE cartridge was conditioned first by washing with 6 mL of methanol followed by 3 mL of 0.1% formic acid. Then 10 mL of the leachate solution was passed through the cartridge at a rate of 1 mL/min followed by washing it with 3 mL of 0.1% formic acid. The cartridge was dried using nitrogen gas followed by eluting the analyte using 3 mL of methanol at

a rate of 1 m/min. The methanol solution was concentrated to approximately 0.5 mL and analyzed via LC/UV/MS system.

Atmospheric pressure ionization was performed in positive ion, negative ion, and sensitivity analyzer modes for QTOF-MS data acquisition. A wide mass range (m/z of 100 to 2500) was selected for the acquisition of data. The corona voltage, sampling cone voltage, source temperature, and desolvation temperature were 3.0 kV, 40 V, 120°C, and 250°C, respectively. Nitrogen (20±2°C at 10 psi) was used for desolvation at 700 L/h, and the cone gas flow rate was 5 L/h. 5 L/h. Argon was used as the collision gas and the collision energy was 15 V to 45 V for high-energy ionizations. Data were acquired and analyzed using MassLynx™ NT 4.1 software. Analyses were performed in full scan mode and the scan time was set to 0.2 s. To ensure mass accuracy and reproducibility of the optimized MS conditions, leucine-enkephalin (m/z 554.2615 in negative mode and m/z 556.2771 in positive mode) was used as a lock mass reference at a concentration of 1 ng/mL and a flow rate of 10 µL/min. The reference was injected into the MS instrument every 30 sec. The instrument was calibrated using sodium format solution as the calibration standard to achieve mass accuracies of <0.5 mDa.

*2.4.5. Isothermal Calorimetry*

During Phase I, IC was used to quantify the hydration kinetics of a Portland cement paste mixed with RAP leachate. Using a fixed liquid-to-cement ratio of 0.5 by mass, a total of six different pastes were prepared: 1) control deionized water with no RAP leachate compounds, 2) control NaOH solution with no RAP leachate compounds, 3) deionized water in contact with RAP for 1 day, 4) deionized water in contact with RAP for 250 days, 5) NaOH solution in contact with RAP for 1 day, and 6) NaOH solution in contact with RAP for 250 days. IC was conducted on 2 replicate samples for each of the control solutions and 3 replicates for the pastes containing

leachate. IC was performed using a Calmetrix I-Cal Flex following ASTM C1679 [124]–[126] procedures to quantify the total heat (J/g binder) and thermal power (W/g binder) of various mixtures. The paste mixtures were manually mixed in 15 mL plastic vials before inserting the vials in the IC at 23˚C. The heat of hydration was measured for up to 48 h.

*2.4.6. X-Ray Photoelectron Spectroscopy (XPS)*

In Phase I, XPS was used to determine the elemental composition of the first few nanometers of the asphalt coating film of RAP aggregates. The XPS was performed on RAP aggregates before and after soaking in solution. XPS characterization of the samples was performed on a PHI VersaProbe III Scanning XPS microscope using a monochromatic Al K-alpha X-ray source (1486.6 eV). XPS spectra were acquired over an area of 1000 μm by 200 μm with dual-beam charge neutralization. All binding energies were referenced to the C─C peak at 284.8 eV. Atomic concentrations of elements were determined from the integrated intensity of the elemental photoemission features corrected by relative atomic sensitivity factors.

*2.4.7. Optical Imaging*

In Phase I, RAP aggregates passing the #200 sieve (75 μm) before and after NaOH soaking were investigated using a Zeiss Axio Observer Z1 optical microscope. A magnification of 100× was used to observe any physical changes to the surface.

*2.4.8. Pore Solution Extraction*

In Phase II, pore solution of hardened mortar samples was extracted from samples made with NaOH-treated RAP, untreated RAP, and natural sand cured for 1 day, 3 days, and 7 days. This analysis was implemented to explore changes in pore solution chemistry as a function of pre-leaching by an NaOH solution. The pore solution extraction device was designed based on the

Barneyback and Diamond design [127]. The extracted pore solution was quantitatively analyzed to measure the pH, the elemental composition by inductively coupled plasma mass spectrometry (ICP-MS), and the organic carbon content by TOC analysis.

The mortar specimens were subjected to high pressure in excess of 300 MPa, resulting in about 5 mL to 10 mL of pore solution. Care was taken to not exceed 420 MPa for two reasons: 1) according to the authors' experience, pressures in excess of 420 MPa risked damaging the piston, and 2) the literature show that the ionic concentration of pore solution is impacted by the magnitude of applied pressure, resulting in a recommendation of not exceeding 500 MPa [128]. The pressure was increased at a rate of approximately 2.8 MPa/s and held constant for several minutes once the maximum pressure was reached.

The extracted pore solution was immediately tested for pH using Apera Instruments PH400S portable pH meter. Subsequently, the pore solution sample was acidified with Nitric Acid (HNO3) hydrochloric acid (HCl) to reach a pH<4 in preparation for ICP-MS and TOC analyses. A Thermo Electron iCAP-RQ ICP-MS was used in accordance with Standard Method 3125-B [129]. The TOC analysis procedure was previously presented in Section. 2.4.1.

*2.4.9. Compressive Strength and Split Tensile Analysis*

In Phase II, the compressive and split tensile strengths were measured per ASTM C39 [129], and ASTM C496 [130], [131], respectively, for the mortar mixture samples. Three replicate samples were tested at 1 day, 3 days, and 7 days of moist curing.

*2.4.10. Contact Angle and Surface Free Energy*

In order to more effectively understand how the NaOH solution treatment affected the cohesive and adhesive properties of the asphalt, a set of experiments in Phase II measured the surface free

energy (SFE) of asphalt surfaces. This methodology followed the procedure by Brand and Roesler [36], where a flat surface of plain asphalt (PG 64-22) was treated in a given solution. Three asphalt samples were prepared: 1) an untreated surface, 2) a surface soaked in deionized water for 10 days, and 3) a surface soaked in NaOH solution for 10 days. Following van Oss-Chaudhury-Good (VOCG) theory [132], [133], a total of three probe liquids with known properties were used: one non-polar liquid (Di-Iodomethane) and two polar liquids (Glycerol and Ethylene Glycol).

The contact angle between the asphalt surface and a sessile drop of the probe liquid was measured by a Biolin Scientific Theta Flow optical tensiometer. A minimum of five sessile drops were measured per probe liquid per surface. From the Young-Dupré equation, the work of adhesion at the liquid-solid interface ($W_{ls}$) is a function of the contact angle of the liquid ($\theta$) and liquid surface tension ($\gamma_l$). From VOCG theory, $W_{ls}$ is a separated into contributions from Lifshitz-van der Waals ($\gamma^{LW}$), Lewis acid electron acceptor ($\gamma^+$), and Lewis base electron donor ($\gamma^-$) components for the liquid (l) and solid (s) phases:

$$W_{ls} = \gamma_l(1 + \cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + 2\sqrt{\gamma_s^+\gamma_l^-} + 2\sqrt{\gamma_s^-\gamma_l^+} \quad (1)$$

Since the probe liquids are of known properties [133] in Equation (1), the three probe liquids to yield three contact angles will result in the surface energy components of the solid (*i.e.*, $\gamma_s^{LW}, \gamma_s^+, \gamma_s^-$). Furthermore, the work of adhesion ($W^A$) between two solids of 1 and 2, in vacuum is also derived as:

$$W_{12}^A = 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + 2\sqrt{\gamma_1^+\gamma_2^-} + 2\sqrt{\gamma_1^-\gamma_2^+} \quad (2)$$

The interfacial energy ($\gamma_i$) between solids 1 and 2 in vacuum is derived as:

$$\gamma_i = \gamma_{12} = \gamma_1 + \gamma_2 - W_{12}^A \quad (4)$$

The work of adhesion between solids 1 and 2 in the presence of a liquid (labeled 3), can also be derived as:

$$W_{123}^A = -\gamma_{12} + \gamma_{13} + \gamma_{23} \quad (5)$$

## 2.5. Results and Discussion

### *2.5.1. Total Organic Carbon (TOC) Analysis*

Table 2 shows the TOC results for the solutions with RAP leachates. Note that the TOC values reported for the reference solutions (0 day soaking) were due to filtering the solutions with plastic syringes during the sample preparation. The results in Table 2 show that, as the time of soaking increased, more organic compounds leached from the RAP aggregates but the largest increase in TOC occurred within the first 24 h. The results are consistent with the literature that the organic content in solution will increase with increasing pH relative to water[101].

***Table 2. TOC analysis results in Phase I (mg/L)***

| Solution | 0 day* | 1 day | 5 days | 15 days | 20 days |
|---|---|---|---|---|---|
| Deionized water | 0.596 | 12.98 | 13.52 | 15.91 | 17.86 |
| NaOH (pH≈12) | 1.35 | 25.61 | 40.48 | 49.12 | 55.29 |

*0-day soaking refers to the reference solution before soaking the RAP in the water or NaOH solution

### *2.5.2. Fourier Transform Infrared (FTIR) Spectroscopy*

The FTIR spectra of the concentrated leachate are shown in Figure 1. By comparing the spectrum of the reference NaOH (without RAP leachates) and the spectrum of the NaOH leaching solution after 55 days, the RAP solution appears to have a number of additional peaks. The peak

at 1716 $cm^{-1}$ is likely attributable carbonyl (C=O) groups [134], which are present in oxidized asphalt [135]. The peak around 3396 $cm^{-1}$ is attributable to hydroxyl (O–H) and/or amine (N–H) groups [134], [136]. The peaks at 2923 $cm^{-1}$ and 2853 $cm^{-1}$ is likely attributable aliphatic (C–H, methyl and methylene) groups [137]. The peak around 1653 $cm^{-1}$ could be attributable to carbonyl and/or amino (C=O) groups [137]. Unsurprisingly, these data are indicative of organic compounds, but given the complex and heterogenous molecular composition of asphalt[138], it is likely that the FTIR data are the culmination of contributions from many organic compounds in the leachate.

Figure 2 shows the changes in the surface chemistry of the asphalt coating film of the RAP aggregates before and after treatment with NaOH. All the changes observed in FTIR peaks before and after treatment refer to alkene and alkane leachates from the asphalt. There is no study in the literature to show how these two compounds can impact cement hydration.

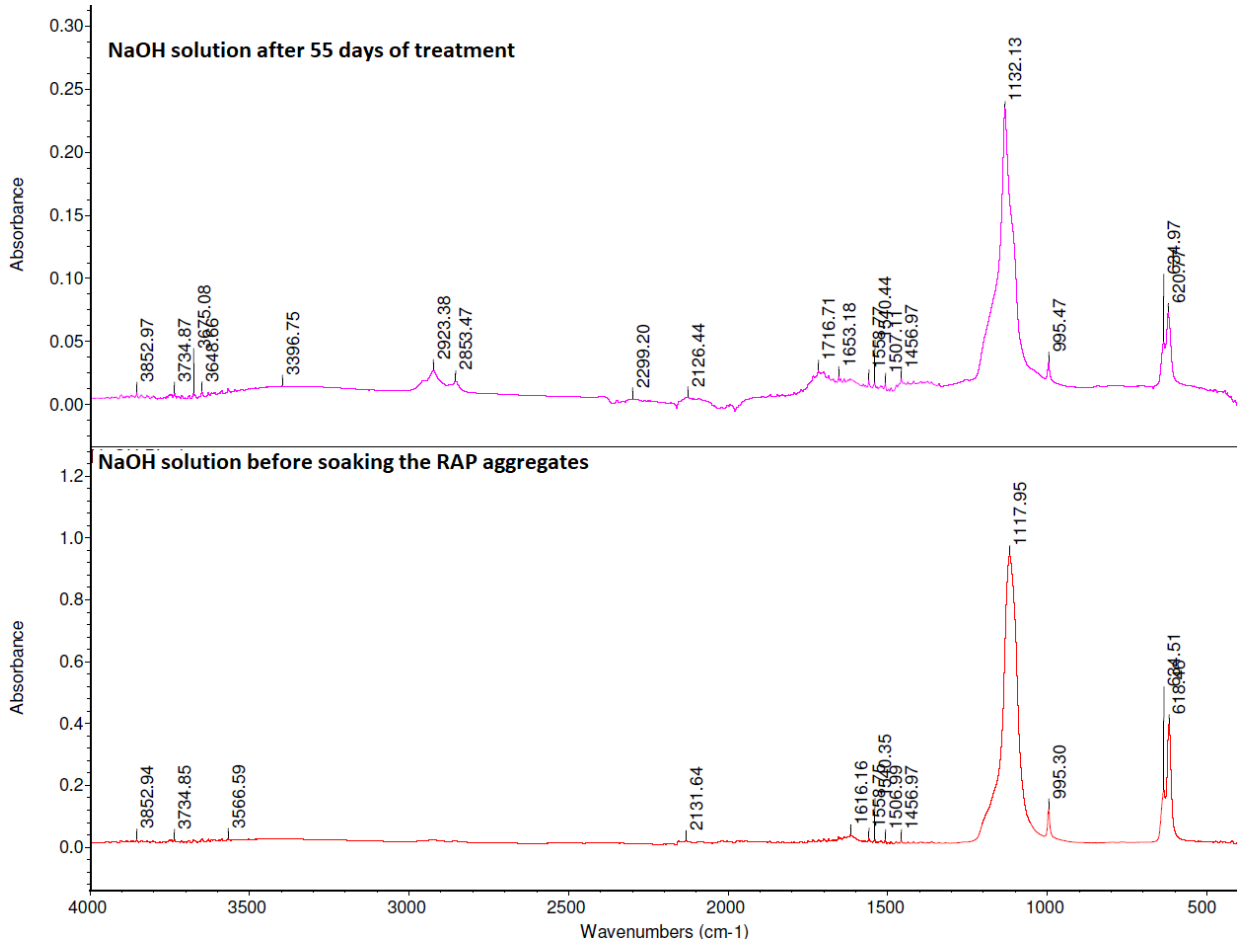



***Figure 1. FTIR spectrum obtained from the NaOH leaching solution after 55 days of RAP aggregates soaking***

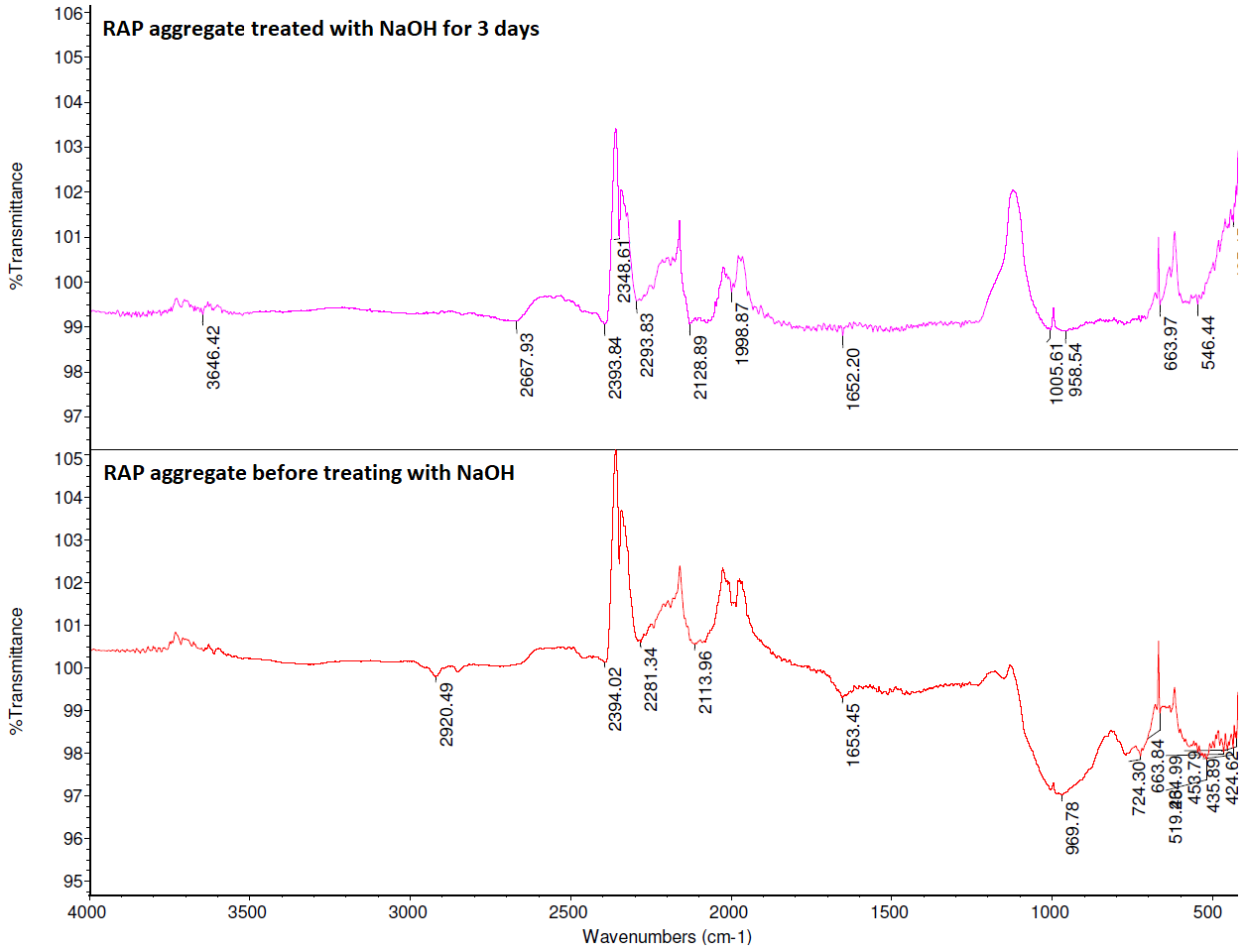



***Figure 2. FTIR spectrums of RAP aggregates before and after treatment with NaOH***

### *2.5.3. Gas Chromatography (GC)*

The results of GC/FID are shown in Figure 3 and Figure 4. The results did not indicate the presence of any VOCs or SVOCs. Therefore, since TOC analysis shows that organic compounds are present in the leachate, the GC/FID indicates that the organic compounds in the leachate are all non-volatile.

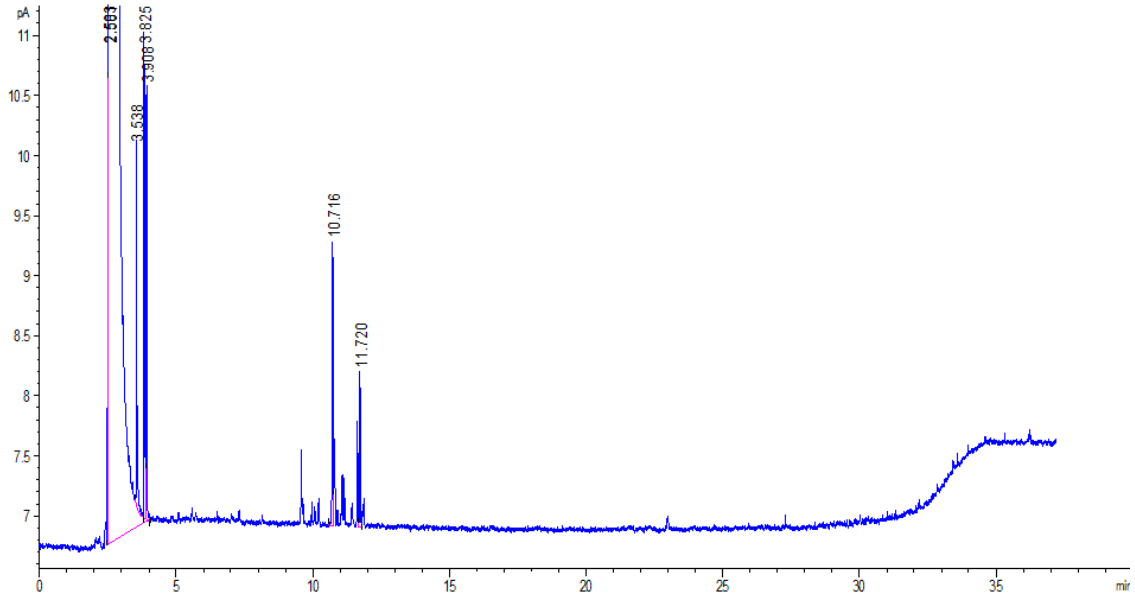



***Figure 3. GC/FID analysis of the reference NaOH solution without RAP.***

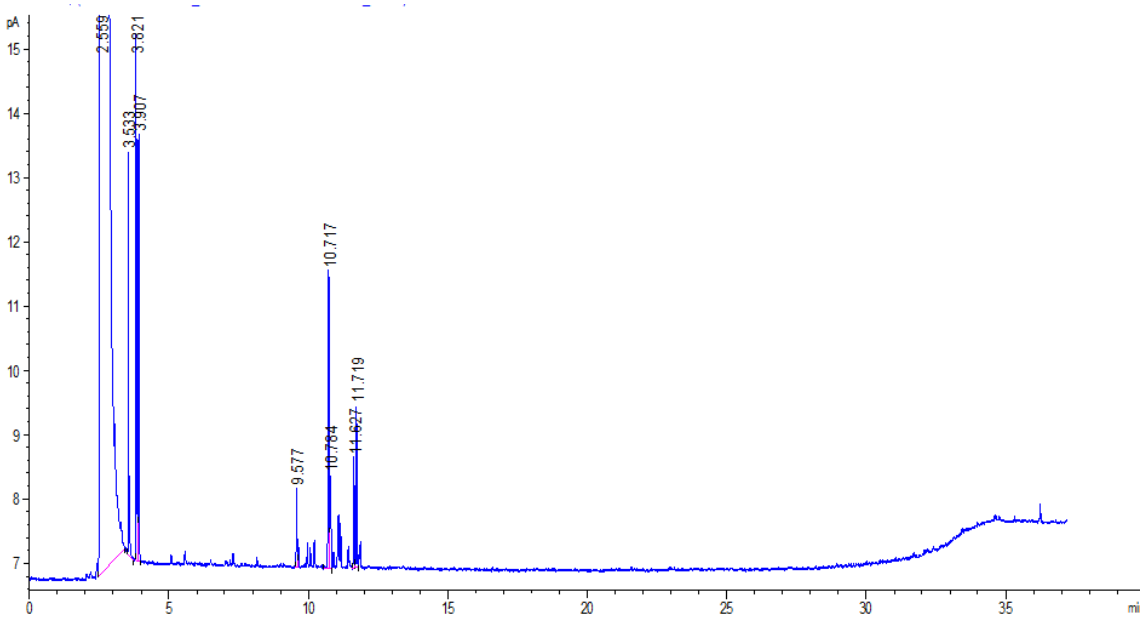
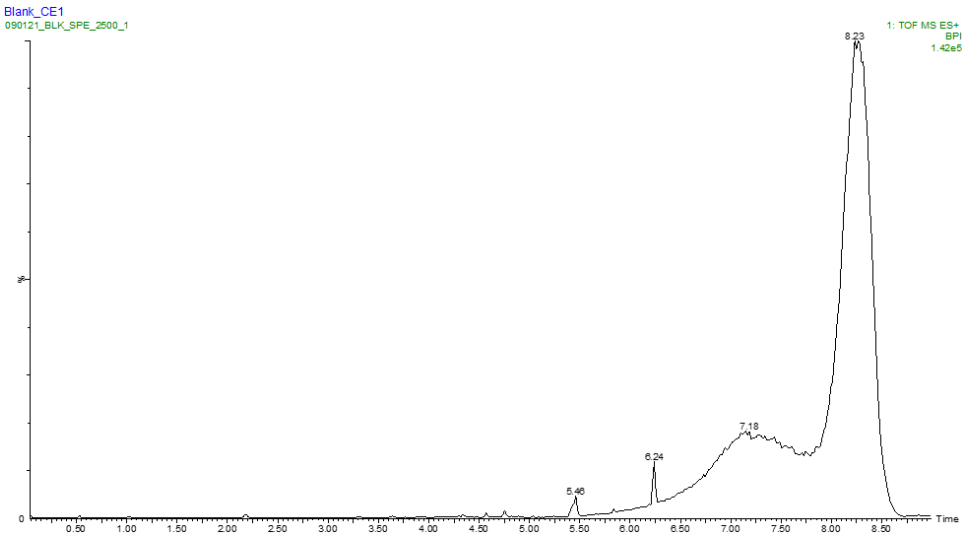


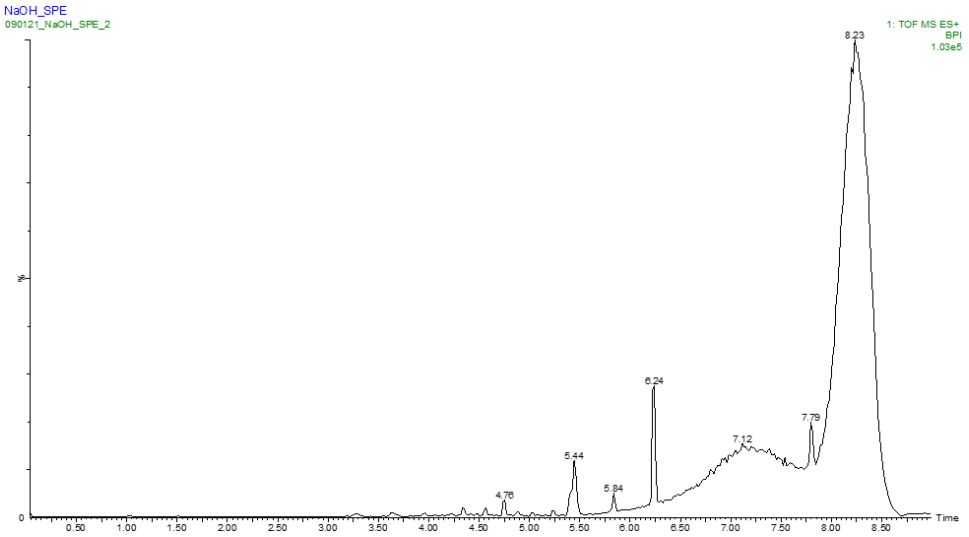

***Figure 4. GC/FID analysis of the concentrated leachate collected after soaking RAP in NaOH solution for 55 days.***

*2.5.4. High-Performance Liquid Chromatography (HPLC)*

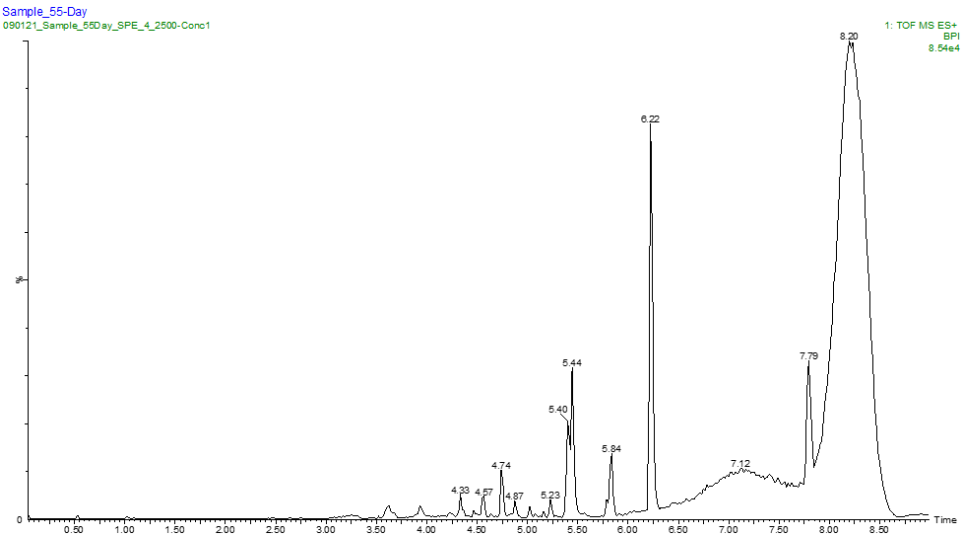
Figure 5 shows the HPLC data in positive mode using the MS detector. Positive mode experiments were also performed with the UV detector set at a wavelength of 254 nm, but no compounds were detected; it is possible that compounds could have been detected at other wavelengths.




(a)




(b)

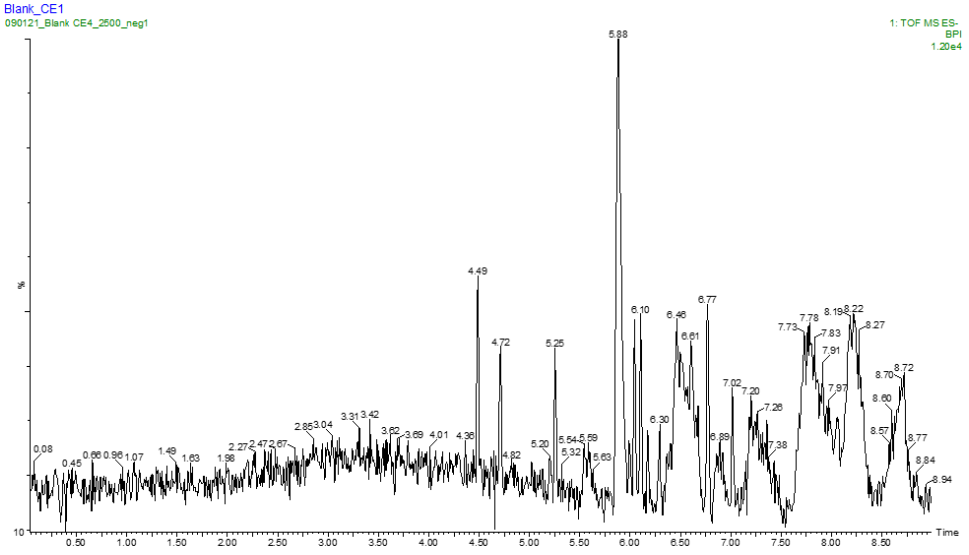



(c)

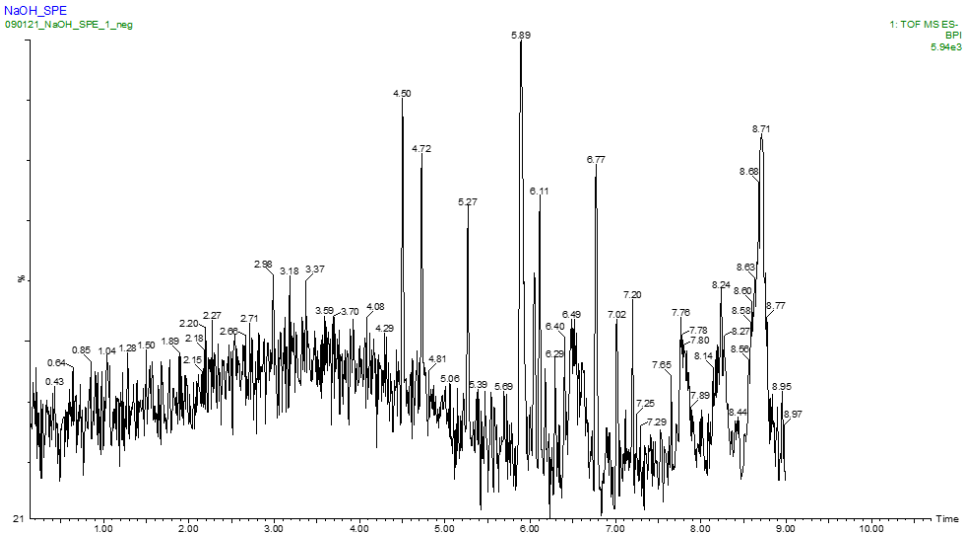
***Figure 5. Positive mode of LC/MS analysis using C18 SPE cartridge(a) blank MeOH (b) 10 mL concentrated reference NaOH solution (c) 10 mL concentrated leaching NaOH solution after 55 days of soaking RAP aggregates***

Figure 6 shows the HPLC data in negative mode using the MS detector. Figure 6a is a blank with methanol, and Figure 6b is the reference NaOH solution without RAP leachates. The peaks in Figure 6a,b are equivalent, indicating that no impurities were present. Figure 6c is the concentrated leachate from NaOH solution with RAP leachates, which indicates that non-volatile polar and/or non-polar organic compounds are present. Comparing Figure 6c and Figure 6b, it is evident that the leachate from RAP contains a number of organic compounds eluted from around 2 min to 5 min. Figure 7 shows the MS spectra after four different times from Figure 6c corresponding to the primary peak at 3.67 min and the minor peaks at 3.49 min, 3.16 min, and 2.60 min. Note that the time of MS data collection in Figure 7 is slightly later than these four peaks in an attempt to fully capture the compounds corresponding to those peaks. Figure 7 clearly demonstrates that a significant number of organic compounds are present, but without further

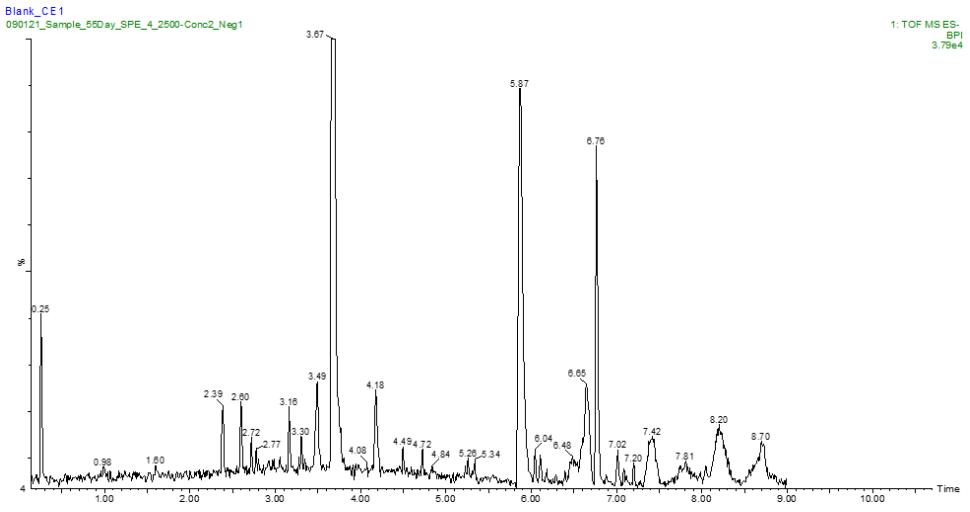
separation of the concentrated leachate, it is impossible at this stage to speculate on the compounds present. However, the mass-to-charge (m/z) ratio of the compounds and fragments appears to tend towards values less than 400.




(a)

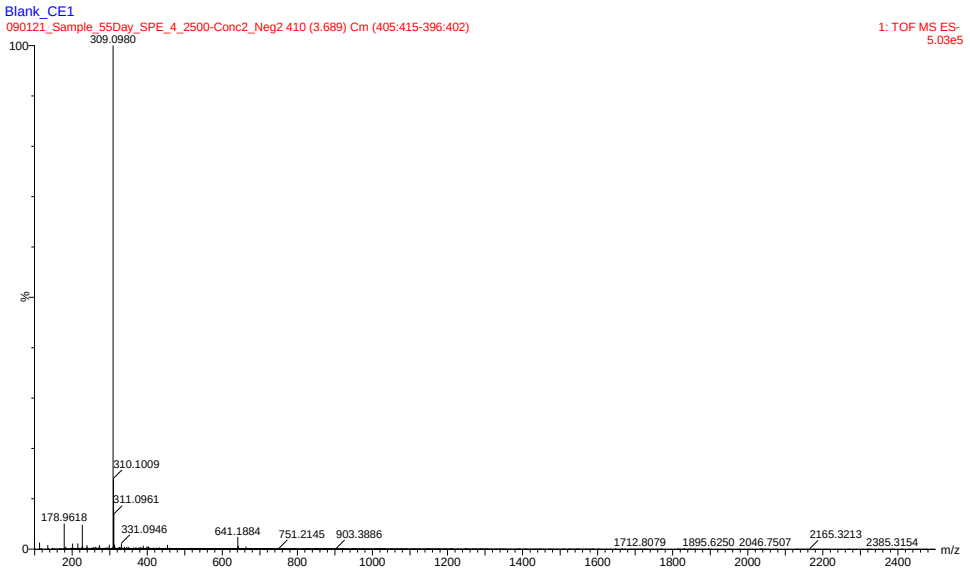



(b)

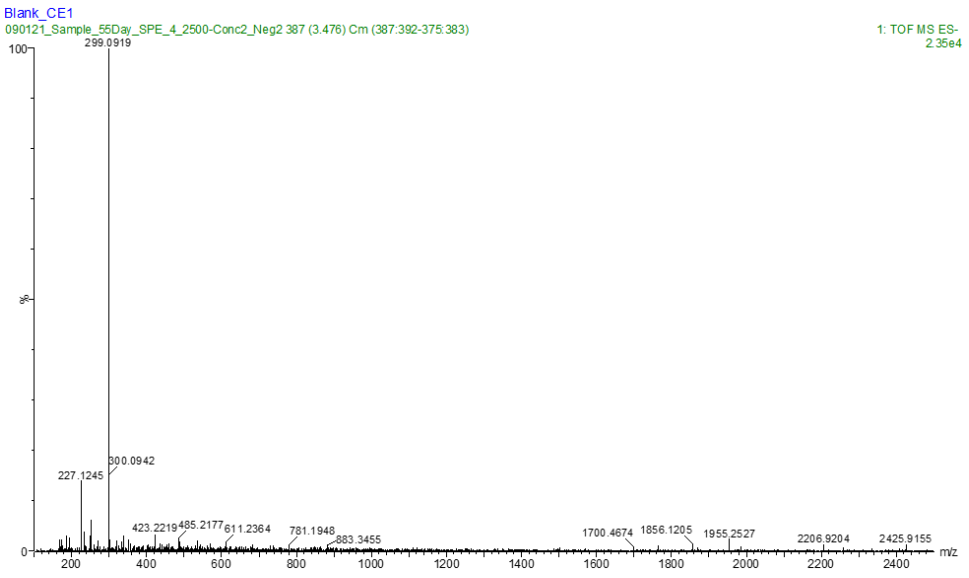



(c)

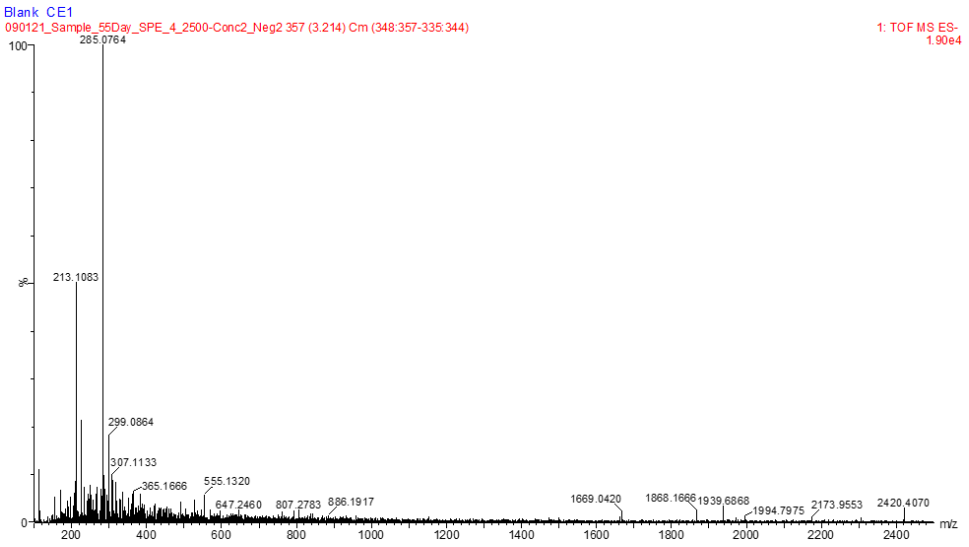
***Figure 6. Negative mode of LC/MS analysis using C18 SPE cartridge (a) Blank methanol (b) 10 mL concentrated reference NaOH solution (c) 10 mL concentrated leaching NaOH solution after 55 days of soaking RAP aggregates***



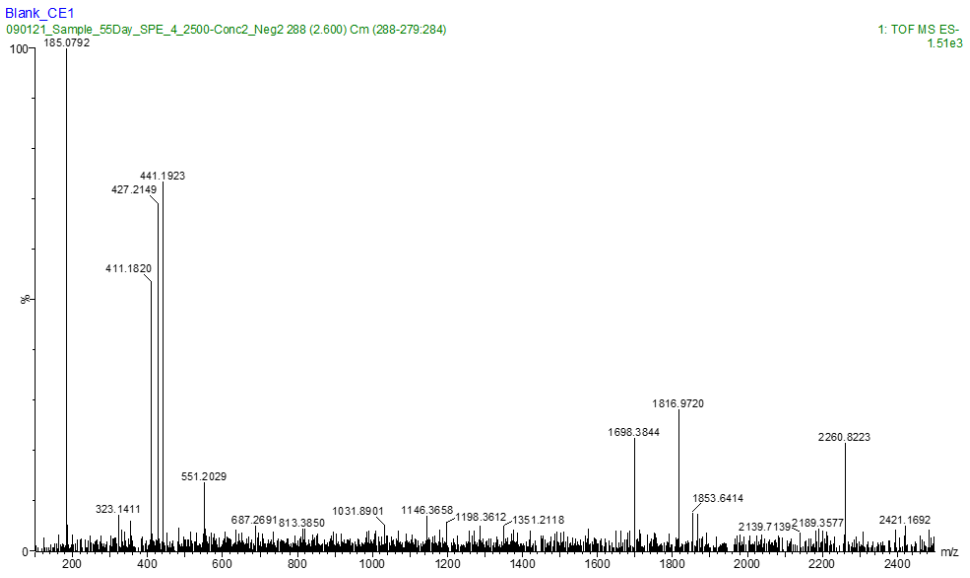

(a)


Blank_CE1
090121_Sample_55Day_SPE_4_2500-Conc2_Neg2 387 (3.476) Cm (387:392-375:383)
1: TOF MS ES-
2.35e4
299.0919
300.0942
227.1245
423.2219
485.2177
611.2364
781.1948
883.3455
1700.4674
1856.1205
1955.2527
2206.9204
2425.9155
m/z

(b)


Blank_CE1
090121_Sample_55Day_SPE_4_2500-Conc2_Neg2 357 (3.214) Cm (348:357-335:344)
1: TOF MS ES-
1.90e4
285.0764
213.1083
299.0864
307.1133
365.1666
555.1320
647.2460
807.2783
886.1917
1669.0420
1868.1666
1939.6868
1994.7975
2173.9553
2420.4070
m/z

(c)




(d)

***Figure 7. Spectra of peak eluted in Figure 6c with retention time of (a) 3.69 min (b) 3.50 min (c) 3.17 min (d) 2.62 min***

### *2.5.5. Isothermal Calorimetry*

The IC results for the six different samples, including three replicate tests, are shown in Figure 8 for up to 48 hours of hydration. In this time frame, all stages of hydration can be observed: Stage I (dissolution), Stage II (dormancy), Stage III (acceleration), Stage IV (deceleration), and Stage V (steady state). Subsets of Figure 8 are identified in subsequent figures in order to better highlight and distinguish the differences. Table 3 shows the average calculated data from the IC curves.

Figure 9 shows the main peak in the hydration curves of the samples made with deionized water, including the control without RAP and RAP leachate in deionized water after 1 day and 250 days of soaking. In general, the solutions with RAP leachate appear to decrease the height of the main peak, with the result from 250 days of RAP soaking showing the greatest decrease relative

to the control. This reduction in the peak height indicates that in the presence of the leachate compounds, less chemical reaction is happening during cement hydration which can be concluded that the leachates may be poisoning the cement paste and preventing hydration.

Figure 10 shows the main peak in the hydration curves of the samples made with NaOH solution, including the control without RAP and RAP leachate in NaOH solution after 1 day and 250 days of soaking. While the trends are not as clear as for deionized water, it does appear that there is a slight decrease in the peak height with samples from RAP.

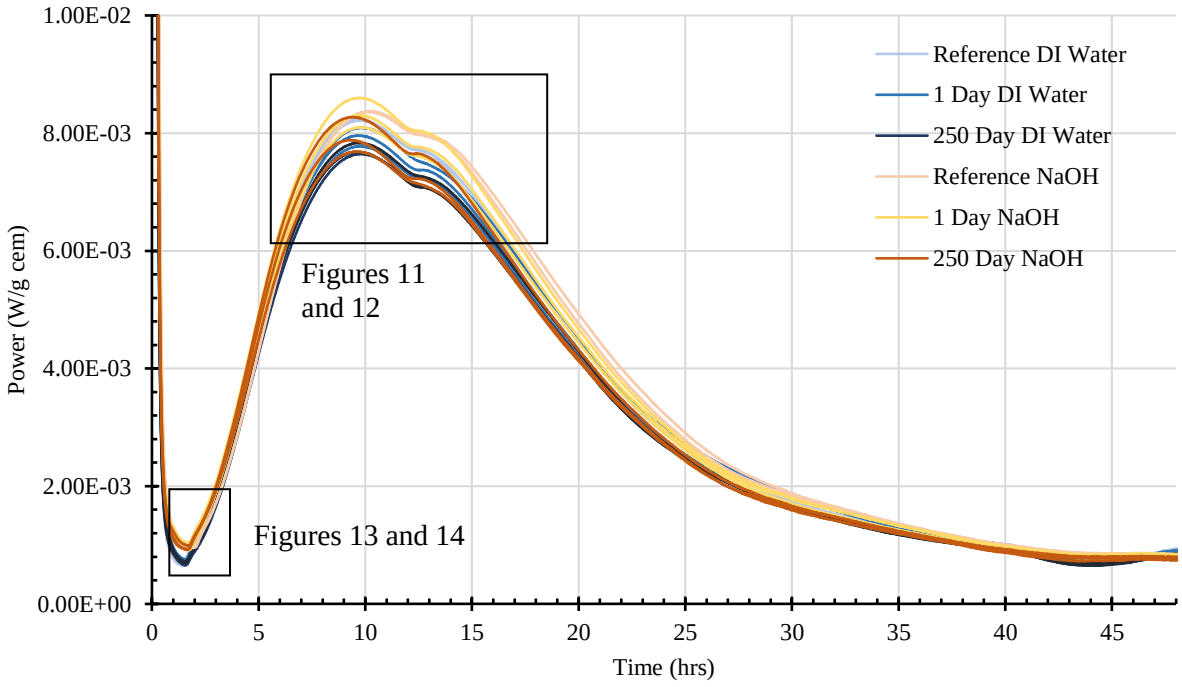



***Figure 8: Isothermal calorimetry results for all samples tested.***

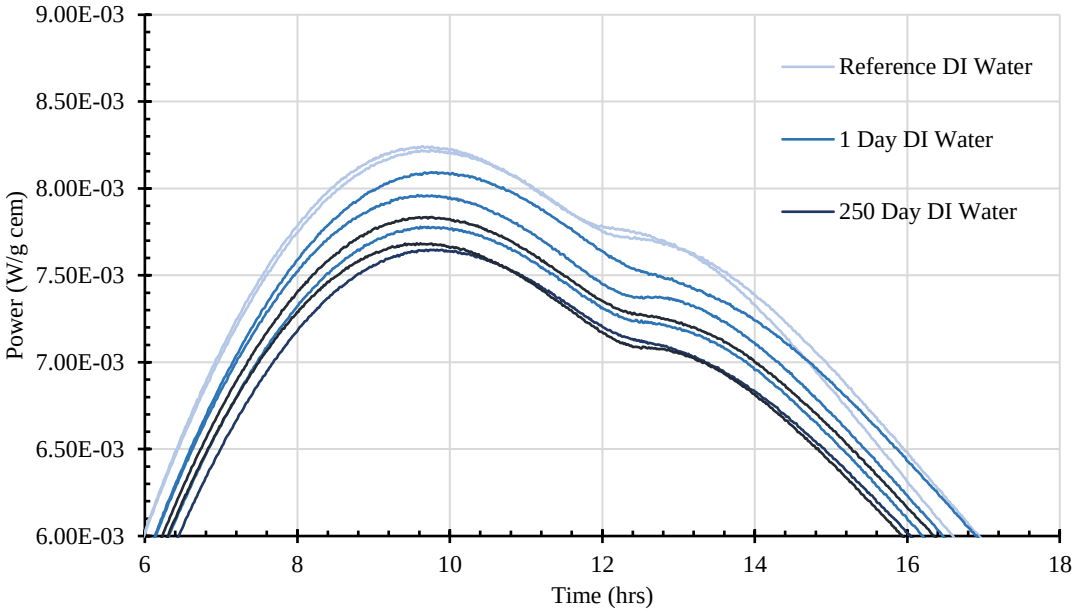



***Figure 9: Main hydration peak for deionized water samples.***

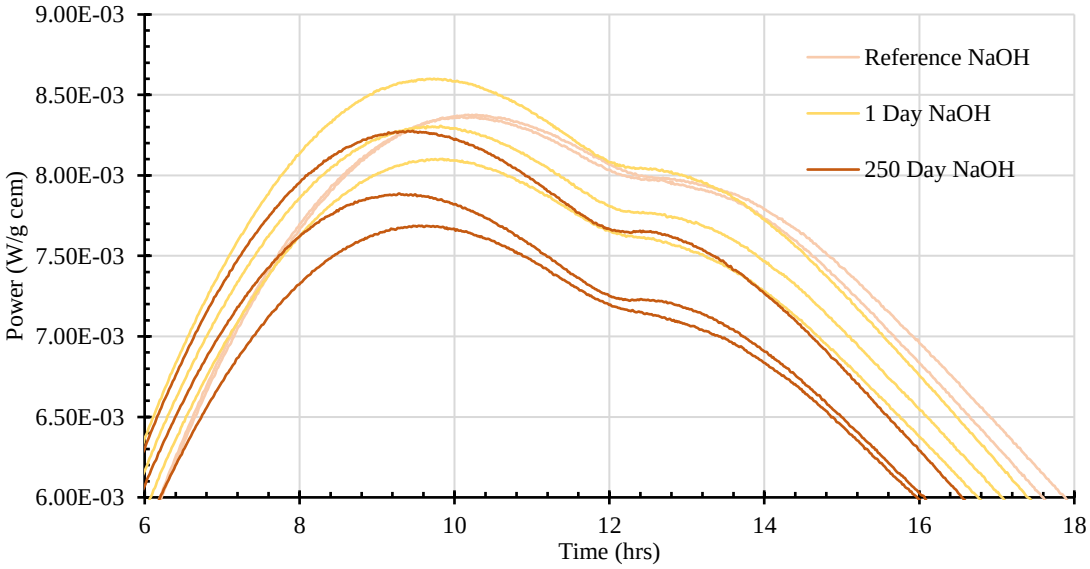



***Figure 10: Main hydration peak for NaOH samples.***

Figure 11 and Figure 12 highlight the transition from Stage II to Stage III for the mixes with deionized water and NaOH solution, respectively. In general, the curves are similar such that it is difficult to observe any trends, although the transition to Stage III may occur sooner for NaOH solutions with RAP relative to NaOH solutions without RAP.

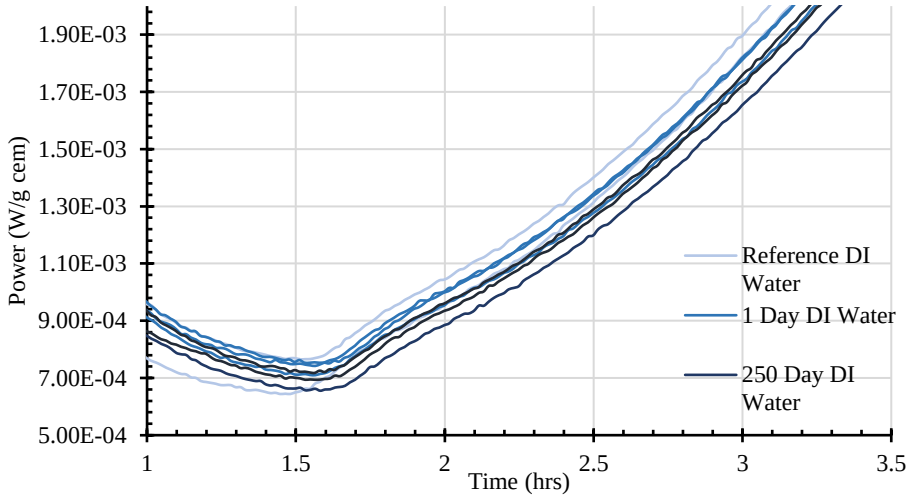



***Figure 11: End of dormancy, beginning of acceleration stage for deionized water samples.***

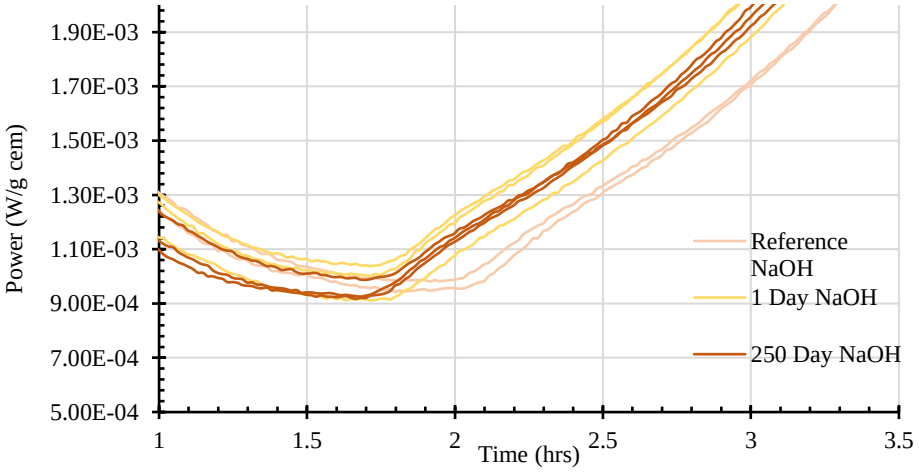



***Figure 12: End of dormancy, beginning of acceleration stage for NaOH samples.***

Figure 14 show the cumulative heat of hydration of all samples tested. It can be seen that the reference samples have greater cumulative energy readings than the samples containing leachate, which further implies that the leachate is inhibiting the formation of hydration products.

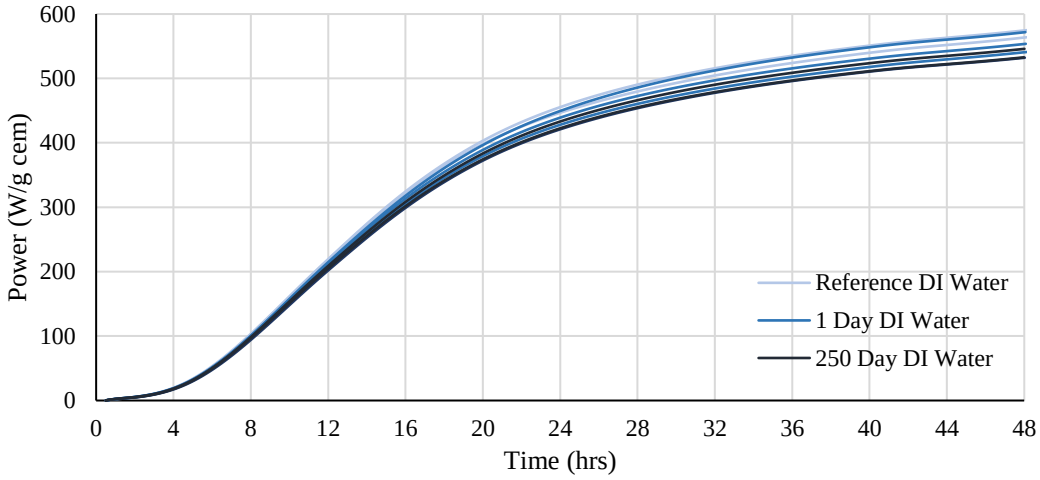



***Figure 13: 48 Hour cumulative heat of hydration for Deionized Water samples***

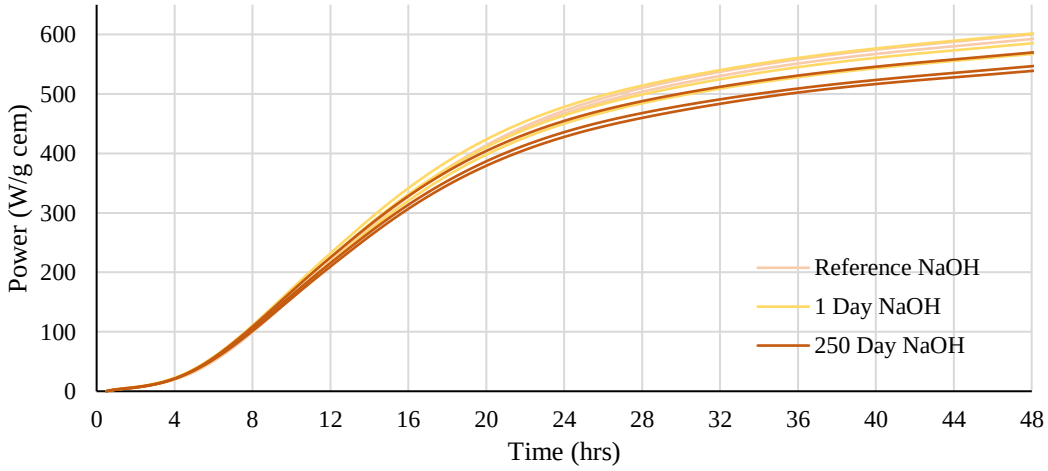



***Figure 14: 48-Hour cumulative heat of hydration for NaOH samples***

Table 3 shows the average and standard deviation of the results from IC. In general, the leachate in deionized water or NaOH solution decreased the maximum heat, although the cement paste with NaOH solution with RAP leachate reached the maximum value faster than the control.

***Table 3: Summary of Isothermal Calorimetry Results***

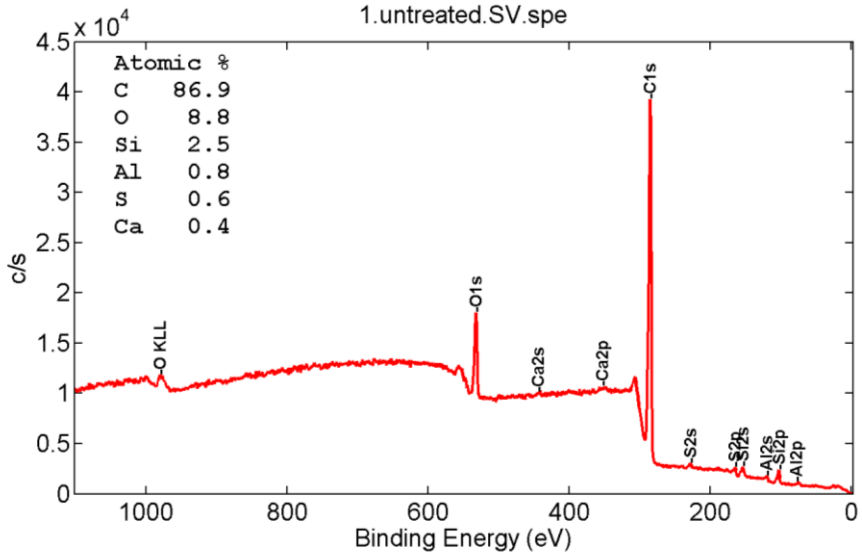
| | Thermal Equilibrium Time (h) | Maximum Heat Flow (mW/g cement) | Time to Maximum (h) | Time to End of Dormancy (h) | Total Heat after 48 hours (W/g cem) |
|---|---|---|---|---|---|
| Reference DI Water | 0.47 | 8.23 ± 0.01 | 9.70 ± 0.07 | 1.48 ± 0.05 | 568.98 ±5.50 |
| 1 Day DI Water | 0.48 | 7.95 ± 0.16 | 9.65 ± 0.10 | 1.58 ± 0.03 | 555.23 ± 12.72 |
| 250 Day DI Water | 0.43 | 7.72 ± 0.10 | 9.72 ± 0.14 | 1.56 ± 0.03 | 536.86 ± 6.37 |
| Reference NaOH | 0.71 | 8.37 ± 0.01 | 10.14 ± 0.06 | 1.79 ± 0.01 | 596.29 ± 3.83 |
| 1 Day NaOH | 0.52 | 8.34 ± 0.25 | 9.80 ± 0.06 | 1.71 ± 0.00 | 584.69 ± 14.05 |
| 250 Day NaOH | 0.80 | 7.95 ± 0.30 | 9.42 ± 0.15 | 1.68 ± 0.02 | 551.71 ± 13.14 |

*2.5.6. X-Ray Photoelectron Spectroscopy (XPS)*

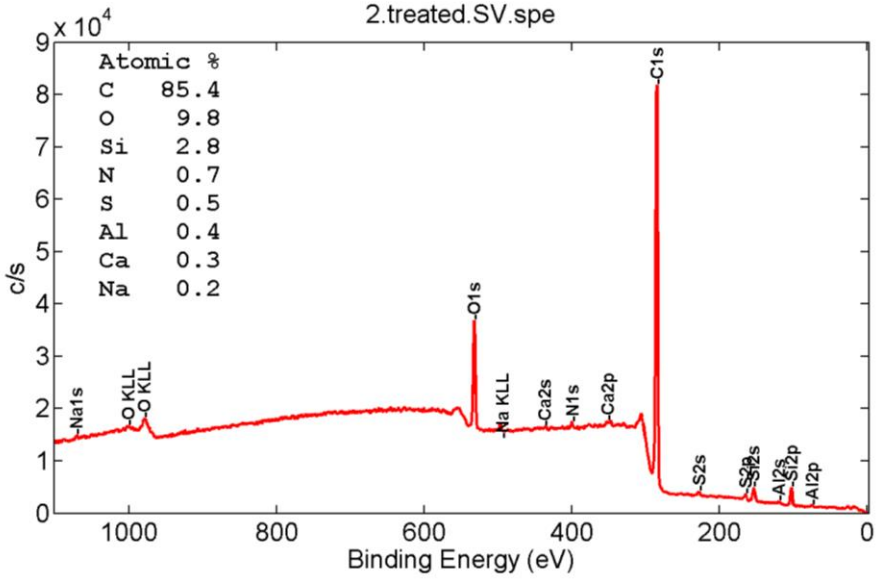
Figure 15 shows the XPS data for RAP aggregates before and after soaking in NaOH solution. After NaOH treatment, there was no obvious change in surface composition including carbon, oxygen and silicon contents, indicating that the asphalt surface coatings were not removed by NaOH. However, the NaOH solution did appear to result in some sodium uptake by the asphalt.

Figure 16 shows a deconvolution of the C 1s peak. A number of carbon functional groups are evident before soaking in NaOH solution, many of which disappear after soaking; this may suggest that the NaOH solution preferentially dissolved the organic compounds with those function groups.

Figure 17 shows a deconvolution of the O 1s peak. Since a larger O 1s fraction is attributable to C=O rather than C–O in the treated RAP aggregate, this may suggest that there is more oxidation of the surface by NaOH. Other studies have suggested that NaOH can increase the oxidation of asphalt, although Brand and Roesler showed a modification to the sulfoxide (S=O) rather than carbonyl groups by FTIR [36].

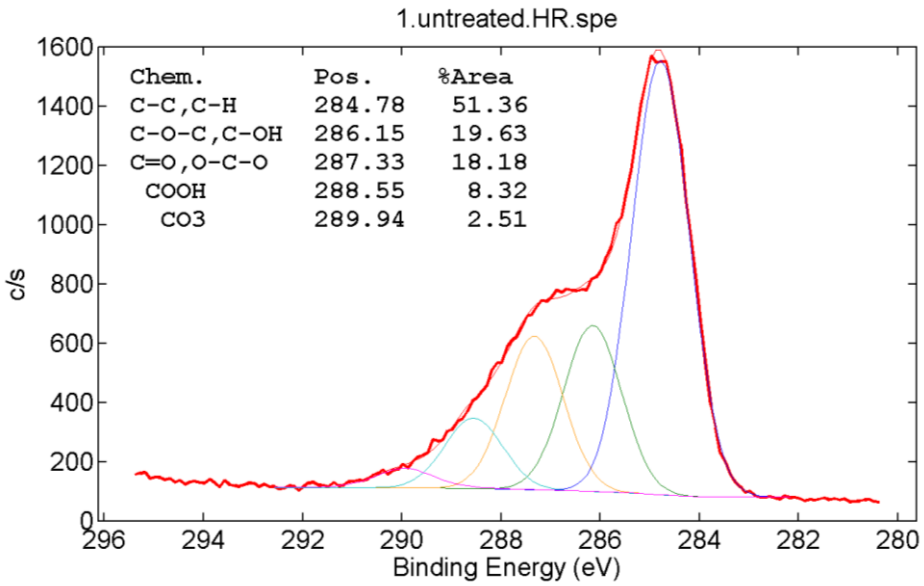



(a)

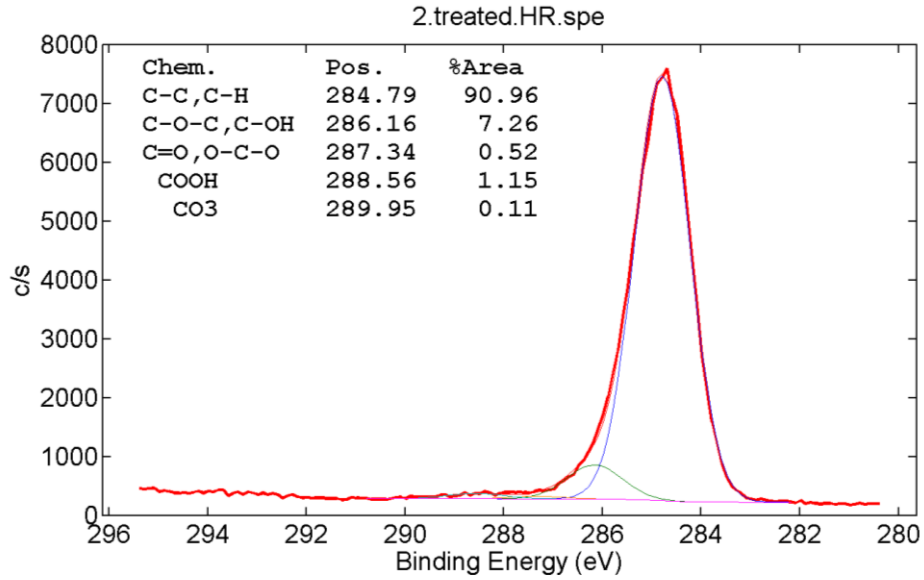



(b)

***Figure 15. Results of XPS analysis on (a) an untreated RAP aggregate (b) a NaOH-treated RAP aggregate***

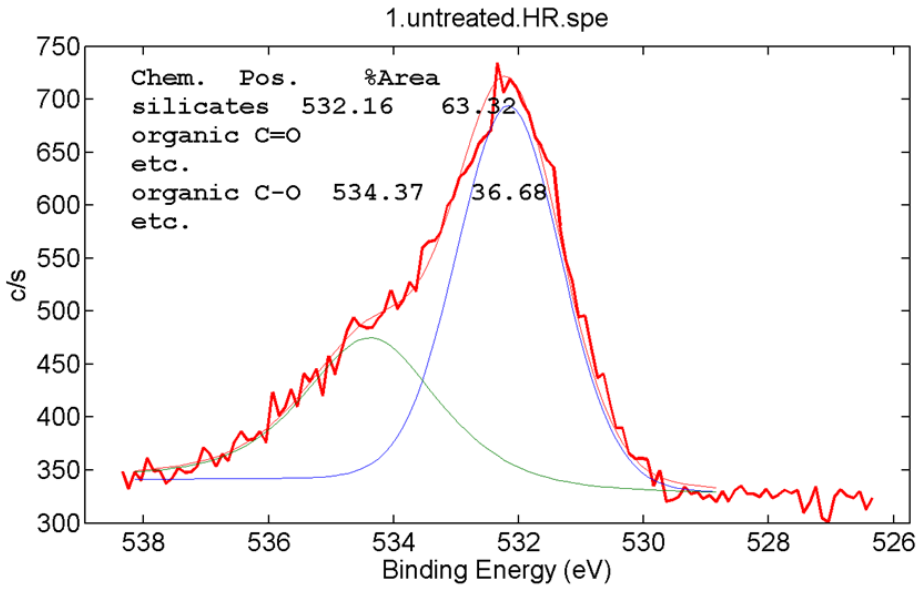



(a)

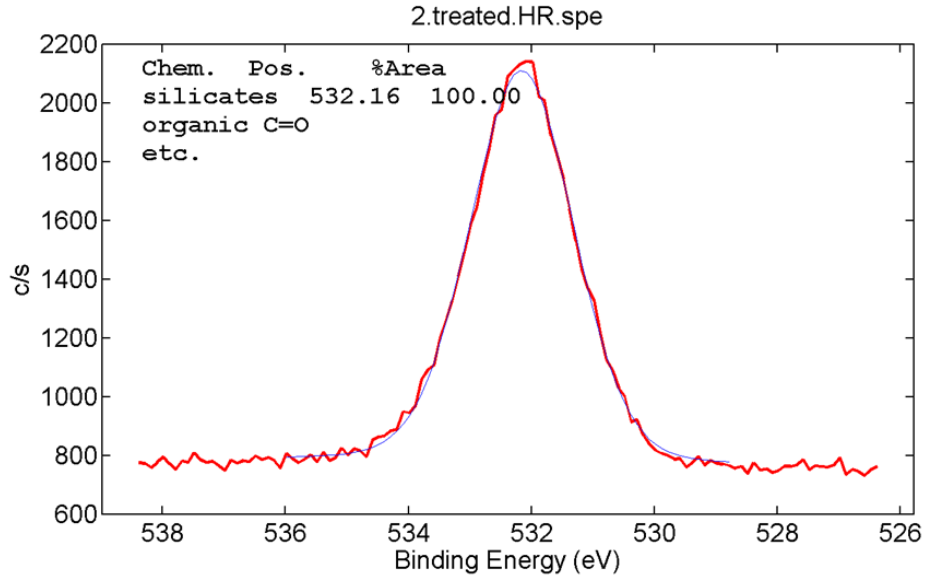



(b)

***Figure 16. Deconvolution of peak C 1s (a) an untreated RAP aggregate (b) a NaOH-treated RAP aggregate***




(a)

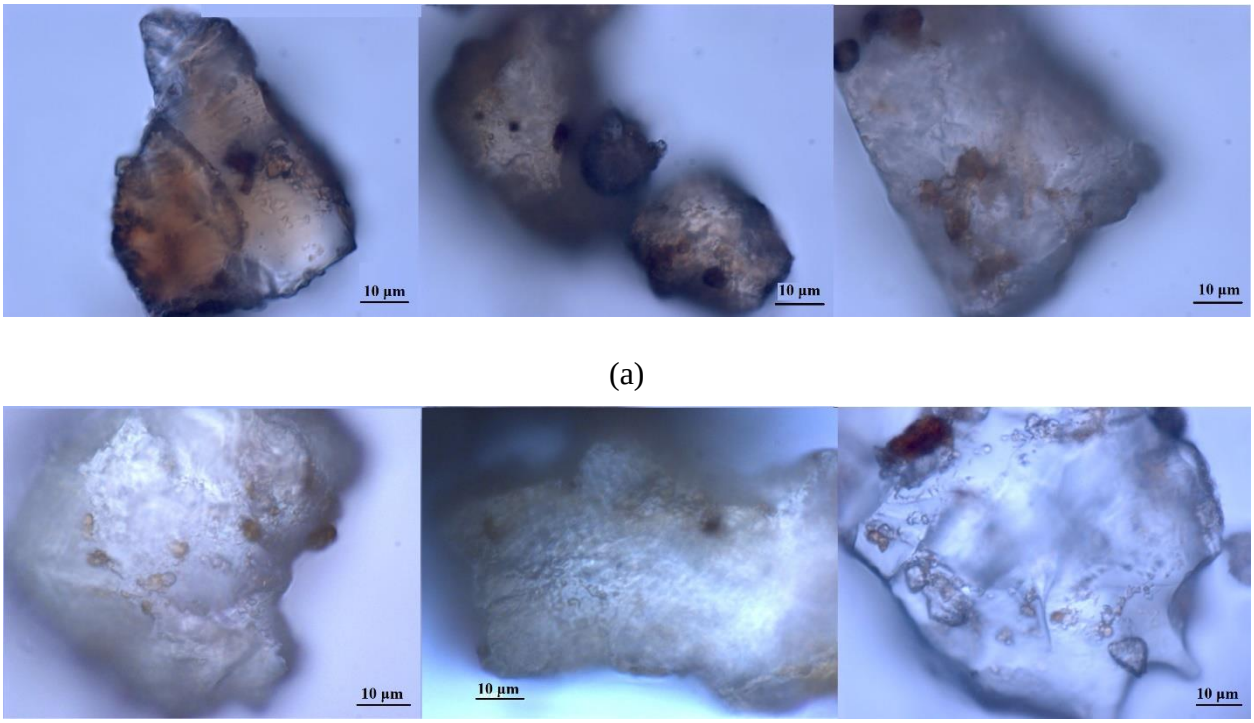



(b)

***Figure 17. Deconvolution of peak O 1s (a) an untreated RAP aggregate (b) a NaOH treated RAP aggregate***

*2.5.7. Optical Imaging*

Figure 18 shows optical imaging at 100× for very fine (<0.3 mm) RAP particles treated by NaOH solution. A discoloration is observable after NaOH soaking, with a brownish color disappearing after NaOH soaking.




(a)

(b)

***Figure 18. Images took by an optical microscope a) untreated RAP aggregates b)NaOH treated RAP aggregates***

*2.5.8. Pore Solution Extraction*

While the results in Table 2 showed that some organic compounds are leached out from the RAP, the NaOH solution is not equivalent in composition to pore solution. For this reason, in Phase II, TOC analysis was completed on the pore solution extracted from the mortar specimens made with untreated RAP, NaOH-treated RAP, and natural sand cured for 3 days and 7 days. The

results of TOC in Phase II performed on pore solution are shown in Figure 19. The relatively high amount of TOC in the natural sand specimen is because of the fluoropolymer dry lubricant used on the pore solution die. Since the fluoropolymer dry lubricant was used for all samples, the natural sand acts as the blank sample, and any differences between specimens containing RAP with the natural sand specimen should be due to the direct impact of organic carbons leachate into the pore solution, assuming that the natural sand contained no organic matter. The results in Figure 19 indicate that the pore solution of the specimens made with NaOH-treated RAP aggregates has a higher amount of TOC compared to the pore solution of the specimens made with untreated RAP aggregates. This implies that NaOH was not effective in pre-leaching those components from the asphalt coating. From Figure 15 and Figure 18 it is demonstrated that the NaOH solution treatment modifies the surface of the RAP aggregates, so perhaps this modifies asphalt compounds at the surface to be readily soluble. It is unknown whether all of the compounds leached from the treated RAP aggregates are the same as compounds leached from the untreated RAP aggregates into the pore solution.

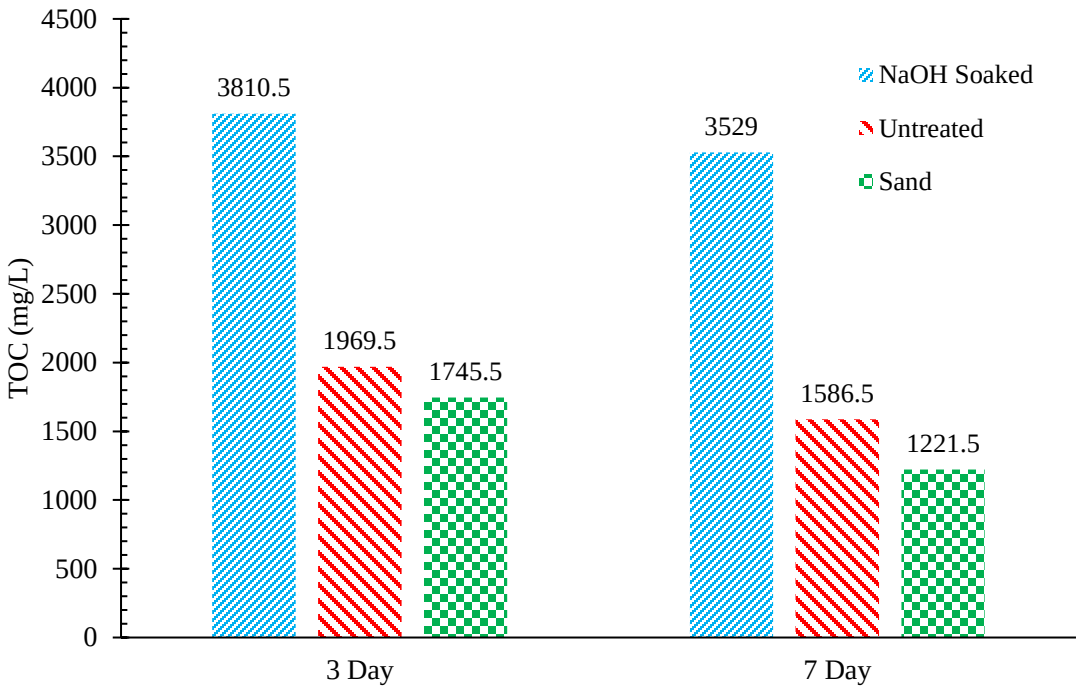
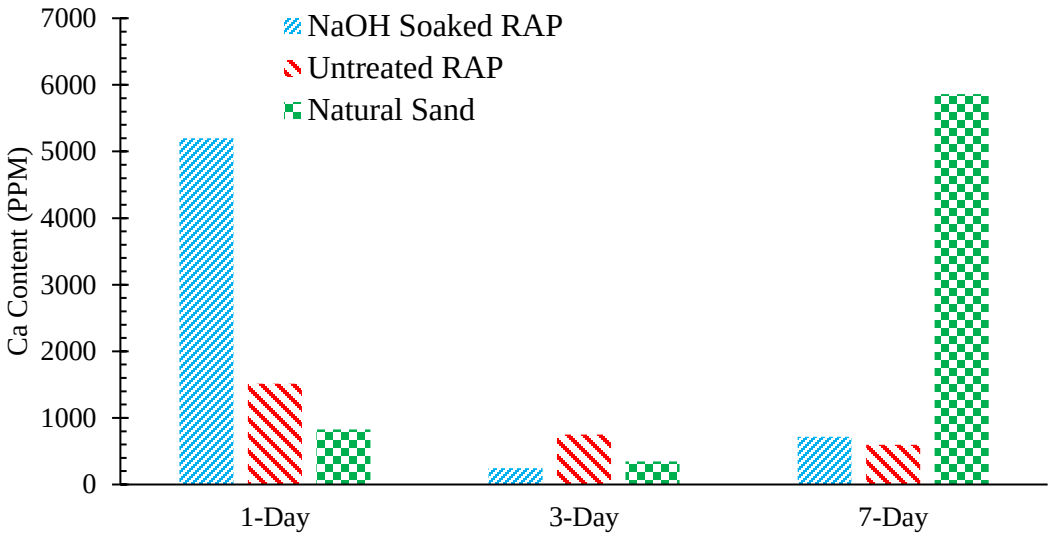



***Figure 19. TOC analysis results performed on pore solution extracted from the mortar specimens in Phase II***

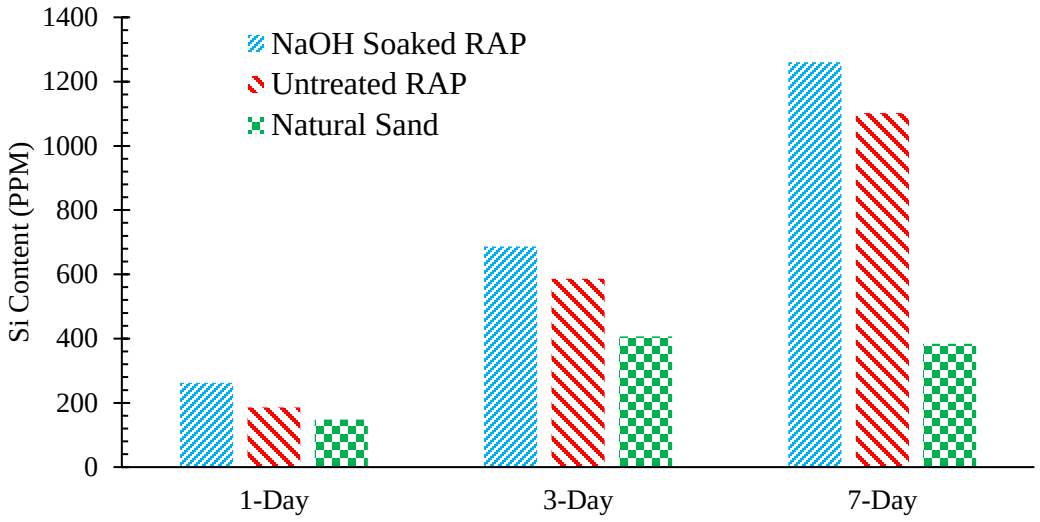
The ICP-MS results for calcium (Ca), silicon (Si), and sulfur (S) analyzed from the extracted pore solutions of different mixtures cured for 1 day, 3 days, and 7 days are shown in Figure 20. Figure 20a shows that on the first day of curing more Ca is present in the pore solution in the case of using RAP in the mortar mixture compared to the time when natural sand has been used. For the mixtures with NaOH-treated RAP aggregates even more Ca is present in the pore solution.

Figure 20b shows that, in general, the mixtures containing RAP have a higher amount of Si compared to the mixture made with natural sand, but the amount of Si in the samples made with treated RAP aggregates was the highest among all mixtures in all curing times. By increasing the curing time in the natural sand mixture, a slight increase in the Si content was observed after the depletion of the calcium sulfate. With increasing the curing time, more Si is present in the pore solution for all mixtures, but for the natural sand mixture, the Si is entered into the cement

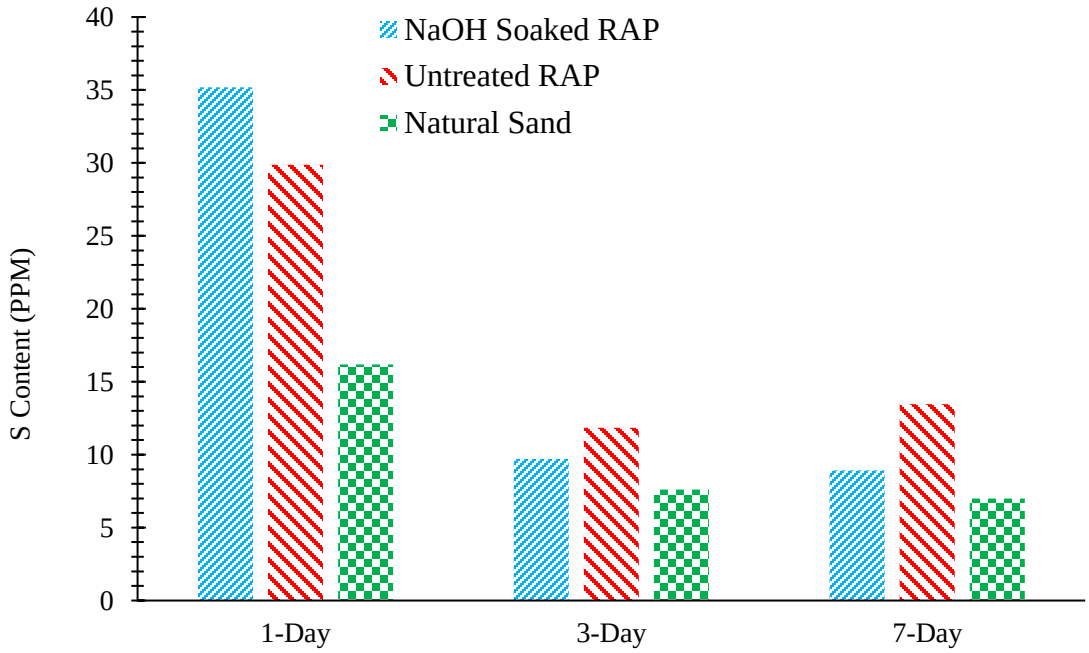
hydration to produce C-S-H while the sharp increase in the content of Si in the RAP aggregates may show that the dissolved Si has not been entered into the cement hydration effectively. It can be supported by the findings from another study where the researchers observed larger and more porous ITZ with RAP aggregates with less C-S-H [35]. The investigation of S, as shown in Figure 20c, shows that more sulfur exists in the pore solution of the sample made with the treated RAP aggregates. Since the aggregate content in all mixtures is the same, the higher S content in the treated RAP sample may be attributed to the existence of more sulfoxide groups on the treated RAP as discussed earlier.




(a)




(b)




(c)

***Figure 20. Results of ICP performed on the extracted pore solutions a) Ca element b) Si element (c) S element***

*2.5.9. Compressive Strength and Split Tensile Analysis*

The compressive strengths after 1 day, 3 days, and 7 days of curing are shown in Figure 21. As expected, based on the literature discussed in Section 1, all mixtures that contained RAP aggregates had lower compressive strength compared to the mixture made with natural sand. The compressive strength of the mixtures made with treated RAP aggregates was slightly higher than mixtures made with untreated RAP aggregates.

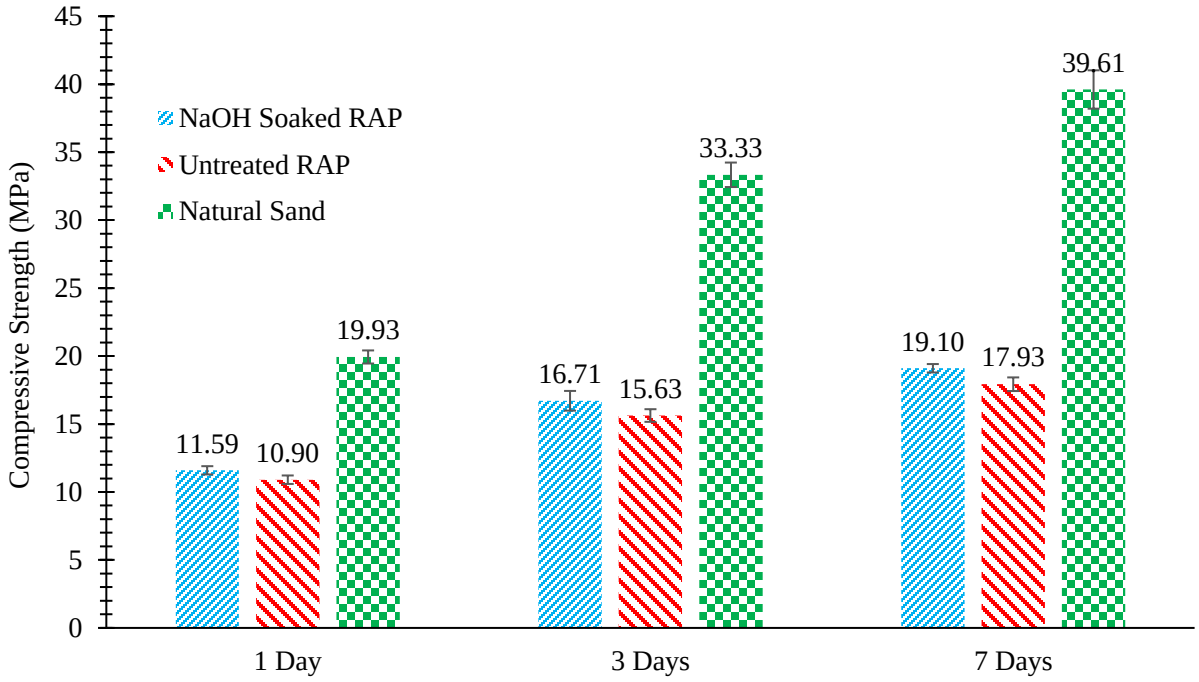



***Figure 21. Compressive strength test results***

The images of the split specimens after 1 day, 3 days, and 7 days of curing are shown in Figure 22. For untreated RAP mixtures, a combination of aggregate fracture and cement-asphalt adhesion and asphalt cohesion failures were observed, but the asphalt cohesion failure was dominant, which agrees with the literature [37]. In the split fracture surfaces, the cohesion failure can be identified as the dark asphalt remaining in mirrored areas on both sides of the failed sample,

implying that the split-tensile failure occurred within the asphalt. For both treated RAP mixtures (NaOH and deionized water treated), a combination of aggregate fracture, cement-asphalt adhesion, and asphalt cohesion failures was observed, but adhesion failure was dominant. Adhesion failure can be characterized by the absence of dark asphalt in mirrored areas on both sides of the split samples.

(a) (b) (c)

***Figure 22: Split tensile samples at different ages (a) 1 day (b) 3 days (C) 7 days. Samples on top contain aggregate soaked in NaOH while the bottom contains aggregate soaked in deionized water.***

*2.5.10. Contact Angle and Surface Free Energy*

To support the discussion in reference to the failure modes in Figure 22, contact angle measurements were performed to quantify the surface free energy. The contact angle results for the three probe liquids are shown in Figure 23. It can be seen that the pretreatment of asphalt samples has an effect on the contact angle for all three liquids. The sample soaked in water for 10 days exhibited lower contact angles than the control, and the sample soaked in NaOH solution appeared to reduce the contact angle lower than the water-treated sample. However, the effect is

minimal, and it should be noted that the error bars representing standard deviations of all samples tested overlap between the various pretreatment methods.

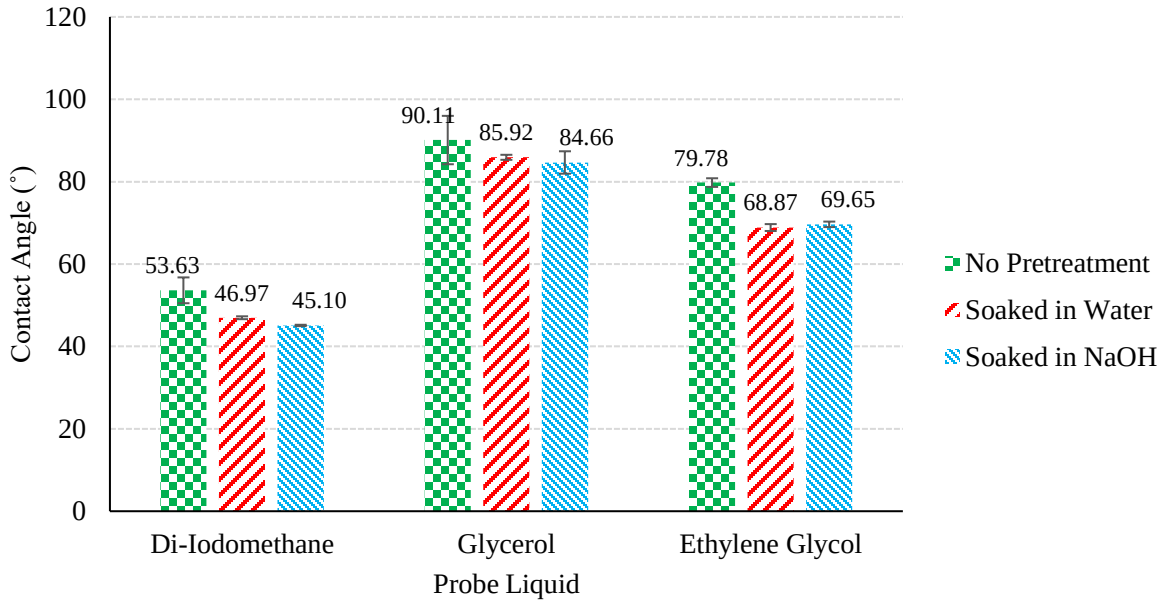



***Figure 23: Average Contact Angle between Probe Liquids and Asphalt Surfaces***

Using VOCG theory and the measured contact angles, the solid properties were calculated, as shown in Table 4. The work of adhesion between cement and the various asphalt samples is then calculated (Table 5) in addition to the work of cohesion of the asphalt. Notably, the pretreatment increased the work of adhesion between asphalt and cement and also increased the work of cohesion of the asphalt. For the control (untreated) asphalt surface, the work of cohesion is less than the work of adhesion, which suggests that cracks will propagate preferentially through the asphalt film due to asphalt cohesion failures; this is consistent with Figure 22 and the results by Brand and Roesler [36], [37]. However, after treatment by soaking in water or in NaOH solution,

the work of adhesion becomes less, suggesting preferential cement-asphalt adhesion failures, which is consistent with Figure 22.

***Table 4: Calculated solid properties based on VOCG theory (mJ/m2)***

| Pretreatment Method | $\gamma_s^{LW}$ | $\sqrt{\gamma_s^+}$ | $\sqrt{\gamma_s^-}$ |
|---|---|---|---|
| No Pretreatment | 32.228 | -0.047 | -0.407 |
| Soaked in Water for 10 Days | 35.946 | -0.117 | 0.104 |
| Soaked in NaOH for 10 Days | 36.959 | -0.048 | -0.056 |
| Hydrated Cement Paste* | 40.6 | 0.05 | 3.5 |

*Values from Brand, 2015 [139]

***Table 5: Work of Adhesion between Asphalt and Portland Cement, given in mJ/m2***

| Pretreatment Method | Work of Adhesion with Cement in a Vacuum | Work of Adhesion with Cement in Water | Work of Cohesion in Asphalt |
|---|---|---|---|
| No Pretreatment | 71.98 | 69.21 | 64.53 |
| Soaked in Water for 10 Days | 75.59 | 69.99 | 71.84 |
| Soaked in NaOH for 10 Days | 77.13 | 71.66 | 73.93 |

## 2.6. Conclusion and Recommendations

A number of conclusions can be drawn from the results of this study. Generally, the incorporation of reclaimed asphalt pavement aggregates has a negative impact on the hydration and strength characteristics of structural concrete. This broadly agrees with existing literature. Isothermal calorimetry results indicated that the presence of leachate from RAP aggregates was detrimental to the heat of hydration, implying that the organic compounds which make up the asphalt binder are hindering the formation of hydration products such as C-S-H and C-H. This was supported by the pore solution analysis which indicated that the presence of RAP aggregates in the mortar samples was increasing the concentration of ions that are crucial in the formation of those hydration products.

Future study of the utilization of RAP aggregates in concrete should include analysis of different pretreatment methods. Additionally, flexural strength, elastic modulus, and other mechanical properties can be tested.

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# 3. Effect of Quarry Fine Substitution on Cement Hydration

## 3.1. Introduction and Literature Review

Quarries around the world are faced with a wide variety of problems related to by-product and waste material management. To produce crushed aggregate that meets gradation requirements, blasting and crushing operations produce a large amount of excess quarry fines. Depending on the rock and crusher types, upwards of 20% to 25% of the final aggregate product may be quarry fines [140]–[141]. In the U.S., the total production amount of quarry by-products, which includes quarry fines, is estimated at 175 Mt/yr [141]. It is important for quarry managers to consider the composition, reactivity, and potential hazards of by-product and waste materials in order to develop safe and sustainable waste management practices. Like many other parts of the United States, the state of Virginia faces the problem of stockpile buildup and the risks that stockpiling materials poses to the natural environment. This study investigates the effect of using quarry fines as filler materials in cement paste and mortar mixes. The quarry fines are used to replace a portion of the Portland cement, between 5% and 20%, in order to reduce the amount of cement used in concrete; essentially, this study explores the use of quarry fines to replace limestone in a Type IL Portland limestone cement.

Many studies have been conducted on the potential use of alternative or waste materials as fillers in concrete. The current existing literature provides analysis of the effects of fillers on cement hydration [142]–[145], mechanical performance [146]–[152], and durability [149], [150], [153]–[155] Many of these studies, however, are conducted using finely ground material that has known composition and properties, whereas the study presented in this paper has been conducted without this knowledge. Many of the techniques and findings still provide some context for the scope of this study. A large number of the studies conducted found that the presence of fillers

impacted both overall heat of hydration and the rate of hydration even though fillers are typically thought to be inert materials. Poppe and De Schutter found that quartzite fillers reduced the heat of hydration and limestone fillers also reduced the total heat of hydration but accelerated the rate of hydration [142]. This indicates the importance of the composition of the filler material. Other studies have confirmed that many of the most common filler materials cause cement hydration to accelerate [143], [145].

In terms of mechanical properties and durability, the majority of existing literature has been conducted with materials that are already known to have desirable qualities. For example, studies have shown that using granite dust in concrete can improve the durability performance of concrete by reducing permeability [149]–[151], [155]. Other studies have analyzed the potential for pozzolanic behavior of certain fine materials [143], [146], [156]. Materials that were found to be pozzolanic caused increased strength and durability characteristics.

While this study is primarily concerned with the use of waste products as filler material, it is worth mentioning a number of other uses that have been developed and investigated. Studies have shown that quarry fine waste material can be repurposed in a number of ways, such as the production of coarse aggregate for concrete or subbase layers [157]–[159]. This practice often involves energy intensive processes to mechanically alter the structure of quarry fine waste to produce pellets. Still more studies have shown that quarry fine waste shows potential for use as replacement of fine aggregate in concretes [147], [160]–[163]. Many of these studies found that partial replacement of fine aggregate resulted in strength gain due to the fact that the aggregate packing was optimized by the presence of quarry fines. It was also found that replacing larger portions of fine aggregate became detrimental to concrete strength.

## 3.2. Test Methods

### *3.2.1. Isothermal Calorimetry*

Isothermal calorimetry was conducted in accordance with ASTM C1679 using a Calmetrix I-Cal Flex instrument. The samples to be analyzed were all cement paste samples. Four replicate samples of ordinary Portland cement and water were analyzed as a reference control. Four samples for each quarry fine were prepared with varying substitutive percentages ranging from 5% to 20% replacement of cement. Isothermal calorimetry provides information of the total heat (J/g cementitious) and thermal power (W/g cementitious). Paste samples were mixed manually and transferred to the calorimeter chamber within 60 seconds of mixing. Heat of hydration was recorded for a minimum of 48 hours for all samples. Quarry fine materials were ground to a fine powder before IC testing to ensure consistent analysis of all samples.

### *3.2.2. Pore Solution Extraction*

Analysis of pore solution from hardened mortar samples was conducted to further understand the physicochemical interactions within the microstructure. Pore solution was extracted using a specially designed device similar to that used by Barneyback and Diamond [127] The device is pictured below and consists of three main components: the base plate with drilled channels, the outer shell, and the piston. Hardened 2x4 in mortar samples are placed within the hardened steel outer shell and subjected to high pressure in excess of 300MPa to extract the pore solution. A pressurized system is then connected to the base plate with drilled channels to help collect the solution in 15ml vials.

During the process of extraction, care was taken to limit the applied pressure to 420MPa. This was done to avoid causing particles to become stuck between the piston and outer shell which

could cause damage to the device. It has also been found that pressures in excess of 500MPa impact the ionic concentrations of the pore solution [127]. The stress rate for pore solution extraction was approximately 2.8 MPa/s. High pressure was maintained for a number of minutes to allow the collection of more than 10mls of solution.

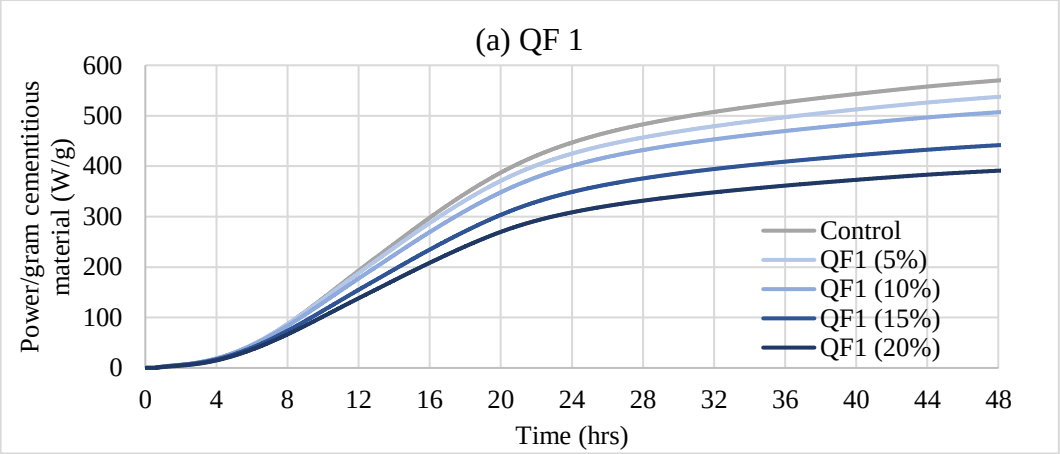
#### *3.2.3. Compressive Strength*

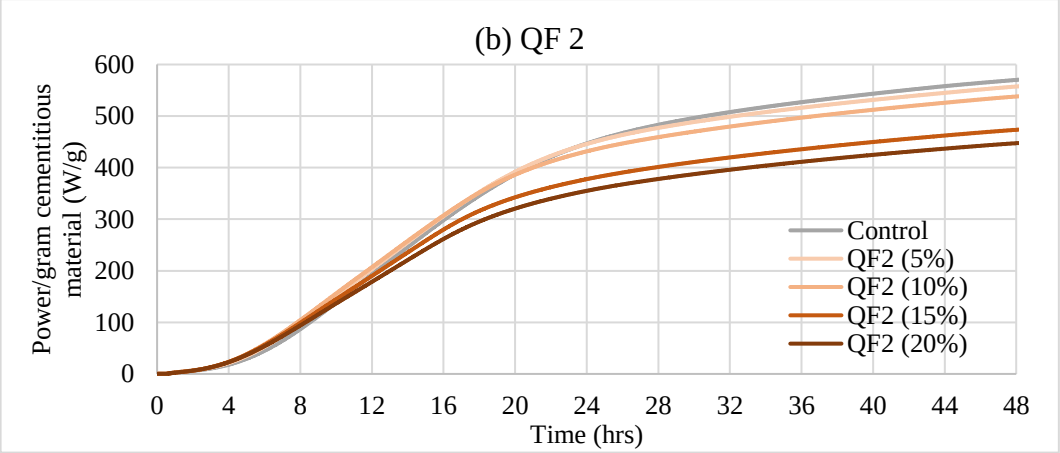
Compressive strength of 2”x4” mortar samples was conducted in accordance with ASTM C39 [130]Control samples were prepared with a simple mix design with a w/c ratio of 0.5 and a paste-to-sand ratio of 0.8. Samples were then prepared with either 5% or 15% of the cement content substituted for quarry fine material. These samples were tested after 14 days of moist curing.

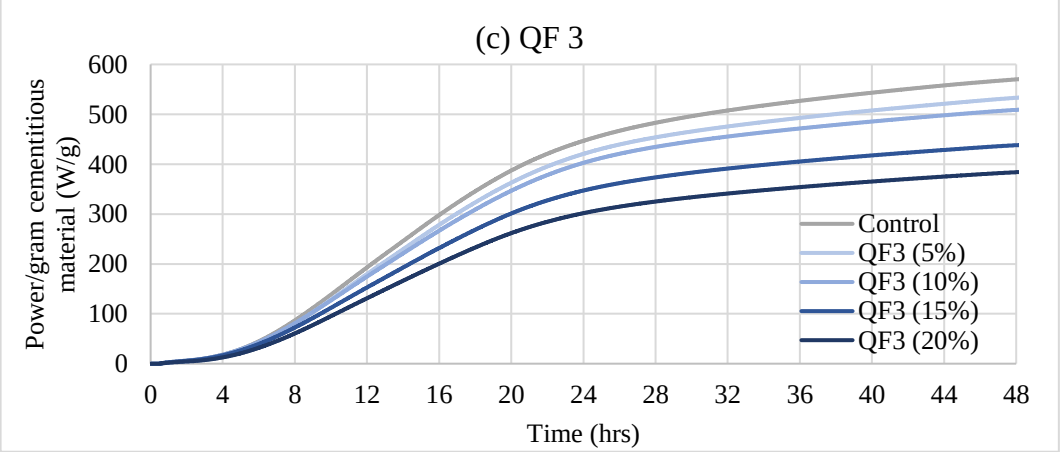
### 3.3. Results and Discussion

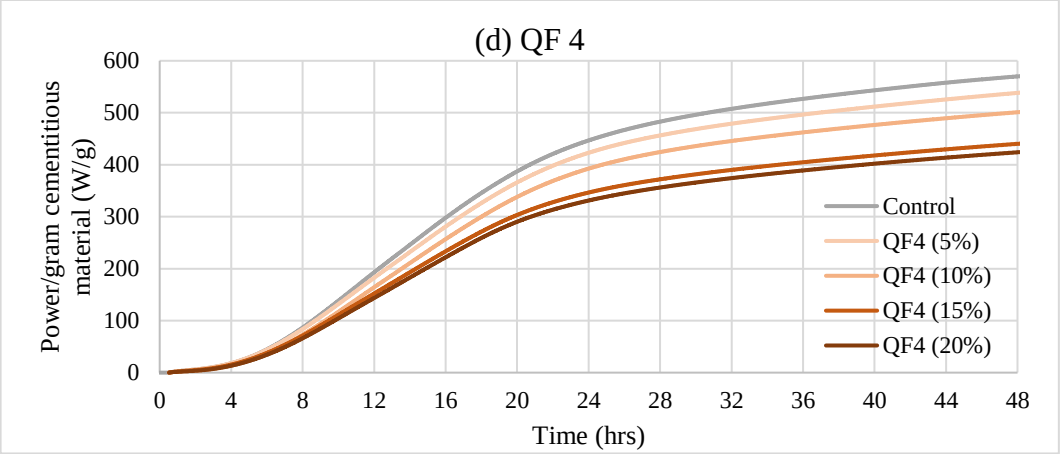
#### *3.3.1. Isothermal Calorimetry*

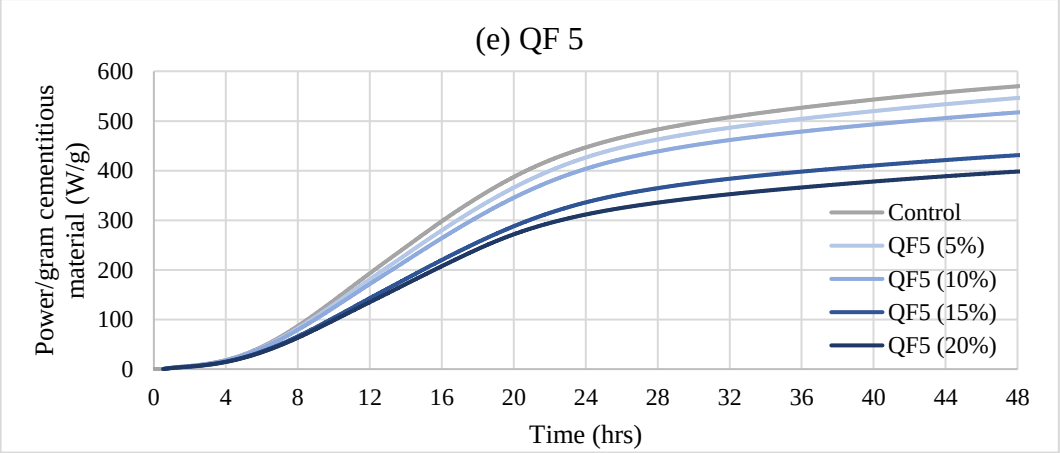
The cumulative heat of hydration of cement paste samples with various percentages of quarry fines is presented in Figure 24 (a-g). Each figure presents the data for one quarry fines source. Four substitutive percentages are presented relative to a reference sample. The trends observed are very similar for all quarry fines. In general, the data clearly indicates that the total heat of hydration decreases as greater percentage of cement is replaced by quarry fines.

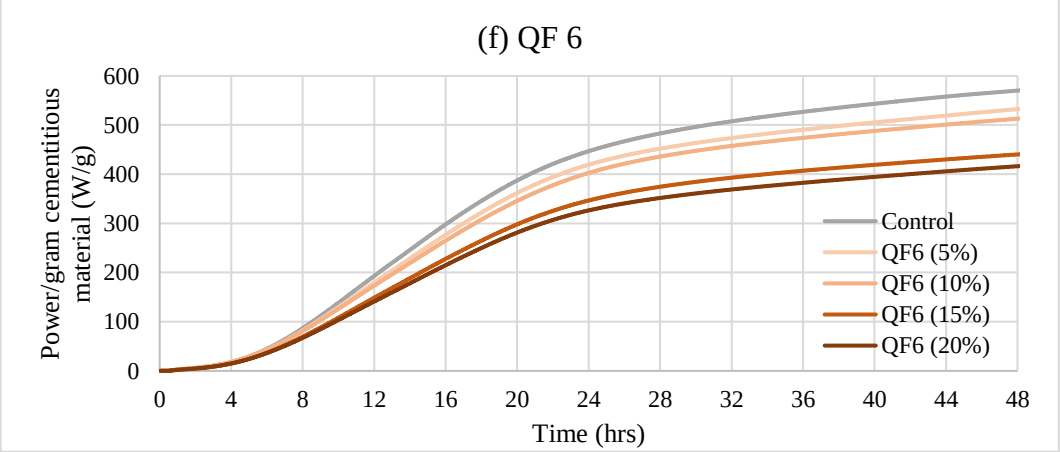

(a) QF 1
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF1 (5%)
QF1 (10%)
QF1 (15%)
QF1 (20%)


(b) QF 2
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF2 (5%)
QF2 (10%)
QF2 (15%)
QF2 (20%)


(c) QF 3
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF3 (5%)
QF3 (10%)
QF3 (15%)
QF3 (20%)


(d) QF 4
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF4 (5%)
QF4 (10%)
QF4 (15%)
QF4 (20%)


(e) QF 5
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF5 (5%)
QF5 (10%)
QF5 (15%)
QF5 (20%)


(f) QF 6
Power/gram cementitious material (W/g)
600
500
400
300
200
100
0
0 4 8 12 16 20 24 28 32 36 40 44 48
Time (hrs)
Control
QF6 (5%)
QF6 (10%)
QF6 (15%)
QF6 (20%)

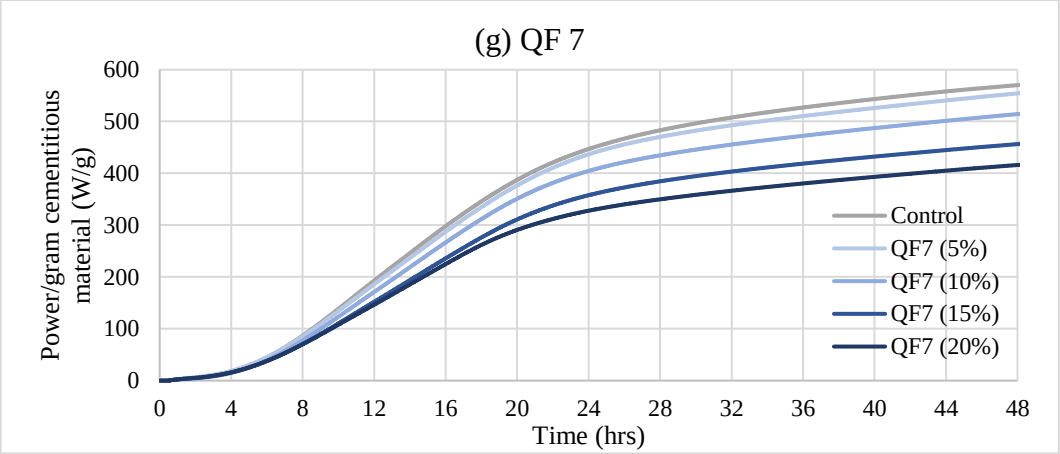



***Figure 24 (a-g): Cumulative heat of hydration data for cement paste samples with quarry fine substitution. Reference line represents the average of 4 replicate samples while each QF line represents one sample of that substitutive percentage.***

For all samples, the tail end of the curve clearly reduces as the substitutive percentage increases from 5% up to 20% in 5% increments. This finding is in good agreement with the existing literature [141]. It is worth noting that some quarry fines perform better than others in terms of hydration energy. For example, quarry fines 2 and 7 seem to perform very similarly to the reference samples at 5% substitution, while quarry fines 1 and 3 seem to be causing the largest reduction in hydration energy. It is noted that there is a major difference between the 10% and the 15% samples for all the quarry fines analyzed. A quantitative comparison of each of the quarry fines is more clearly visualized by analyzing the cumulative heat energy at set intervals of time, as shown in Table 6.

***Table 6: Incremental comparison of Hydration Data with Performance Indicators. Typical error margin is ±12W/g at 24 hours and ±15W/g at 48 hours.***

| QF | Substitutive Percentage (%) | Heat after 24 Hours (W/g) | Heat after 48 Hours (W/g) | 24 Hour Performance Indicator | 48 Hour Performance Indicator |
|---|---|---|---|---|---|
| **Reference** | | 449 | 570 | N/A | N/A |
| **1** | 5 | 425 | 537 | 0.24[1] | 0.79 |
| | 10 | 401 | 507 | 0.59 | 1.05 |
| | 15 | 349 | 442 | 7.19 | 7.46 |
| | 20 | 309 | 391 | 11.10 | 11.40 |
| **2** | 5 | 446 | 557 | -4.44 | -2.72 |
| | 10 | 432 | 538 | -6.32 | -4.39 |
| | 15 | 378 | 473 | 0.72 | 2.02 |
| | 20 | 355 | 447 | 0.85 | 1.58 |
| **3** | 5 | 421 | 533 | 1.13 | 1.49 |
| | 10 | 403 | 509 | 0.14 | 0.70 |
| | 15 | 347 | 438 | 7.63 | 8.16 |
| | 20 | 302 | 384 | 12.66 | 12.63 |
| **4** | 5 | 423 | 538 | 0.69 | 0.61 |
| | 10 | 393 | 501 | 2.37 | 2.11 |
| | 15 | 347 | 440 | 7.63 | 7.81 |
| | 20 | 331 | 424 | 6.20 | 5.61 |
| **5** | 5 | 427 | 546 | -0.21 | -0.79 |
| | 10 | 404 | 517 | -0.08 | -0.70 |
| | 15 | 336 | 431 | 10.08 | 9.39 |
| | 20 | 312 | 398 | 10.43 | 10.18 |
| **6** | 5 | 419 | 532 | 1.58 | 1.67 |
| | 10 | 403 | 513 | 0.14 | 0.00 |
| | 15 | 347 | 440 | 7.63 | 7.81 |
| | 20 | 326 | 416 | 7.31 | 7.02 |
| **7** | 5 | 437 | 554 | -2.44 | -2.19 |
| | 10 | 405 | 514 | -0.30 | -0.18 |
| | 15 | 358 | 456 | 5.18 | 5.00 |
| | 20 | 328 | 416 | 6.87 | 7.02 |

The "Performance Indicator" in Table 6 is a measure of how the quarry fine performed relative to a theoretical filler material which has no effect on hydration. The performance indicator

[1] Performance indicator calculated as: $\left(\frac{Control\ 24hr\ Heat - Sample\ 24hr\ Heat}{Control\ 24hr\ Heat} * 100\right) - Substitutive\ \%$

For QF1 at 5% substitution, this is: $\left(\frac{449\ W/g - 425\ W/g}{449\ W/g} * 100\right) - 5 = 0.24$

is the difference between the percentage reduction in hydration energy and the substitutive percentage. Negative values, highlighted in green, indicate that the reduction in hydration energy was less than the quarry fine substitutive percentage for that sample. Based on these performance indicators, it appears that quarry fines 2 and 7 perform well at low substitutive percentages of 10% or less, while quarry fine 5 has reasonable performance at 10% substitution or less. The data in Table 6 are visually displayed in Figure 25 (a, b), below.

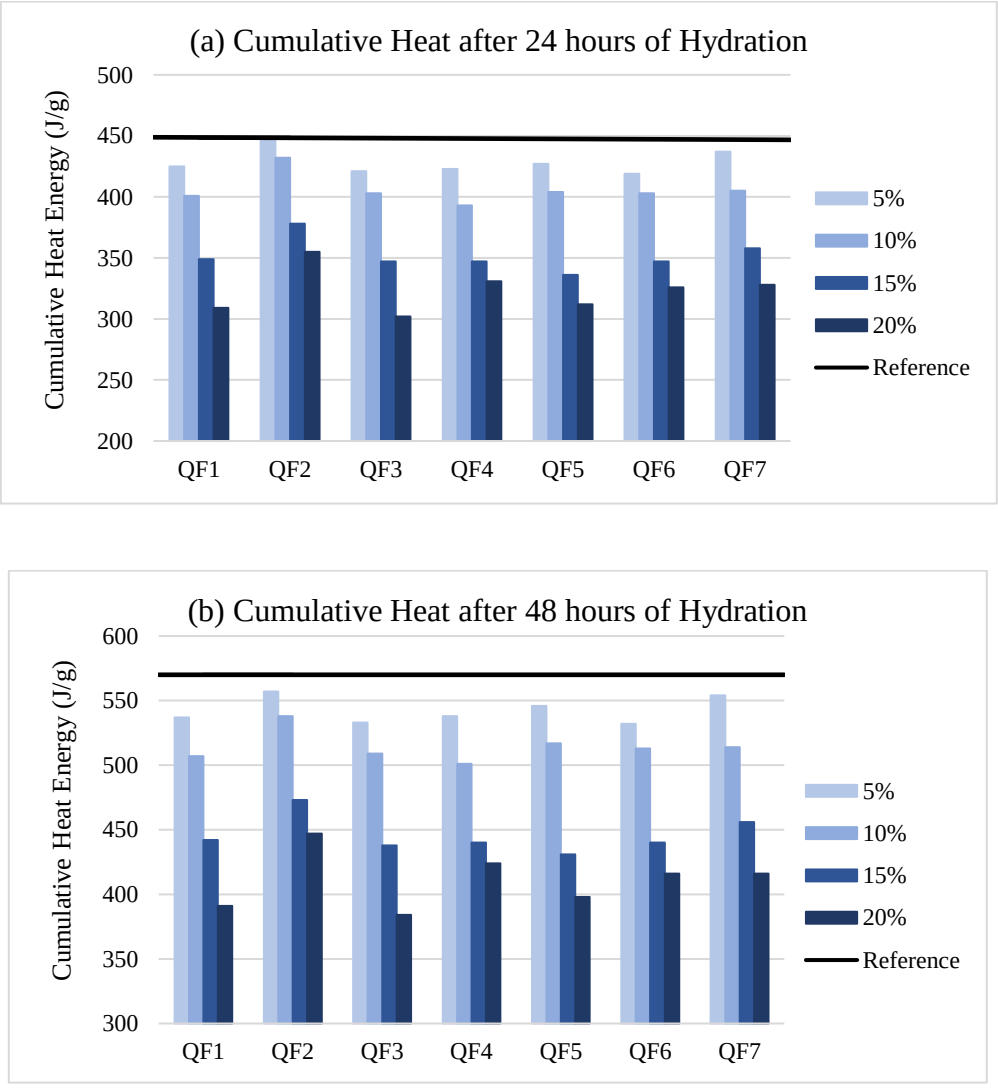
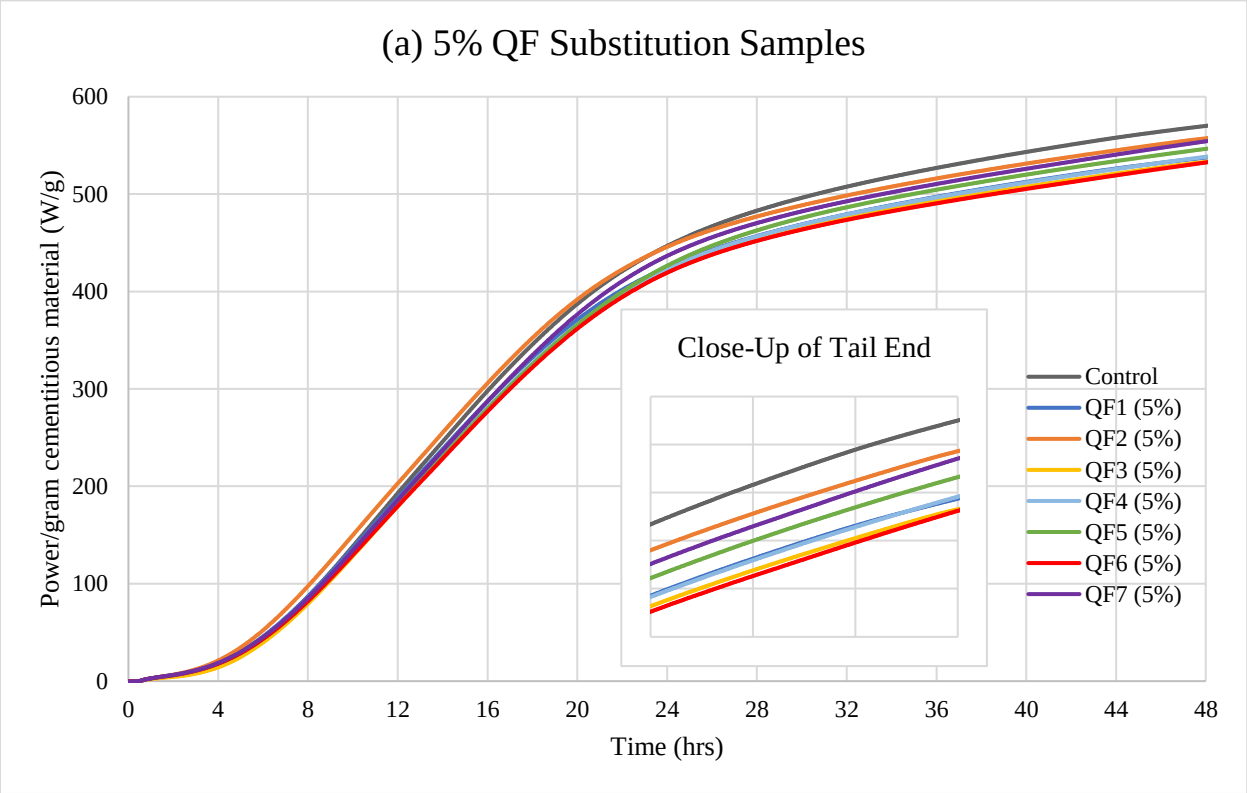
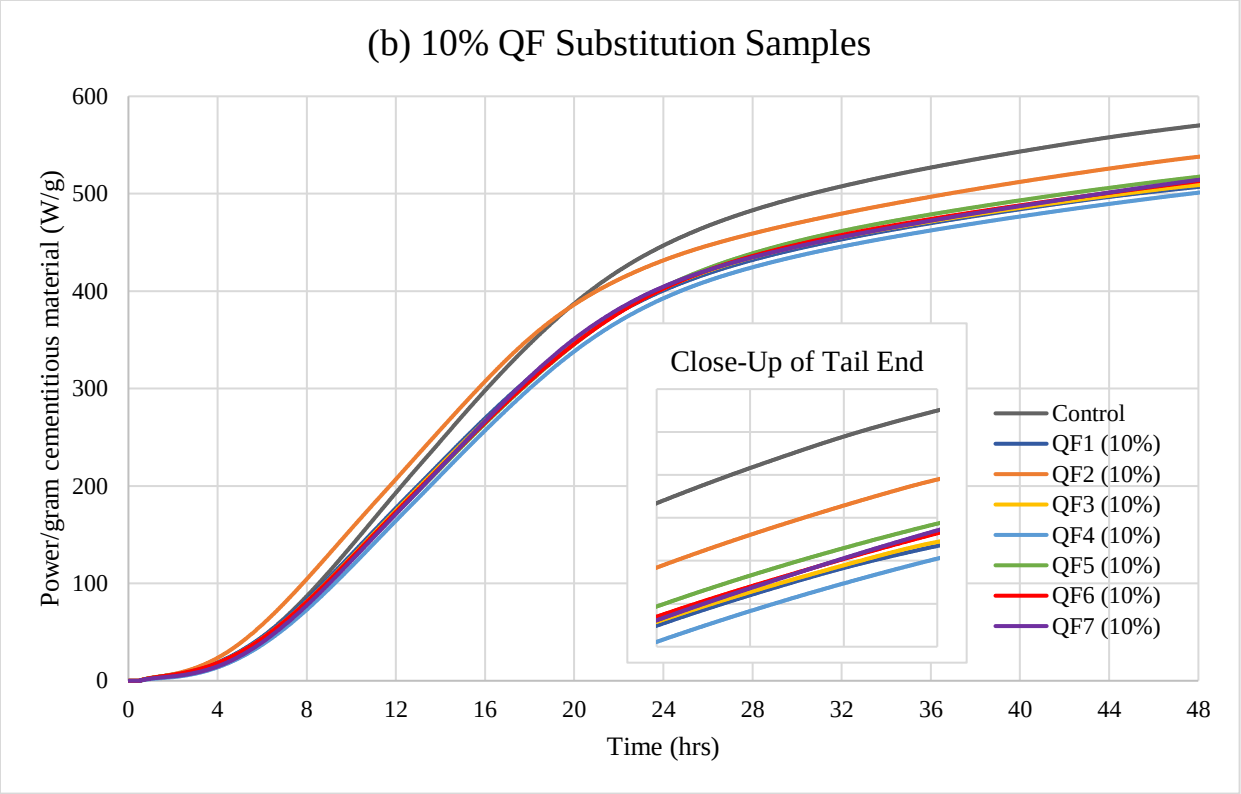
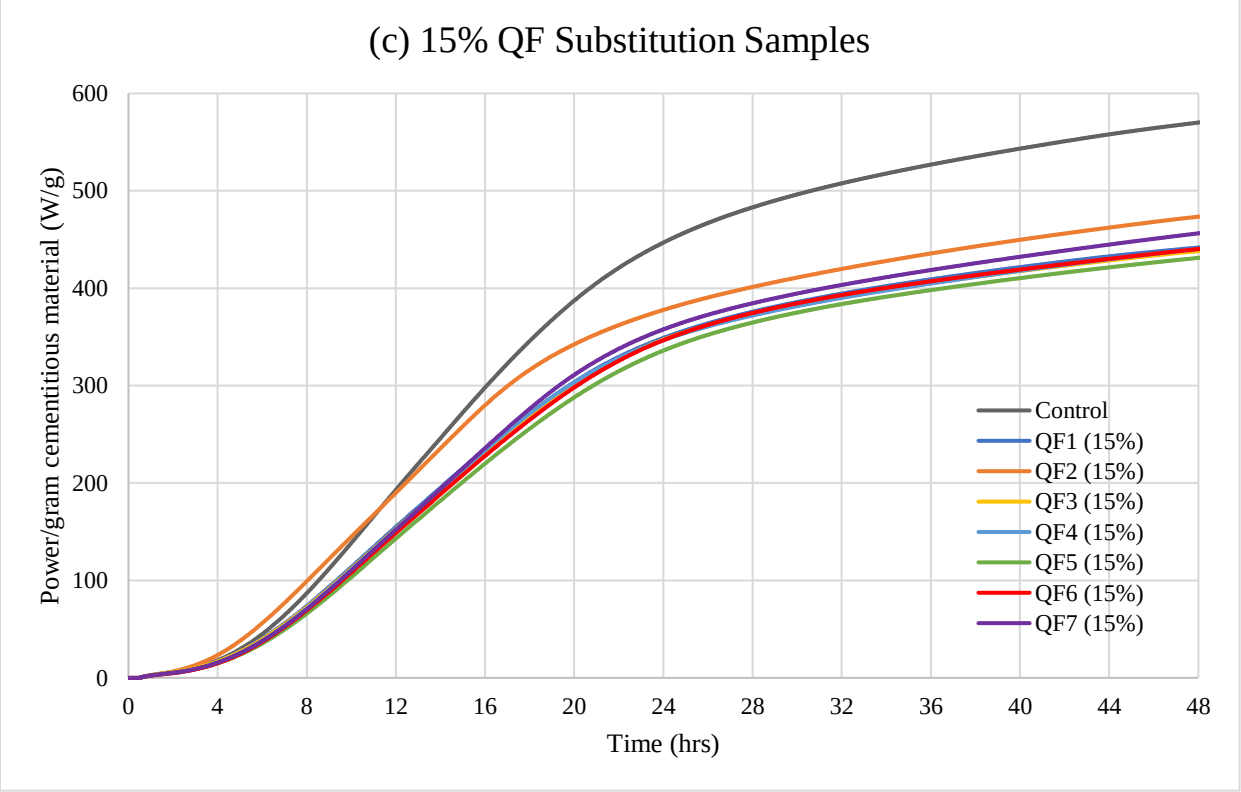



***Figure 25 (a, b): Cumulative heat of hydration of samples with quarry fine substitution compared to reference sample.***

In order to clearly compare the various quarry fines, the cumulative hydration curves for each quarry fine on the same plot is presented in Figure 26. Close-up views of the tail end of the data are provided for the 5% and 10% samples because the data is very close together and difficult to read without a magnified view.




(b) 10% QF Substitution Samples
Power/gram cementitious material (W/g)
Time (hrs)
Close-Up of Tail End
Control
QF1 (10%)
QF2 (10%)
QF3 (10%)
QF4 (10%)
QF5 (10%)
QF6 (10%)
QF7 (10%)


(c) 15% QF Substitution Samples
Power/gram cementitious material (W/g)
Time (hrs)
Control
QF1 (15%)
QF2 (15%)
QF3 (15%)
QF4 (15%)
QF5 (15%)
QF6 (15%)
QF7 (15%)

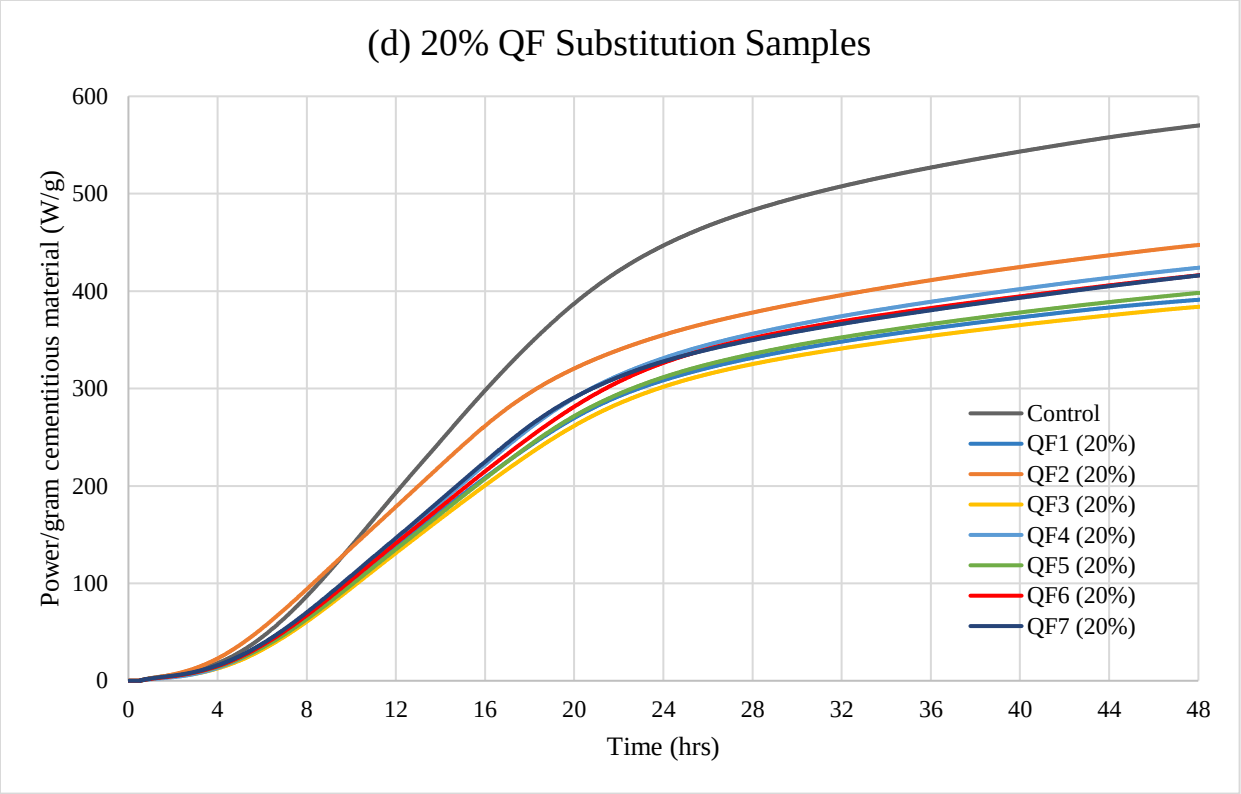
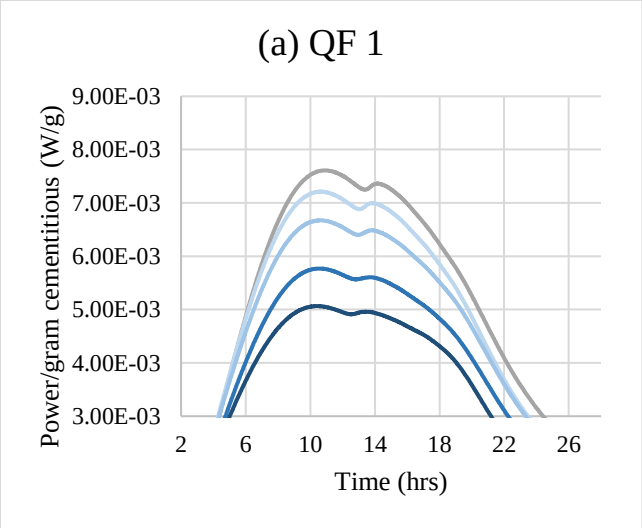
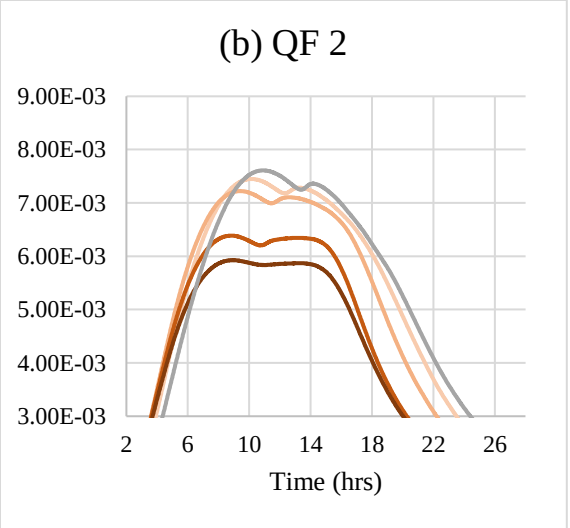
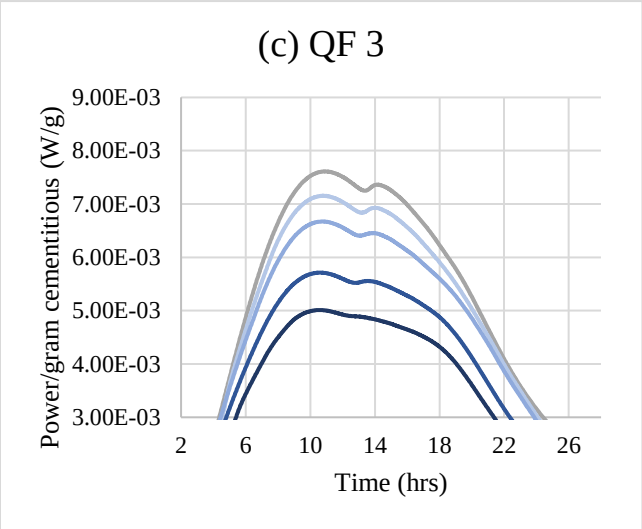


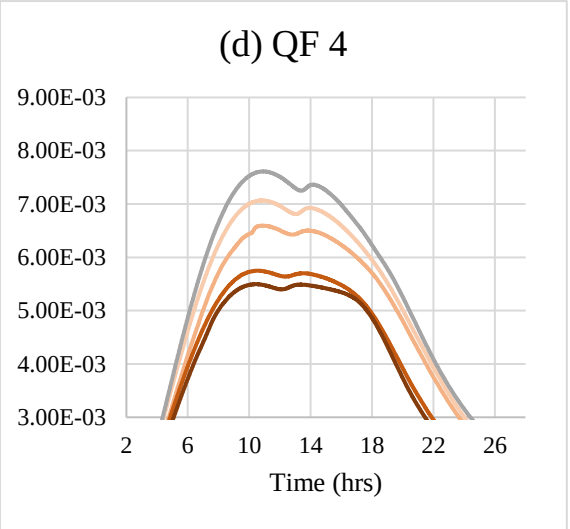

***Figure 26 (a-d): Comparative cumulative hydration data for quarry fine samples at various substitutive percentages.***

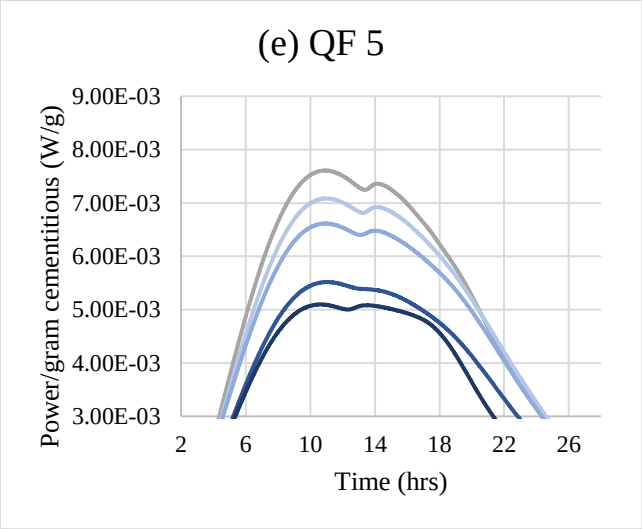
In addition to cumulative heat data, Figure 27 (a-g) shows the main peak of hydration for cement paste samples prepared with various quarry fine substitutive percentages. As previously noted, higher percentages of quarry fine substitution caused a decrease in hydration energy. It appears that for all quarry fines, there is a large reduction in hydration energy when the replacement percentage is increased from 10% to 15%. The 5% replacement curves have a very slight effect on hydration. As a result, it was determined that further testing would be conducted on samples which had substitutive percentages of 5% and 15%.

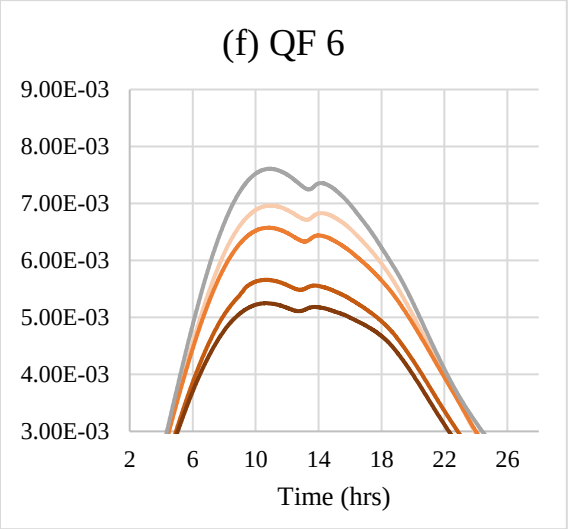

(a) QF 1
Power/gram cementitious (W/g)
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)


(b) QF 2
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)


(c) QF 3
Power/gram cementitious (W/g)
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)


(d) QF 4
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)


(e) QF 5
Power/gram cementitious (W/g)
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)


(f) QF 6
9.00E-03
8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2
6
10
14
18
22
26
Time (hrs)

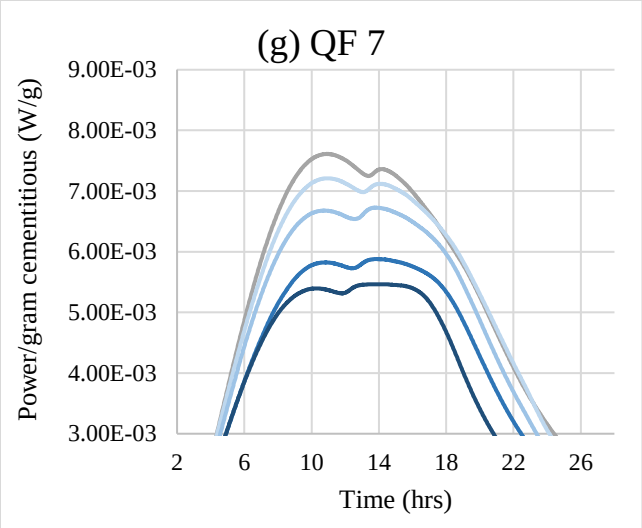



***Figure 27 (a-g) : Main hydration peak for Quarry Fines at substitutions of 5% to 20%, compared to reference cement paste samples.***

Looking at the main hydration peak gives a greater understanding of the effect that the quarry fines have on the rate of hydration. While the majority of the samples do not appear to have any effect, quarry fine 2 appears to have a significant effect on the rate of hydration. At higher percentages of 15% and 20% substitution, the main hydration peak occurs about 2 to 3 hours before the reference sample, indicating an accelerated rate of hydration.

Another observation from Figure 27, is the relative size of the two main hydration peaks. The first peak indicates the hydration of Alite ($C_3S$), while the second peak represents the hydration of Aluminate ($C_3A$). Quarry fines 7 and 2 (to a lesser extent) appear to have much more prominent second peaks which may indicate higher aluminum content in those quarry fines which results in the formation of more aluminate. This higher production of aluminate may explain why quarry fine 2 and 7 had the best performance indication in Table 6 and had the smallest reduction in total hydration energy.

### *3.3.2. Pore Solution Extraction*

Pore solution extracted from hardened mortar samples was analyzed for pH immediately after extraction. The pH results are shown below in Table 7, and are also visually represented in the figures that follow.

***Table 7: pH of extracted pore solution***

| QF # | % Substitution | 1 Day | 3 Day | 7 Day |
|---|---|---|---|---|
| N/A | 0 | 13.36 | 13.33 | 13.26 |
| 1 | 5% | 13.35 | 13.24 | 13.08 |
| | 15% | 13.27 | 13.11 | 12.96 |
| 2 | 5% | 13.33 | 13.27 | 13.24 |
| | 15% | 13.22 | 13.15 | 13.11 |
| 3 | 5% | 13.34 | 13.19 | 13.07 |
| | 15% | 13.23 | 12.92 | 12.87 |
| 4 | 5% | 13.36 | 13.29 | 13.22 |
| | 15% | 13.28 | 13.2 | 13.16 |
| 5 | 5% | 13.32 | 12.98 | 13.08 |
| | 15% | 13.24 | 12.5 | 12.96 |
| 6 | 5% | 13.36 | 13.32 | 13.26 |
| | 15% | 13.28 | 13.18 | 13.14 |
| 7 | 5% | 13.32 | 12.92 | 13.04 |
| | 15% | 13.4 | 12.85 | 13.04 |

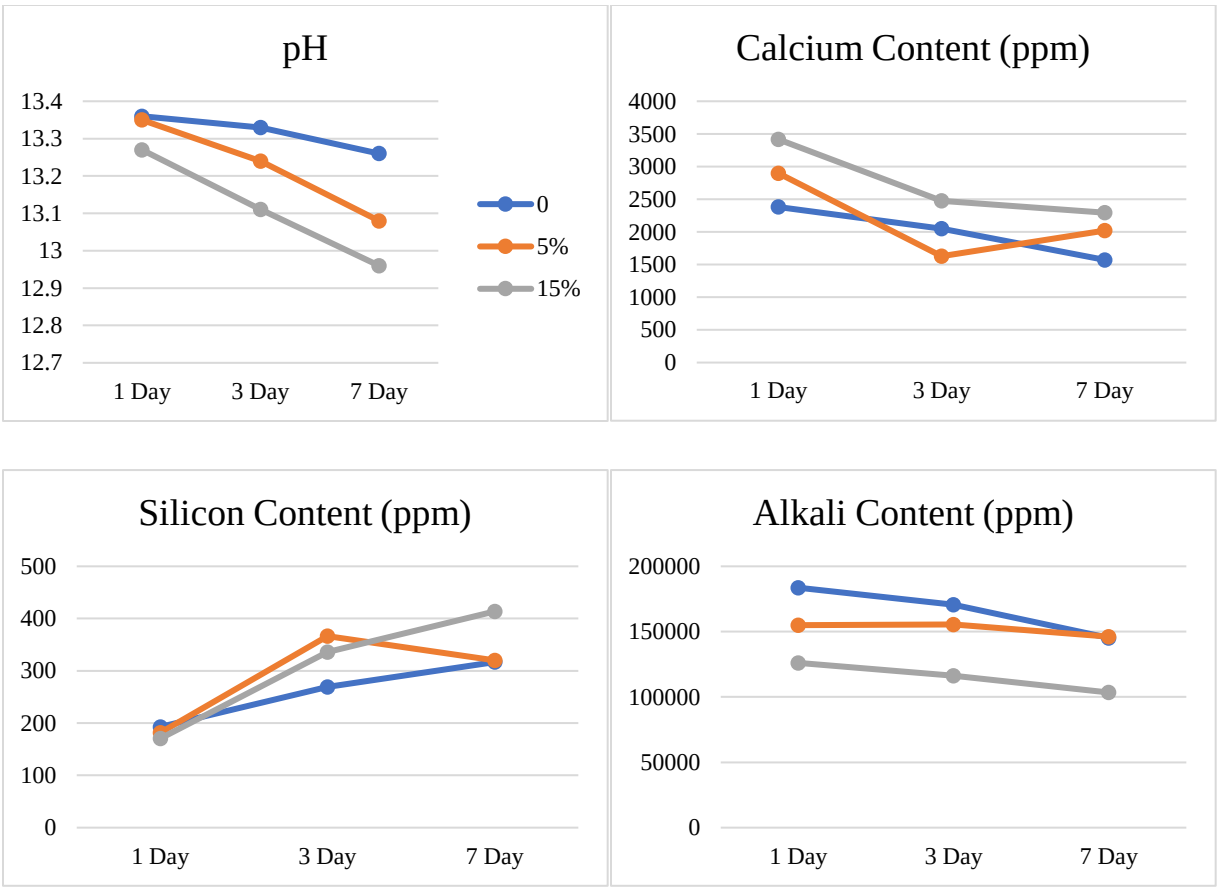



***Figure 28: Pore solution pH values and key elemental quantities for samples containing quarry fine 1.***

Noticeably, the calcium and silicon contents of the pore solution extracted from mortar samples containing quarry fine 1 are higher as compared to reference samples. The exception is the silicon content at 1 day of curing and the calcium content of the 5% samples after 3 days of curing, but in general the trend is upheld. The implication of having higher Ca and Si concentrations in the pore solution is that there is lower concentration in the solid phases [164]. Calcium and silicon are fundamental components of cement hydration product C-S-H. It can be deduced, therefore, that the presence of quarry fine 1 is negatively impacting the formation of C-S-H, resulting in a greater concentration of Ca and Si in the pore solution. Alkali content refers to the concentration of Sodium Oxide ($Na_2O$) and Potassium Oxide ($K_2O$). In the figures, the

total Na and K contents from ICP analysis were summed as a comparative measure. It is noted that the alkali content of the pore solution is less than that of the reference samples. Studies have found that alkali content may be impacted by the presence of pozzolanic materials. The presence of pozzolans reduces the C/S ratio of C-S-H in the microstructure which allows more alkalis to be incorporated into the C-S-H [164]. This may imply that quarry fine 1 exhibits pozzolanic activity at early ages because a decreased alkali content of pore solution relates to an increased content in the solid phases. However, pozzolanic activity is typically evident later, so this cannot be stated at early ages. It should also be noted that a reduction in alkali content is expected as a result of the decrease in Portland cement as it is substituted by quarry fine materials [165].

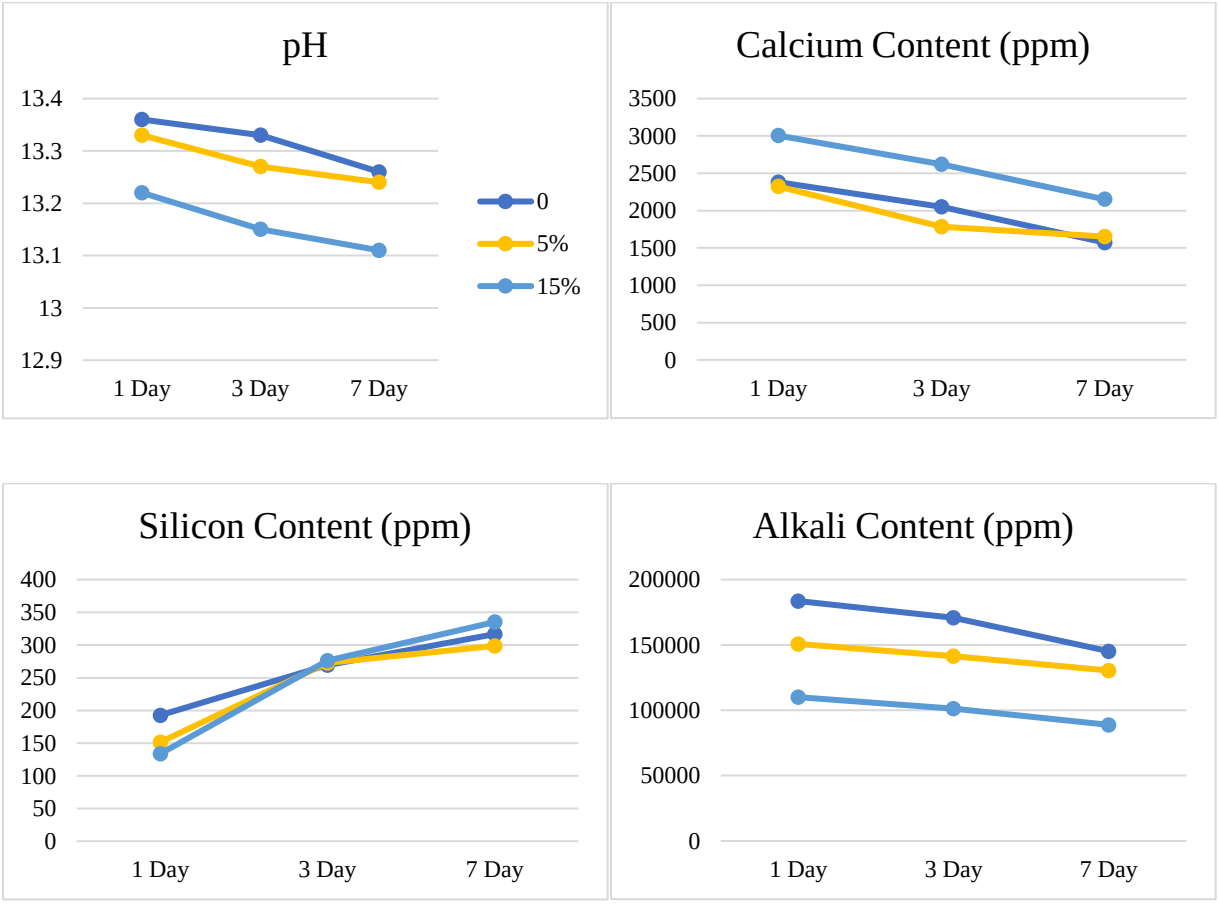



***Figure 29: Pore solution pH values and key elemental quantities for samples containing quarry fine 2.***

Unlike quarry fine 1, the presence of quarry fine 2 in small portions (5% substitution) seems to have minimal effect on the Ca and Si content of the extracted pore solution. This would imply that at early ages, the presence of this material is not adversely affecting the formation of hydration products. However, the 15% substitution samples show a significantly higher Ca content in the pore solution which implies that greater presence of quarry fine 2 begins to negatively impact the C-S-H in the microstructure. These findings are supported by the isothermal calorimetry results. Of note in those results, the 5% sample showed very little difference in heat of hydration as compared to the reference samples. The 15% sample, however, showed a significant difference, as the peak heat of hydration was reduced by about 15-20% as compared to reference samples. The trend in Alkali content is similar to quarry fine 1 but to an even greater extent. The alkali content is reduced by the presence of quarry fine 2 which may imply pozzolanic activity, but further study is required to state this conclusively.

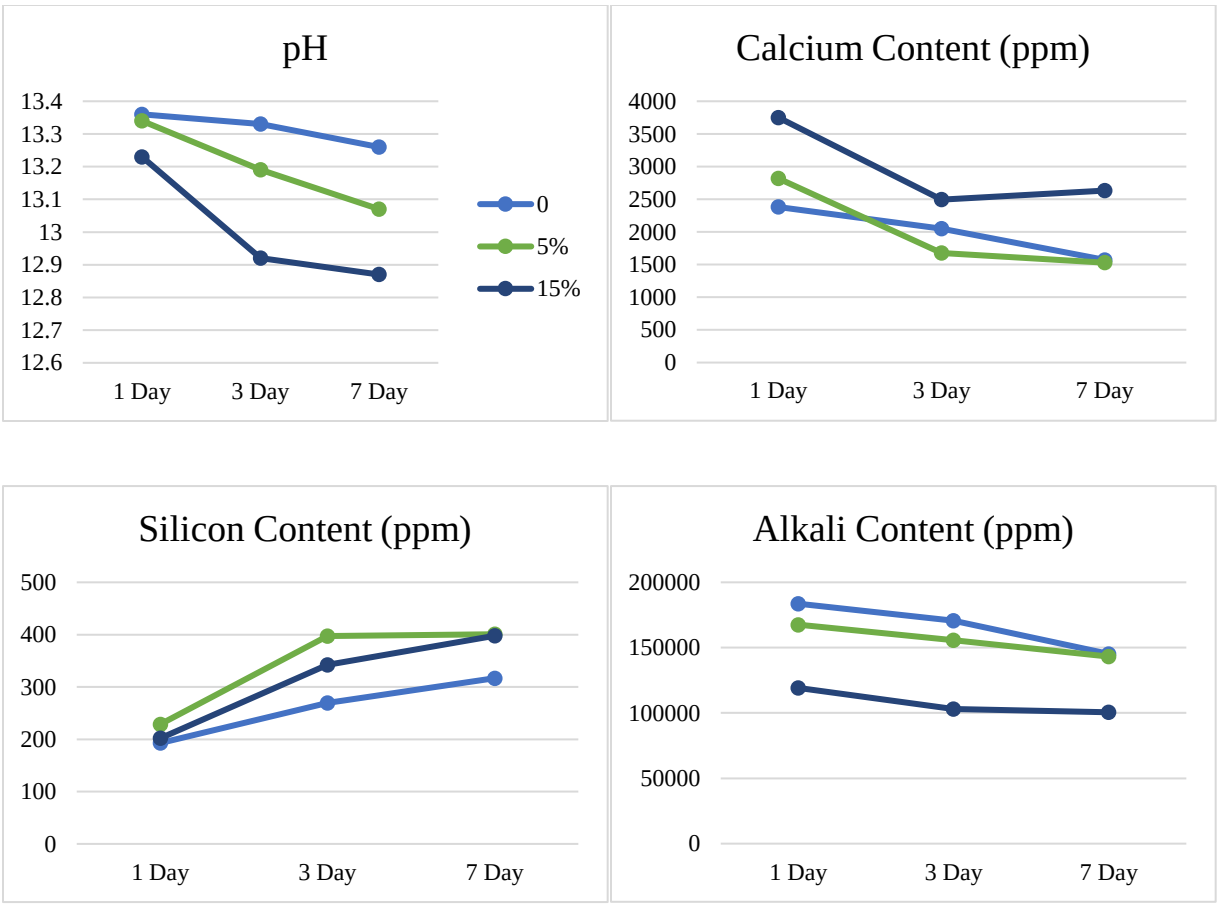



***Figure 30: Pore solution pH values and key elemental quantities for samples containing quarry fine 3.***

Very similar to quarry fine 1, quarry fine 3 exhibits an increase in dissolved Si and Ca in the pore solution, implying that this material is negatively impacting the formation of C-S-H in the concrete microstructure. Once again, this information is supported by calorimetry data.

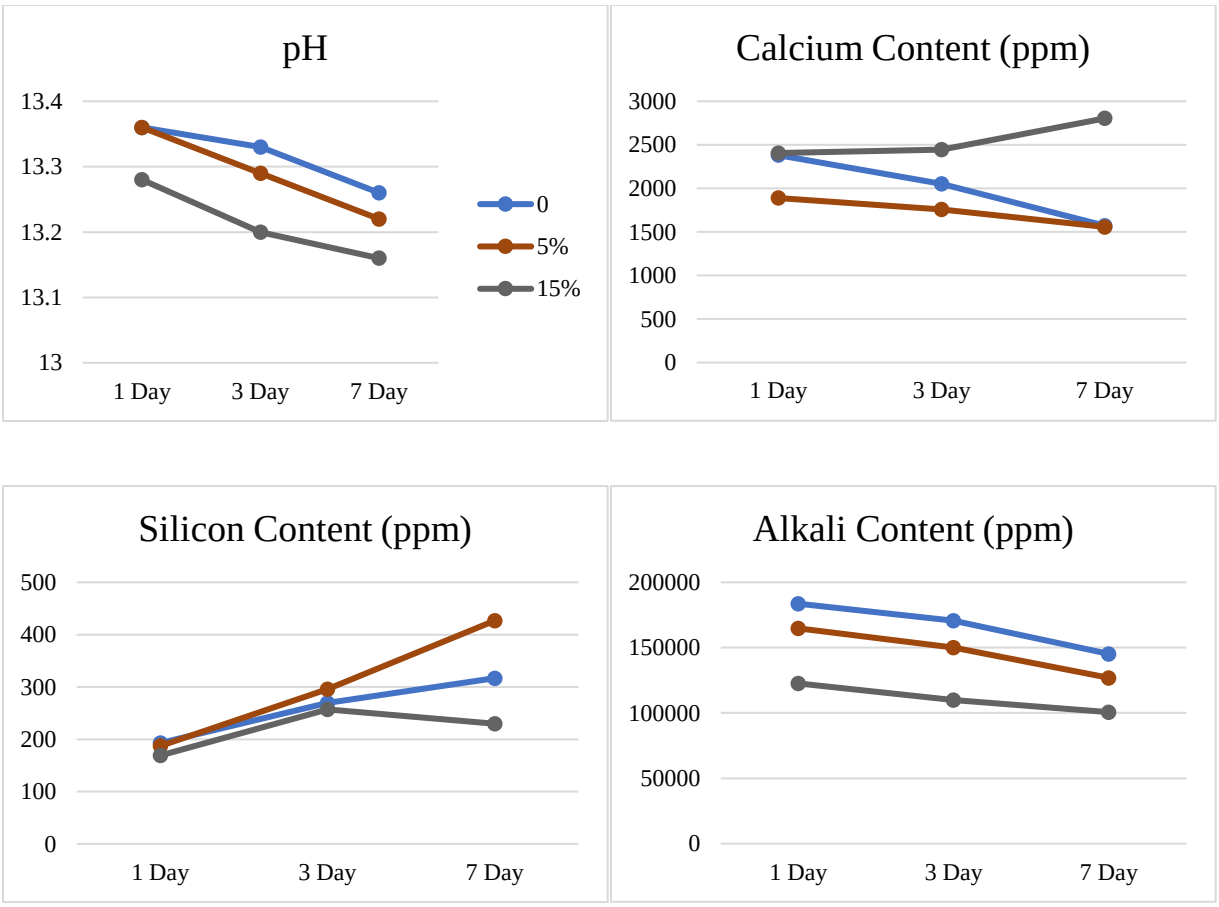



***Figure 31: Pore solution pH values and key elemental quantities for samples containing quarry fine 4.***

Quarry fine 4 results show that at 5% substitution, the pore solution contains lower concentrations of calcium but higher concentrations of silicon. At 15% substitution, the opposite is observed. These contradictory findings may indicate that there are additional reactions taking place as a result of the chemical makeup of this particular quarry fine material. While it is unclear what these reactions are, the calorimetry data supports the hypothesis that the hydration process is being negatively impacted.

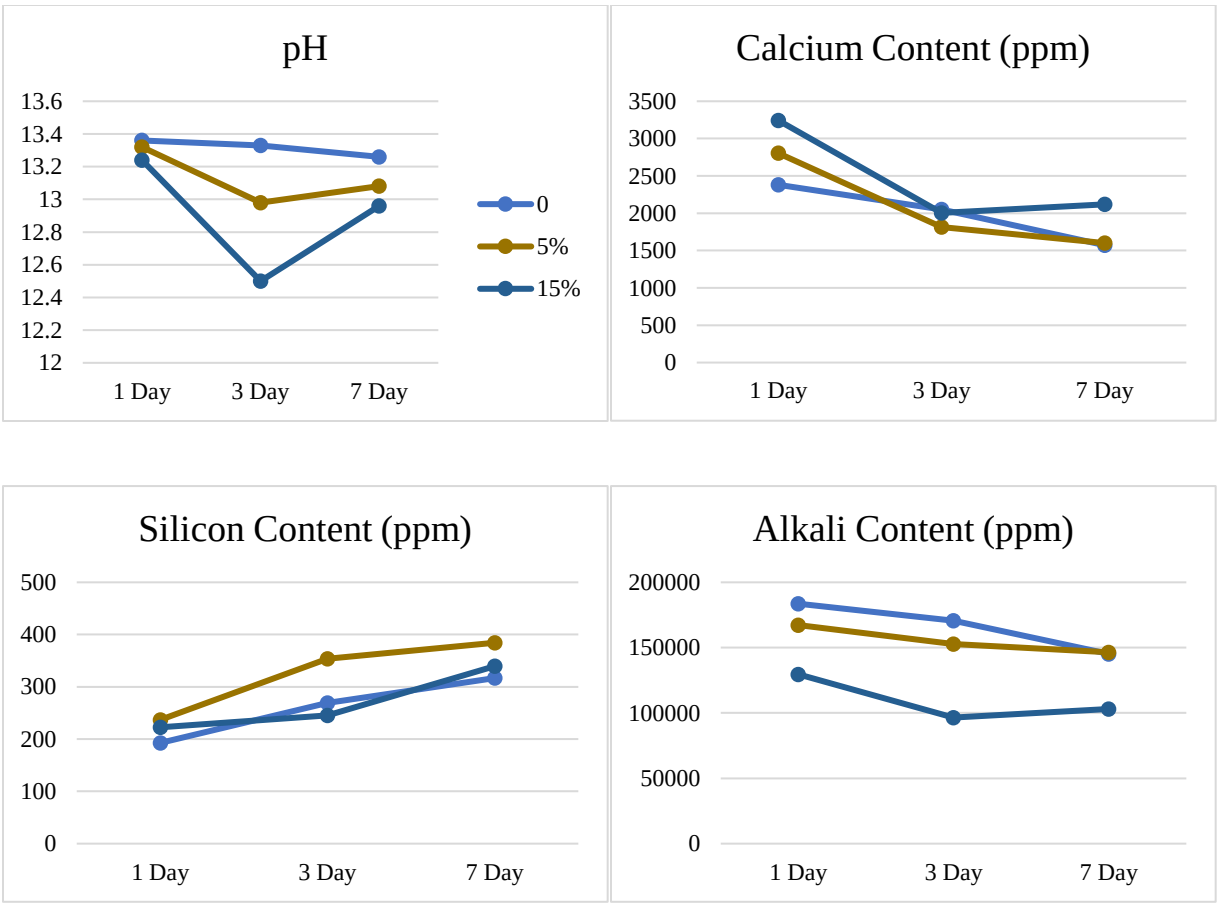



***Figure 32: Pore solution pH values and key elemental quantities for samples containing quarry fine 5.***

The trends for quarry fine 5 are very similar to those observed in quarry fines 1 and 3, though to a lesser extent. Even at 15% substitution, the silicon and calcium contents are only slightly higher than the reference samples. This implies that similar quantities of these elements are being used in the formation of hydration products. This is once again supported by calorimetry data. Quarry fine 5 was one of the best performers in isothermal calorimetry, along with quarry fines 2 and 7. The trend in alkali content is also the same as with quarry fine 1 and all the others thus far.

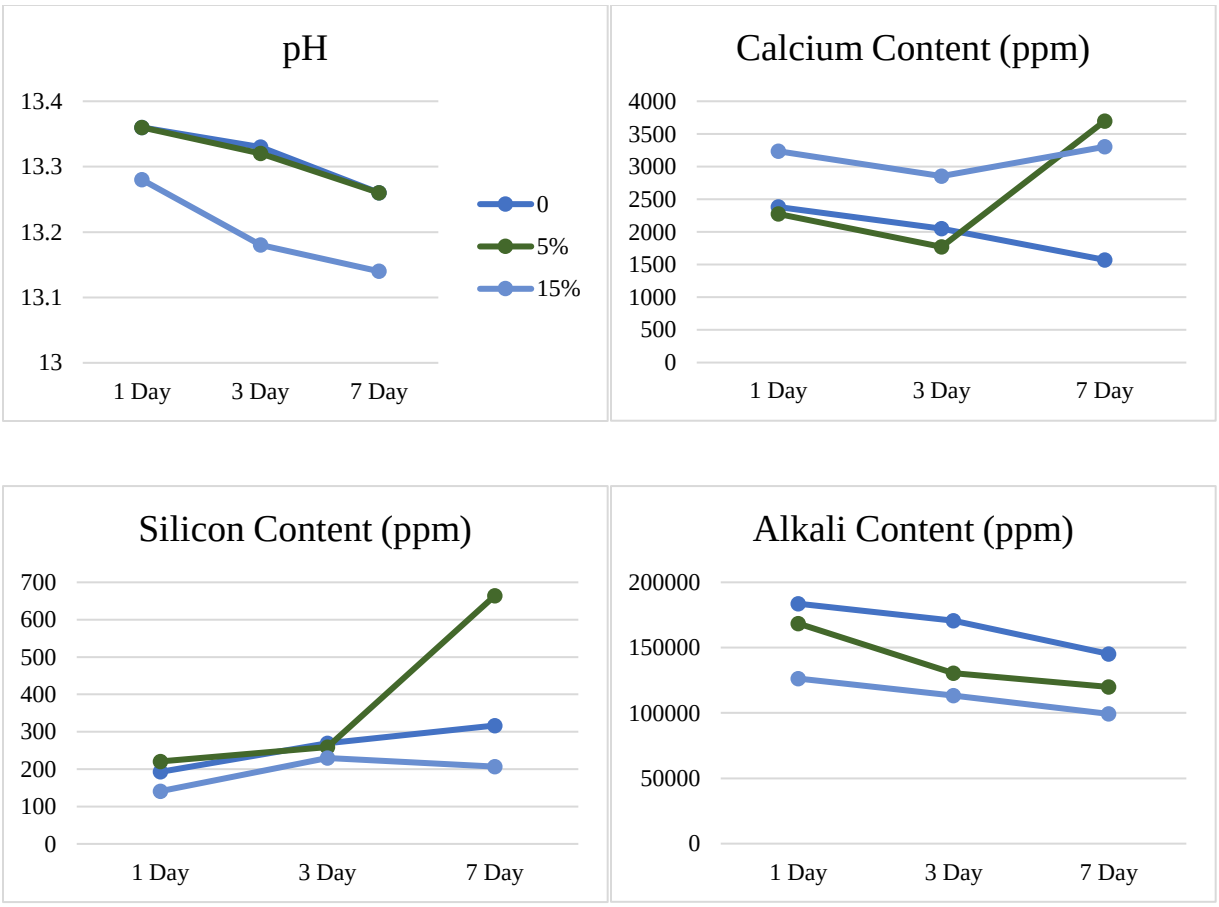



***Figure 33: Pore solution pH values and key elemental quantities for samples containing quarry fine 6.***

Results for quarry fine 6 are similar to quarry fine 4, in that there are a number of contradictory trends. Again, this implies that numerous reactions may be taking place in the microstructure that are not fully understood but that are expected to have a detrimental effect on hydration, as shown in the calorimetry data.

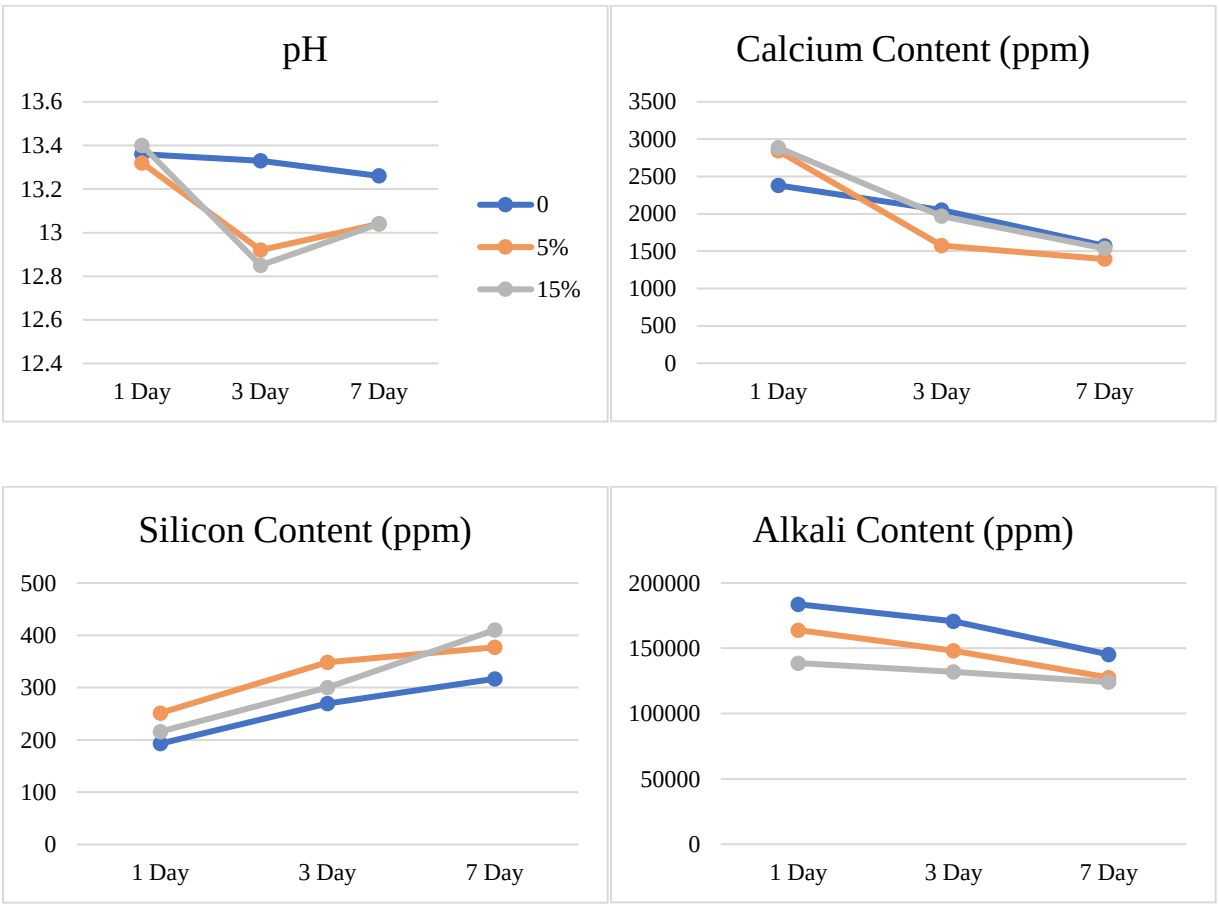



***Figure 34: Pore solution pH values and key elemental quantities for samples containing quarry fine 7.***

Quarry fine 7 results show higher silicon content but similar calcium content when compared to reference samples. This implies a reduction in the formation of hydration products to a limited extent. Notably, the reduction in alkali content is significantly less than many of the other quarry fines. This may imply that quarry fine 7 has a higher alkali content in its composition. Further characterization studies would be needed to confirm this.

*3.3.3. Compressive Strength*

After IC results indicated that 5% quarry fine replacement of cement had minimal effect on hydration and 15% had a magnified effect (See Section 4.1) it was decided that further strength testing should be done on samples of both 5% and 15% replacement. Compressive strength results are presented in Figure 35.

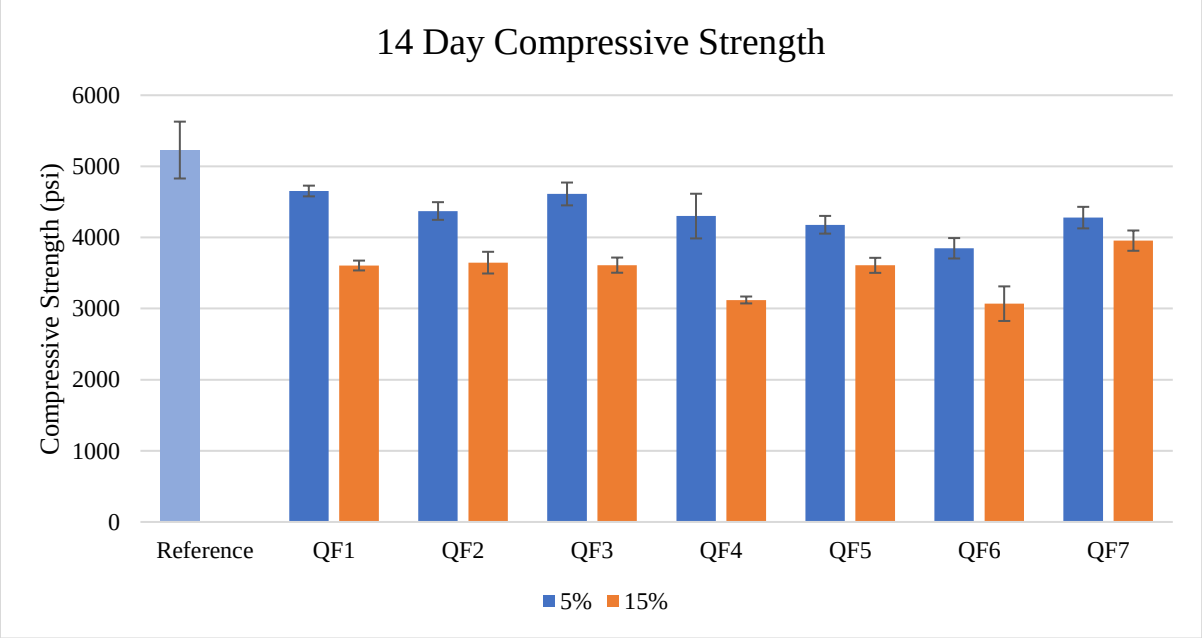



***Figure 35: 14-day compressive strength of hardened mortar samples prepared with 5 and 15% quarry fine replacement of cement. w/c ratio = 0.5. Error bars represent the standard deviation amongst the 3 replicate samples.***

It is noted that increasing percent substitution of quarry fines resulted in decreased compressive strength. As compared to reference mortar samples with no quarry fines, the strength reduction of samples tested is presented in Table 8.

***Table 8: Percent Reduction in Strength Compared to Control Sample***

| | **QF1** | **QF2** | **QF3** | **QF4** | **QF5** | **QF6** | **QF7** |
|---|---|---|---|---|---|---|---|
| **5%** | 11.0 | 16.4 | 11.8 | 17.8 | 20.1 | 26.4 | 18.2 |
| **15%** | 31.1 | 30.3 | 31.0 | 40.3 | 31.0 | 41.3 | 24.4 |

Quarry fines 1 and 3 appear to perform reasonably well at low substitutive percentages, causing a strength reduction of less than 12%. Interestingly, quarry fine 7 has relatively minimal difference in performance between samples with 5% quarry fines and samples with 15%. This may indicate that quarry fine 7 contains a compound that reacts to form strength when in large quantities. Quarry fine 6 appears to cause the greatest reduction in strength.

It is important to note that quarry fines 1 and 3 are saturated slurries when in field conditions. In order to correct for the moisture content, the mix design was altered for those two mixes. It is possible that the saturation of those fines resulted in improved strength characteristics which is evident in Figure 35. With the exception of those two, quarry fines 2 and 7 performed best which is supported by both the hydration data and the analysis of pore solution.

## 3.4. Conclusion and Recommendations

In analyzing a large number of different materials at various substitutive percentages, it is helpful to summarize the general trends and major findings. In general, the addition of quarry fine material as a replacement of Portland cement, caused a reduction in the overall heat of hydration as compared to reference samples. Quarry fines 2, 5, and 7 had the least reduction in hydration energy. Pore solution analysis revealed that many of the samples exhibited increased Ca and Si concentrations in the pore solution, implying that the hydration of C-S-H had been inhibited by the presence of quarry fines. Strength testing supported the physicochemical data as it showed a decrease in strength with an increasing percentage of cement replacement by quarry fines. Quarry fines 2 and 7 exhibit the most potential for use as filler materials in Portland cement.

The preliminary investigation presented in this study is not sufficient to make conclusive arguments for or against the use of any of these quarry fine materials. While it seems that some of

the materials are promising, this investigation should be considered in conjunction with characterization data and further testing. Other than characterization techniques, it is recommended to conduct long term strength testing which could potentially reveal pozzolanic behavior which often only develops at later ages. Based on existing literature, it would be valuable to investigate the use of quarry fines as replacement for fine aggregate, instead of replacing cement. Many of the quarry fines appear to have gradations similar to that of fine aggregate and they may be feasible in situations where good quality fine aggregate is not available.

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# 4. Conclusions and Recommendations

## 4.1. Summary of Findings

As sustainability in the concrete industry becomes a critical industry priority, the utilization of recycled aggregates and cement alternatives or fillers will become more of a necessity. The state of Virginia will need to make progress in that direction, and the utilization of recycled asphalt pavement aggregates or waste quarry fine materials may help in this effort.

In general, RAP aggregates are already a well utilized material as they are recycled for use in making new asphalt or as aggregate in subbase roadway layers. The research conducted in Chapter 2 of this study suggests that the utilization of RAP as an aggregate in concrete would not be as effective as its current uses. While pretreatment appears to make marginal improvements to mechanical performance, it is not where it needs to be. Significant reduction in heat of hydration and mechanical strength were indicative of the RAP aggregates poor performance. Additionally, analysis of the pore solution of hardened mortar samples revealed that the presence of RAP aggregates hinders the formation of hydration products.

In Chapter 3, it was determined that many of the quarry fine materials from sources around Virginia did not improve the mechanical properties of mortar samples when incorporated into the mix as a substitution for cement. This was evident in the reduction of hydration energy, and the reduced mechanical strength. That being said, quarry fines 2 and 7 did show potential for use as filler materials, as they only showed a small decrease in cement hydration and mechanical properties.

## 4.2. Recommendations for Future Work

For the portion of the study that considered the use of RAP as aggregate in concrete, it is recommended that further investigation should involve the following:

- Alternative pretreatment methods to investigate whether there are other methods that may improve the mechanical properties of the aggregate. For example, soaking the RAP aggregates in calcium hydroxide.
- Additional mechanical testing could be conducted on concrete prepared with RAP aggregates. This could include flexural strength testing and elastic modulus testing.
- A carbon footprint analysis to quantify the benefits of using RAP aggregates in concrete.
- Analysis of concrete or mortar prepared with a combination of RAP and various supplementary cementitious materials (SCMs).

Future work for the portion of the study that considered the use of quarry fines as cement replacement could include the following:

- Further investigation could involve characterization studies to determine the chemical composition of these materials in order to better hypothesize ways for them to be utilized in a productive way.
- Future studies could also compare the quarry fine samples to a control sample prepared using equal proportions of an inert material.
- Long term testing to investigate the potential of pozzolanic activity in the quarry fines.
- The quarry fines materials could also be investigated for their feasibility as fine aggregate substitution.

- Samples prepared with a combination of quarry fines and SCMs could be analyzed for mechanical strength to see if notable changes occur.
- Conduct a carbon footprint analysis of the utilization of quarry fines. If it is determined that the reduction in carbon output is significant, it will be more feasible to utilize the quarry fine materials, even if they result in strength reductions as observed in this study.