Chemistry of recycled concrete aggregate leachate in pavement base course applications

By

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EXECUTIVE SUMMARY

Uncertainty regarding the environmental implications of high pH, high alkalinity recycled concrete aggregate (RCA) leachate limits the use of RCA as a substitute for virgin aggregate in pavement base course. The purpose of this work is to understand the time-dependent behavior of leachate chemistry from RCA in pavement base course applications and the persistence of high pH leachate in the environment.

A state-of-the-art review of the existing laboratory and field investigations of RCA leachate chemistry, provided in Chapter I, identifies discrepancies in field and laboratory measurements of RCA leachate pH. Critical evaluation of the existing investigations indicates that conventional laboratory methodology, which employs abrasive, closed system batch reactors, is not representative of field conditions. Long-term highway field studies of RCA leachate illustrate that an initially high leachate pH approaches neutral within approximately one to two years of construction. Conversely, laboratory investigations of RCA leachate pH using batch reactor leaching tests and column leaching tests measure consistently high leachate pH (pH >10). In designing laboratory investigations of RCA leachate chemistry, particle abrasion should be limited to represent the development and preservation of RCA surface carbonation. Additionally, RCA-leachate contact times should be based on field drainage times and the availability of atmospheric carbon should be considered throughout the leaching experiment. Laboratory methodology employed in this work uses non-abrasive, open system batch reactor leaching experiments to evaluate RCA leachate pH and alkalinity.

In order to understand the physicochemical factors that control RCA leachate pH and alkalinity the physical properties, solid phase chemistry, and time-dependent leachate chemistry were evaluated for ten RCA samples. The physicochemical properties informed the development of a geochemical model using Geochemist's Workbench, introduced in Chapter II. Integrating the physicochemical properties and the geochemical model, the factors that control RCA leachate chemistry can be described by two parameters: portlandite content of RCA available for dissolution, and the availability of carbon dioxide. These two time-dependent controlling parameters counteract one another, such that portlandite content governs the peak pH associated with RCA leachate, and the availability of carbon dioxide governs the neutralization of leachate pH.

To extend the fundamental understanding of time-dependent behavior of RCA leachate chemistry to applications in pavement base course, non-abrasive, open system batch reactor leaching experiments were used with different RCA-leachate contact times according to AASHTO base course drainage quality standards (e.g., 2 hours, 1 day, 1 week, and 1 month), presented in Chapter III. The contact time experiments indicate that longer contact times do not increase peak pH associated with RCA leachate pH, such that using RCA in base course applications poses no additional concern regarding drainage quality. Following the contact time experiments, the liquid leachate was separated into a clean beaker, no longer in contact with the RCA material, and the time-dependent pH and alkalinity of the leachate was monitored after phase separation. The phase separation experiments demonstrate that RCA leachate pH will equilibrate to a near-neutral value, pH 7.7 and pH 8.5, regardless of the physicochemical properties of the initial RCA sample, given sufficient exposure to atmospheric carbon dioxide or soil acidity. Therefore, drainage system designs for RCA base course should consider the availability of carbon dioxide and/or soil acidity, especially in sensitive areas.

The findings of this study can be used to provide guidelines for practice to ensure safe and wise use of RCA base course. The pH measured after 24 hours of RCA-leachate contact, referred to as the 24-hour pH, was found to be a useful parameter to characterize an RCA sample because it can be directly correlated with peak pH and portlandite content available for dissolution. The 24-hour pH can be used in practical applications of RCA base course as a straightforward parameter to assess readiness of the RCA for construction and whether stockpiling, artificial carbonation of the material are required before construction.

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TABLE OF CONTENTS

Executive Summary i

Acknowledgements iii

List of Tables viii

List of Figures x

Acronyms xiv

Introduction 1

- Construction applications of RCA 1
- RCA in pavement base course applications 1
- Fundamental chemistry related to RCA leachate chemistry 2

Research objectives 5

Overview of thesis 6

1. Recycled concrete aggregate in base course applications: a State-of-the-Art review of field and laboratory investigations of leachate pH 7

- Abstract 8
- Introduction 9
- Chemical characteristics of RCA 11
- Existing body of work 14
  - Laboratory investigations of leachate pH 14
  - Column Leaching Tests 17
  - Field-scale studies of leachate pH 21
- Conclusions and recommendations 23

2. Integrating physicochemical properties and batch reactor leaching experiments to predict recycled concrete aggregate leachate chemistry – Part I 27

Abstract 28

Introduction 29

Recycled concrete aggregate leachate chemistry 30

Materials and methods 32

RCA samples 32

Methods 33

Results and Discussion 38

Modifying existing batch reactor methodology 38

Physicochemical properties affecting RCA leachate pH and alkalinity 44

Conclusions 47

3. The influence of contact time and base course drainage on recycled concrete aggregate leachate chemistry 48

Abstract 49

Introduction 50

Material and Methods 52

Materials 52

Methods 53

Results and Discussion 54

The influence of contact time on RCA leachate chemistry 54

The influence of RCA-leachate phase separation on leachate chemistry 62

RCA leachate neutralization in the environment 65

Conclusions 67

Conclusions and Recommendations 69

Future Research Opportunities 71

References 73

A. Appendix A 84

B. Appendix B 100

C. Appendix C 106

Field determination of leachate pH 107

Introduction 107

Materials 107

Methods 108

Results and Discussion 110

Conclusions 110

LIST OF TABLES

Table 1.1. Summary of existing field and laboratory determinations of RCA leachate pH. 26

Table 2.1. Sample source information. 33

Table 2.2. Physical properties of sample suite. 34

Table 2.3. Mineral percentages from XRD (Figure A.1). 36

Table 2.4. Carbonate mineral percentages from XRD and TGA (Table A.9, Table A.10). 36

Table 2.5. Comparison of field-measured leachate pH, conventional batch reactor leaching experiments, and batch reactor leaching experiments of the MnROAD RCA samples (Chen et al. 2012, 2013; Madras Natarajan et al. 2019). 40

Table 2.6. Leachate pH and alkalinity of RCA leachate for sample suite, as determined by modified batch reactor leaching experiments. Reported as median of three trials. 43

Table 3.1. AASHTO classifications of pavement drainage quality for use in pavement drainage design. Adapted from (AASHTO 1993). 52

Table 3.2. Summary of physicochemical properties of RCA samples ((Sanger et al. 2019c). 53

Table 3.3. Neutralization pH of leachate after phase separation and the time to reach neutralization pH.65

Table A.1. Atterberg limits for base course sample suite. 85

Table A.2. Specific gravity (G_s) and absorption for base course sample suite. 85

Table A.3. Grain size properties. 85

Table A.4. Friction angle from direct shear. Courtesy of Soil Mechanics. 86

Table A.5. Optimum water content and maximum dry unit wright from modified Proctor compaction. 86

Table A.6. Compression indices from one-dimensional compression. 86

Table A.7. Hydraulic conductivity from falling head and constant head rigid wall permeameters. 87

Table A.8. Grain size distribution data. 87

Table A.9. Mineral percentages from XRD. 87

Table A.10. Carbonate mineral percentages from XRD and TGA, and portlandite percentage from geochemical model. 88

Table B.1. Kinetic rate laws and masses used in the model for each RCA sample tested. 101

Table B.2. Percent portlandite, carbon dioxide contact area, neutralization time, and neutralization pH as calculated by the GWB model which would not have been available with only the experimental data. Peak pH, 24-hour pH, and neutralization pH serve as the boundaries of the two regions of the time-dependent pH curve for the leachate. 101

Table C.1. Alkalinity measurements of Ultrapure MQ equilibrated with atmospheric carbon dioxide in an open system batch reactor. 104

Table D.1. pH indicator results for sample CT18. 112

Table D.2. pH indicator results for sample PR18. 113

Table D.3. pH indicator results for sample ML18. 114

Table D.4. pH indicator results for sample WS18. 115

Table D.5. pH indicator results for sample CT17. 116

Table D.6. pH indicator results for sample OC17. 117

Table D.7. pH indicator results for sample WA17. 118

Table D.8. pH indicator results for sample 16C. 119

Table D.9. pH indicator results for sample 16D. 120

Table D.10. pH indicator results for sample 16P. 121

Table D.11. pH indicator results for sample VA. 122

LIST OF FIGURES

Figure 1.1. Pavement profile schematic. 11

Figure 1.2. RCA leachate chemistry (a) carbonate system of natural waters; (b) dissolution of calcium hydroxide and calcium carbonate from RCA surface; (c) carbonation of RCA surface as represented by the black layer. 14

Figure 1.3. Additional processes that reduce leachate pH for different base course drainage designs (a) subbase drainage; (b) edgedrain/underdrain outlet. 20

Figure 2.1. Grain size distribution for sample suite (Table A.8). Samples 16C, and 16D, and 16P from (Madras Natarajan et al. 2019). 35

Figure 2.2. pH of sample suite from continuous monitoring batch reactor leaching experiments. Results reported as median of three trials with range bars to illustrate the minimum and maximum measured leachate pH. 41

Figure 2.3. Alkalinity of sample suite from continuous monitoring batch reactor leaching experiments. Results reported as median of three trials with range bars to illustrate the minimum and maximum measured leachate pH. 42

Figure 2.4. Relationship between 24-hour leachate pH, peak pH, and 48-hour pH. Peak pH fit: $y = 0.5055x + 5.4795$ ($R^2 = 0.8158$); 48-hour pH fit: $y = 0.4057x + 5.0031$ ($R^2 = 0.7091$). 46

Figure 3.1. pH vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured pH values. 56

Figure 3.2. pH vs. contact time for all samples, subplots for each time (a) 2 hour (b) 1 day (c) 1 week (d) 1 month. Results reported as the median of three trials. 57

Figure 3.3. Alkalinity vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured alkalinity values. 58

Figure 3.4. Calcium ion concentration vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured calcium ion concentration. 59

Figure 3.5. Effects of stirring (pH vs. contact time for all samples) (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as the median of three trials. 61

Figure 3.6. Post-drainage pH vs. time for all samples, all times on each plot (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials. 63

Figure 3.7. Post-drainage alkalinity vs. time for all samples, all times on each plot (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials. 64

Figure 3.8. Acidity required to neutralize RCA leachate pH. Curve fit: H+ [M] = 0.0006x - 0.0052 R^2 = 0.7453. 67

Figure A.1. Relative mineral percentages. 88

Figure A.2. CT18 XRD Trace. 89

Figure A.3. PR18 XRD Trace. 89

Figure A.4. ML18 XRD Trace 90

Figure A.5. WS18 XRD Trace. 90

Figure A.6. CT17 XRD Trace. 91

Figure A.7. OC17 XRD Trace. 91

Figure A.8. WA17 XRD Trace. 92

Figure A.9. 16C XRD Trace. 92

Figure A.10. 16D XRD Trace. 93

Figure A.11. 16P XRD Trace. 93

Figure A.12. VA XRD Trace. 94

Figure A.13. All XRD Traces. 94

Figure A.14. CT18 TGA Trace. 95

Figure A.15. PR18 TGA Trace. 95

Figure A.16. ML18 TGA Trace. 96

Figure A.17. WS18 TGA Trace. 96

Figure A.18. 16C TGA Trace. 97

Figure A.19. 16D TGA Trace. 97

Figure A.20. 16P TGA Trace. 98

Figure A.21. Monitoring time-dependent pH of sample OC17 in a non-abrasive, open system batch reactor (Chapter II), then allowing that sample to air-dry in the laboratory and conducting a second time-dependent batch reactor leaching experiment. Singular experiment conducted on sample OC17. Demonstrates carbonation. 99

Figure B.1. Laboratory data compared to model outputs for the ten RCA samples used. 102

Figure B.2. Relationship between percent portlandite to the 24-hour pH and peak pH, peak pH fit: y = 9.21x+9.3 (R^2=0.91), 24-hour pH fit: y = 12.86x+8.1 (R^2 = 0.68) 103

Figure B.3. Linear relationship between carbon dioxide contact area and the rate of pH, fit: y = -11,928x + 91.5 (R^2 = 0.95) 103

Figure B.4. Monitoring pH of Ultrapure MQ equilibrated with atmospheric carbon dioxide in an open system batch reactor. 104

Figure B.5. Monitoring time-dependent pH of calcium carbonate powder and calcium hydroxide powder in an open system batch reactor. 105

Figure C.1. Fisherbrand Litmus paper (“Fisherbrand^{TM} pH Test Paper Rolls” 2019). 109

Figure C.2. pH indicator color chart (“pH Indicator Chart” 2019). 109

Figure C.3. pH indicators corresponding to 24-hour pH. 111

ACRONYMS

AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
C&D	Construction and demolition
C-S-H	Calcium silicate hydrate
GWB	Geochemist's Workbench
GSD	Grain size distribution
MnROAD	Minnesota Road Research Facility
RCA	Recycled concrete aggregate
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
USCS	Unified Soil Classification System

INTRODUCTION

Construction applications of RCA

To maintain the public highway system public highway system in the United States, approximately one billion tons of virgin aggregate are consumed annually (Willett 2017). Virgin aggregate is quarried rock, usually a limestone or similar, that must be mined and transported to the construction site. Simultaneously, 157 million tons of concrete waste is produced from the demolition of existing roadways and bridges produces approximately annually in the United States that has to be transported from the site (EPA 2016). In-situ concrete recycling eliminates the most capital- and carbon-intensive components of pavement construction: mining and transportation of virgin aggregate to the construction site (Robinson and Brown 2002). Substituting RCA for virgin aggregate conserves finite natural aggregate resources, thereby reducing the energy consumption (20%), water usage (11%), carbon dioxide emissions (16%), and life-cycle economic cost (21%) associated with highway construction (Lee et al. 2010; Del Ponte et al. 2017). Additionally, the relatively low aggregate density of RCA compounds the economic and environmental savings from material transport, should there be any material transport (FHWA 2016; Saeed et al. 2006; Serres et al. 2016). Because using recycled concrete as a substitute for virgin aggregate in construction applications yields environmental and economic benefits, it is becoming more prevalent, particularly in pavement base course applications (Bozyurt et al. 2012).

RCA in pavement base course applications

The purpose of the base course layer in pavement systems is two-fold: to provide strength and drainage to the pavement surface (FHWA 2017). Much work has been done to evaluate the mechanical properties of RCA in base course applications, and the consensus is that RCA is a mechanically sufficient base course substitute for virgin aggregate. RCA has a higher resilient modulus (Bennert et al. 2000; Bestgen et al. 2016; Bozyurt et al. 2012; Edil et al. 2012; Kuo et al. 2002; Vieira and Pereira 2015), higher shear strength

(Saeed et al. 2006; Vieira and Pereira 2015), lower plastic strain (Bozyurt et al. 2012; Edil et al. 2012), lower permanent deformation (Bennert et al. 2000; Saeed et al. 2006), and higher California Bearing Ratio (Bestgen et al. 2016; Saeed et al. 2006; Vieira and Pereira 2015) than virgin aggregate. In addition to exceeding the mechanical performance of virgin aggregate, RCA base course exhibit less loss of stiffness than that of the natural aggregate (Edil et al. 2017).

The secondary function of the base course layer is to provide drainage to the pavement profile. Base course drainage can be designed in several different ways, including subbase layers, edgedrains, and daylighting. By controlling the engineering properties of the subbase layer, base course drainage systems can be designed to facilitate water flow vertically through the pavement profile and into the subsurface. Conversely, edgedrains and daylighting facilitate water flow from the base course layer into the drainage ditch.

When RCA becomes saturated in a precipitation event, it produces a high pH, high alkalinity leachate. Uncertainties regarding the environmental implications of RCA leachate limit widespread use of RCA base course. RCA leachate generation from stockpiles and pavement systems is unavoidable, and therefore it is of great interest to understand the generation and fate of the leachate.

Fundamental chemistry related to RCA leachate chemistry

When RCA becomes saturated in a precipitation event, it produces a high pH, high alkalinity leachate. Uncertainties regarding the environmental implications of RCA leachate limit widespread use of RCA base course. RCA leachate generation from stockpiles and pavement systems is unavoidable, and therefore it is of great interest to understand the generation and fate of the leachate.

pH

pH is defined as the negative log of hydrogen ion activity in an aqueous solution (Equation 1) (Brezonik and Arnold 2011). pH is used to define a solution as acidic or basic, such that a solution with pH

7 is a neutral solution, and is the pH of pure water, a solution with pH less than 7 is an acid, and a solution with pH greater than 7 is a base.

$$pH = -\log[H^+] \tag{1}$$

Throughout this thesis, pH will be referred to in many contexts: peak pH describes the highest pH of the leachate recorded for the leachate over the duration of the experiment; 24-hour pH describes the pH of the leachate after 24 hours RCA-leachate contact time; and the neutralization pH describes the pH of the leachate when the leachate is no longer in contact with RCA, and the leachate has reached equilibrium with atmospheric carbon dioxide.

Alkalinity

Alkalinity is a capacity term that is a measure of a solutions ability to resist pH change (Brezonik and Arnold 2011). Alkalinity describes the acid neutralization capacity of a solution (Equation 2).

$$Alkalinity = \sum[strong\ bases] + \sum[weak\ bases] - \sum[strong\ acids] \tag{2}$$

Carbonate system of natural waters

In base course applications, RCA surfaces are exposed to atmospheric carbon dioxide and the carbonate present in rainwater, described by Equations 3 through 7. The pH of rainwater is approximately pH 5.5, and the alkalinity is approximately 10 mg $CaCO_3$/L (Brezonik and Arnold 2011).

$$2H^+ + 2OH^- \rightarrow 2H_2O \tag{3}$$

$$CO_2(g) \leftrightarrow CO_2(aq) \tag{4}$$

$$H_2O + CO_2(aq) \rightarrow H_2CO_3^* \tag{5}$$

$$H_2CO_3^* + OH^- \rightarrow H_2O + HCO_3^- \tag{6}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{7}$$

Solid phase chemistry of RCA

At the end of its usable life as a monolith, Portland cement concrete is crushed to create RCA and the uncarbonated inner matrix is exposed (Van Gerven et al. 2006; Groves et al. 1990). Portland cement concrete is a mixture of coarse and fine aggregate in Portland cement paste consisting of calcium carbonate ($CaCO_3$), ettringite (Afm), monosulfate (Aft), calcium hydroxide, known as portlandite ($Ca(OH)_2$), and calcium-silicate hydrate (C-S-H) ($3CaO•2SiO_2•3H_2O$) (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Engelsen et al. 2009; Groves et al. 1990, 1991; Hidalgo et al. 2007; Hyun Nam et al. 2016; Matschei et al. 2007; Papadakis et al. 1989). Saturation of the fresh surfaces facilitates dissolution/precipitation and other chemical interactions between the water and base course material. The high pH, high alkalinity of RCA leachate is dominated by dissolved carbonate and hydroxide species released from portlandite and calcium carbonate dissolution. The solid phase chemistry of the cement paste changes after emplacement by several processes, namely through carbonation.

Cement paste carbonation

Intermittent saturation and exposure to atmospheric carbon dioxide promotes carbonation of the hardened cement phases in RCA, such as calcium hydroxide and calcium-silicate-hydrate, are converted to calcium carbonate in vaterite and calcite forms (Arandigoyen et al. 2006; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006; Groves et al. 1991; Papadakis et al. 1989, 1992; Šavija and Luković 2016; Silva et al. 2015). Calcium carbonate nucleates on the surface of portlandite crystals, forming masses around small amounts of calcium hydroxide (Galan et al. 2015; Groves et al. 1990, 1991). Carbonation rate and depth depends on carbon dioxide diffusion, relative humidity, and intermittent wetting and drying cycles (García-González et al. 2006; Van Gerven et al. 2006). Although AFm/Aft carbonation and dissolution may contribute leachate pH, dissolution of portlandite and the release of hydroxide ions are required to achieve the high pH observed in RCA leachate chemistry. Carbonation progressed inward from the aggregate surface, creating zonation: a carbonated outer zone, a partially-carbonated transition zone, and an uncarbonated inner matrix (Van Gerven et al. 2006; Groves et al. 1990). The carbonated outer zone limits the mass transport and dissolution of calcium hydroxide into the leachate, therefore the relative amounts of unreacted calcium hydroxide and calcium carbonate control the alkalinity and pH of RCA leachate (Galan et al. 2015; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006).

Trace element leaching

Dissolution of RCA cement paste also introduces trace elements and heavy metals into RCA leachate. Elements of interest include Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, V, and Zn (Chen et al. 2012, 2013, Engelsen et al. 2006, 2009, 2010). Much of the existing work regarding RCA leachate chemistry evaluates the risk of element leaching from the cement matrix. Investigations of the mobilization of major and trace elements from RCA leachate are not discussed within the scope of this thesis. Generally, heavy metal leaching from RCA decreases with increasing pH (Engelsen et al. 2009, 2010; Galvín et al. 2014; Hillier et al. 1999; Kosson et al. 2014; Lewis et al. 2015; Müllauer et al. 2015; Sanchez et al. 2002, 2009).

RESEARCH OBJECTIVES

The purpose of this thesis is to understand the time-dependent behavior of leachate chemistry from recycled concrete aggregate (RCA) in pavement base course applications, and the persistence of high pH leachate in the environment through the following objectives: 1) identify and address the discrepancies in previous laboratory and field investigations of RCA leachate chemistry; 2) isolate the physicochemical parameters that control RCA leachate chemistry; 3) determine the influence of contact time and base course drainage on RCA leachate chemistry.

OVERVIEW OF THESIS

The motivation for the work presented in this thesis is to understand the generation, fate, and transport of leachate from recycled concrete aggregate (RCA) in pavement base course applications. Chapter I provides a state-of-the-art review of the existing laboratory and field investigations of RCA leachate chemistry. Critical evaluation of the existing laboratory and field measurements of RCA leachate pH identified inadequacies in the conventional laboratory methodology and informed the development of laboratory methodology for the following chapters of this thesis. Chapter II presents an investigation of time-dependent RCA leachate chemistry and the physicochemical parameters that control RCA leachate chemistry. Using the physical properties, solid phase chemistry, and time-dependent leachate pH and alkalinity measured in Chapter II, a geochemical model was developed to describe RCA leachate chemistry. Supplementary information for Chapter II is Appendix A and Appendix B. Chapter III evaluates the influence of contact time on RCA leachate chemistry as well as the time-dependent leachate chemistry after RCA leachate drains from the base course layer. Ultimately, understanding the time-dependent behavior of leachate chemistry and the persistence of high pH leachate in the environment will inform the safe and responsible use of RCA as base course. There is interest to be able to determine RCA leachate pH in field applications of RCA base course to assess whether pre-treatment, prescribed aging, or remediation is necessary before construction; the use of pH indicators to determine RCA leachate pH in field applications was evaluated, and the results are presented in Appendix C. The practical implications and recommendations for future work are provided in the Conclusion of this thesis.

1. RECYCLED CONCRETE AGGREGATE IN BASE COURSE APPLICATIONS: A STATE-OF-THE-ART REVIEW OF FIELD AND LABORATORY INVESTIGATIONS OF LEACHATE PH

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Author contribution statement

Bharat Madras Natarajan conducted a preliminary literature review of field and laboratory investigations of leachate pH which served as the foundation and motivation for the critical review presented in this manuscript. Bu Wang, Tuncer Edil, and Matthew Ginder-Vogel provided technical review of the manuscript.

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ABSTRACT

The prevalence of construction and demolition (C&D) waste and the concurrent demand for construction aggregate presents the opportunity to recycle C&D waste materials as substitutes for virgin aggregate. Commonly, recycled concrete aggregate (RCA) is used as base course in pavement construction. Environmentally responsible applications of RCA must consider the high pH leachate and trace element leaching risks reported in the literature. This state-of-the-art review presents the methodology, results, and limitations of the existing laboratory and field investigations of RCA leachate chemistry. Long-term highway field studies of RCA leachate illustrate that an initially high leachate pH approaches neutral within approximately one to two years of construction. Conversely, laboratory investigations of RCA leachate pH using batch reactor leaching tests and column leaching tests measure consistently high leachate pH (pH >10). The discrepancies between field and laboratory measurements of RCA leachate pH suggest that the current laboratory methodology inadequately describes leachate conditions in the field. The authors recommend that future laboratory investigations consider intermittent wetting and drying cycles, eliminate particle abrasion, employ relevant contact times, and consider additional environmental processes that reduce leachate pH such as soil acidity and carbonation.

INTRODUCTION

In 2015, construction and demolition (C&D) waste debris in the United States exceeded 548 million tons, more than twice the amount of total municipal solid waste (EPA 2015). Concrete composes 70% of all C&D waste, with 41% of concrete C&D waste generated from the construction and maintenance of roads and bridges (EPA 2016). Concurrently, 1.48 billion tons of crushed stone was consumed in the United States in 2016, nearly 76% of which was used in road construction and maintenance (Willett 2017). As population density increases, loss of viable land for aggregate mining in populous regions will result in longer hauling distances of aggregate material and an increase in expenses associated with road construction (Robinson and Brown 2002; Vieira and Pereira 2015).

The supply of C&D waste, particularly concrete, and simultaneous aggregate demand for construction purposes presents the opportunity to recycle C&D waste materials as a substitute for virgin aggregate. Recycling asphalt, crushed stone, and Portland cement concrete for recycled aggregate – although not a novel idea – remains limited across much of the United States (Silva et al. 2017). Some identified barriers to recycling C&D aggregate for use in road construction applications include: few or limiting standards and specifications; insufficient financial incentive; long hauling distance to recycling plants; variable supply and demand; client perception and preconceptions; variable quality; and environmental concerns (Silva et al. 2017). Despite these identified barriers, recycling of C&D waste materials is on the rise; the reported amount of asphalt, crushed stone, and Portland cement concrete recycled in the United States increased by nearly 4% between 2015 and 2016 (Willett 2017).

Recycled substitutes for virgin aggregate in pavement construction applications are becoming more prevalent, particularly as granular and stabilized base course. Most commonly, recycled concrete aggregate (RCA) and recycled asphalt pavement aggregate are used as unbound base course in pavement construction (Figure 1.1) (Bozyurt et al. 2012). The primary functions of pavement base course are to provide structural support, stiffness, and drainage (FHWA 2017). A well-designed base course system is constructed with a well-graded, durable material and is freely draining (FHWA 2017). Many studies have evaluated the use of RCA as pavement base course material, and in general, RCA is recognized as a mechanically sufficient base course substitute for virgin aggregate. RCA has a higher resilient modulus (Bennert et al. 2000; Bestgen et al. 2016; Bozyurt et al. 2012; Edil et al. 2012; Kuo et al. 2002; Vieira and Pereira 2015), higher shear strength (Saeed et al. 2006; Vieira and Pereira 2015), lower plastic strain (Bozyurt et al. 2012; Edil et al. 2012), lower permanent deformation (Bennert et al. 2000; Saeed et al. 2006), and higher California Bearing Ratio (Bestgen et al. 2016; Saeed et al. 2006; Vieira and Pereira 2015) than virgin aggregate. In addition to exceeding the mechanical performance of virgin aggregate, RCA base course are more resistant than virgin aggregate to stiffness loss from freeze/thaw cycles (Edil et al. 2017).

Known benefits of using RCA as base course substitute extend beyond the mechanical suitability. In-situ concrete recycling eliminates the most capital- and carbon-intensive components of pavement construction: mining and transportation of virgin aggregate to the construction site (Robinson and Brown 2002). Substituting RCA for virgin aggregate conserves finite natural aggregate resources, thereby reducing the energy consumption (20%), water usage (11%), carbon dioxide emissions (16%), and life-cycle economic cost (21%) associated with highway construction (Lee et al. 2010; Del Ponte et al. 2017). Additionally, the relatively low aggregate density of RCA compounds the economic and environmental savings from material transport, should there be any material transport (FHWA 2016; Saeed et al. 2006; Serres et al. 2016).

Although RCA base course exhibits desirable mechanical properties and life-cycle benefits, environmentally responsible applications of RCA must consider the high pH leachate and trace element leaching risks. RCA leachate generation from stockpiles and pavement systems is unavoidable, and therefore it is of great interest to understand the fate and transport of the leachate. Existing laboratory investigations consistently measure high leachate pH, pH 10 to 14; conversely, long-term highway field studies demonstrate that, after an initial phase of high pH, leachate approaches neutral pH within one to two years of construction (Chen et al. 2012, 2013, Engelsen et al. 2006, 2012, 2017). Discrepancies in leachate pH from laboratory and field studies suggest that the laboratory methodology does not accurately represent field conditions. Many of the existing laboratory investigations of RCA leachate chemistry are designed to investigate the pH-dependent release of major and trace elements; future investigations of RCA leachate pH should be motivated by the physicochemical conditions of base course systems in designing the laboratory methods. The purpose of this paper is to provide a state-of-the-art review of the existing laboratory and field investigations of RCA leachate chemistry, and to provide recommendations to modify laboratory methods in future investigations of RCA leachate pH. The authors recommend that future laboratory investigations consider intermittent wetting and drying cycles, eliminate particle abrasion, employ relevant contact times, and consider additional environmental processes that reduce leachate pH.

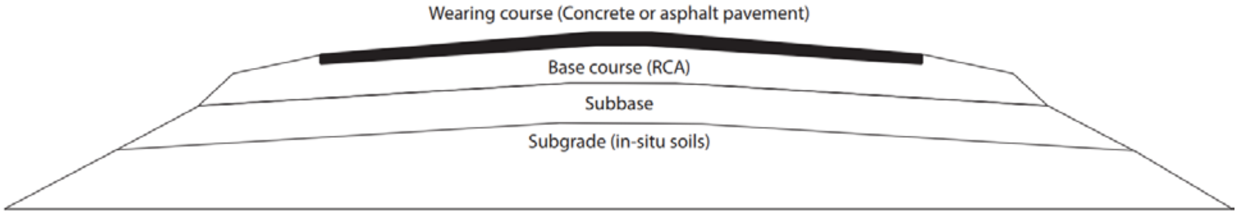

Figure 1.1. Pavement profile schematic.

CHEMICAL CHARACTERISTICS OF RCA

Portland cement concrete becomes RCA when it is crushed after its usable life as a monolith. Portland cement concrete is a mixture of coarse and fine aggregate in Portland cement paste consisting of calcium carbonate ($CaCO_3$), ettringite (Afm), monosulfate (Aft), calcium hydroxide, known as portlandite ($Ca(OH)_2$), and calcium-silicate hydrate (C-S-H) ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Engelsen et al. 2009; Groves et al. 1990, 1991; Hidalgo et al. 2007; Hyun Nam et al. 2016; Matschei et al. 2007; Papadakis et al. 1989). Initially, completely hydrated cement paste contains up to 15% to 25% calcium hydroxide present in macrocrystalline, microcrystalline, slightly crystalized, and/or amorphous forms (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Hidalgo et al. 2007). The solid phase chemistry of the cement paste changes after emplacement by several processes, namely through carbonation.

During carbonation, cement hydrate phases in hardened cement pastes, such as calcium hydroxide and calcium-silicate-hydrate, are converted to calcium carbonate in vaterite and calcite forms (Arandigoyen et al. 2006; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006; Groves et al. 1991; Papadakis et al. 1989, 1992; Šavija and Luković 2016; Silva et al. 2015). Calcium carbonate nucleates on the surface of portlandite crystals, forming masses around small amounts of unreacted calcium hydroxide (Galan et al. 2015; Groves et al. 1990, 1991). Carbonation requires diffusion of carbon dioxide into water in contact with calcium hydroxide, where the reaction takes place in the aqueous phase. Carbonation rate and depth depends on carbon dioxide diffusion, relative humidity, and intermittent wetting and drying cycles (García-González et al. 2006; Van Gerven et al. 2006). Optimal conditions for conversion of calcium hydroxide to calcium carbonate occur at 20 degrees Celsius and 40-80% relative humidity (Abbaspour et al. 2016; Galan et al. 2015).

Carbonation begins at the exposed surface of the concrete monolith and progresses inward. At the end of its usable life as a monolith, concrete is crushed to create RCA and the uncarbonated inner matrix is exposed (Van Gerven et al. 2006; Groves et al. 1990). In base course applications, RCA surfaces are exposed to atmospheric carbon dioxide and the carbonate present in rainwater (Figure 1.2). Saturation of the fresh surfaces facilitates dissolution/precipitation and other chemical interactions between the water and base course material. The characteristic high pH and alkalinity (acid neutralization capacity) of RCA leachate is dominated by dissolved carbonate and hydroxide species released from portlandite and calcium carbonate dissolution (Figure 1.2); therefore, differences in solid phase composition of RCA will control the differences in RCA leachate pH. Although AFm/Aft carbonation and dissolution may contribute leachate pH, dissolution of portlandite and the release of hydroxide ions are required to achieve the high pH observed in RCA leachate chemistry.

With intermittent saturation and exposure to atmospheric carbon dioxide, the process of carbonation continues for RCA, progressing inward from the aggregate surface and creating zonation: a carbonated outer zone, a partially-carbonated transition zone, and an uncarbonated inner matrix (Van Gerven et al. 2006; Groves et al. 1990). Carbonation and the formation of the protective carbonate surface layer, the carbonated outer zone, limits the mass transport and dissolution of calcium hydroxide into the leachate, therefore the relative amounts of unreacted calcium hydroxide and calcium carbonate influence the alkalinity and initial pH of RCA leachate (Figure 1.2) (Galan et al. 2015; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006). Carbonation of the RCA material should be a critical consideration in RCA leachate investigations and in RCA construction applications, as the aggregate surface chemistry, not the bulk mineral composition, governs the leaching behavior (Abbaspour et al. 2016; Bestgen et al. 2016; Engelsen et al. 2009; Ginder-Vogel et al. 2005; Loncnar et al. 2016; Mulugeta et al. 2011; Sanchez et al. 2002).

Dissolution of the cement matrix also introduces trace elements and heavy metals into RCA leachate. Elements of interest include Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, V, and Zn (Chen et al. 2012, 2013, Engelsen et al. 2006, 2009, 2010). Much of the existing work regarding RCA leachate chemistry evaluates the risk of element leaching from the cement matrix. Investigations of the pH-dependent release of major and trace elements from RCA leachate are not discussed within the scope of this literature review, but may be of interest to some readers (Engelsen et al. 2009, 2010; Galvín et al. 2014; Hillier et al. 1999; Kosson et al. 2014; Lewis et al. 2015; Müllauer et al. 2015; Sanchez et al. 2002, 2009).

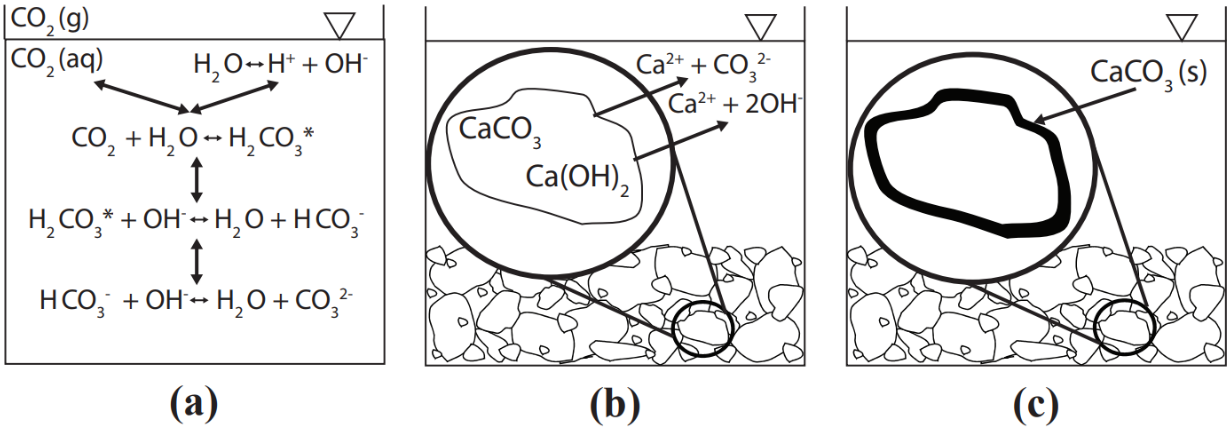

Figure 1.2. RCA leachate chemistry (a) carbonate system of natural waters; (b) dissolution of calcium hydroxide and calcium carbonate from RCA surface; (c) carbonation of RCA surface as represented by the black layer.

EXISTING BODY OF WORK

The following literature review presents the existing RCA leachate investigations, including long-term field monitoring, batch reactor tests, and column leaching tests methodologies. RCA leachate pH measurements determined by the existing field and laboratory investigations are summarized in Table 1.1.

Laboratory investigations of leachate pH

Methodology used in batch reactor investigations of leachate pH

Batch reactor leaching experiments are the most common method for investigating RCA leachate chemistry because the methodology is inexpensive, straightforward, and yields reasonably reproducible results in waste or soil leaching experiments (Kalbe et al. 2007). The existing studies of RCA leachate chemistry follow one of the following standard methods: *SR002.1 – Alkalinity, Solubility, and Release as a function of pH* (Kosson et al. 2002); *European Committee for Standardization Technical Standard CEN/TS 14429 pH dependence leaching test* (CEN 2005); *European Committee For Standardization CEN 12457-1 Characterisation of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges*

– Part 1 (CEN 2002); *Liquid-solid partitioning as a function of liquid-to-solid ratio in solid materials using a parallel batch reactor procedure - Method 1316* (EPA 2012); *ASTM D3987 Standard Practice for Shake Extraction of Solid Waste* (ASTM 2012); *ASTM D5233 Standard Test Method for Single Batch Extraction Method for Wastes* and *ASTM D4793 Standard Test Method for Sequential Batch Extraction of Waste with Water* (ASTM 2017a; b); and *USGS Field Leach Test for Assessing Water Reactivity and Leaching Potential of Mine Wastes, Soils, and Other Geologic and Environmental Materials Techniques and Methods 5-D3* (Hageman 2007).

Each of the commonly-used standards employs a fundamentally similar procedure: construction of a batch reactor at a prescribed liquid-to-solid ratio, vigorous agitation of the batch reactor, and extraction of a leachate sample for analysis. Specifically, the SR002.1 method recommends batch reactors with a liquid-to-solid ratio of 10 are agitated in an end-over-end tumbler at 28 rpm (±2 rpm) (Kosson et al. 2002). The European standards for leaching tests also recommends batch reactors with a liquid-to-solid ratio of 10 (CEN 2005) or with a liquid-to-solid ratio of 2 are agitated in an end-over-end tumbler (CEN 2002). Similarly, the United States Environmental Protection Agency (EPA) Method 1316 recommends five parallel batch leaching extractions at varying liquid-to-solid ratios (0.5, 1, 2, 5, and 10) that are agitated in an end-over-end tumbler at 28 rpm (±2 rpm) (EPA 2012). ASTM standard methods recommend batch reactors with a liquid-to-solid ratio of 10 to 20 are agitated in an end-over-end tumbler at 29 rpm (±2 rpm) for 18 hours to 72 hours (ASTM 2012, 2017a; b). The United States Geological Survey (USGS) 5-D3 method is designed to determine leaching potential in the field, and therefore recommends batch reactors constructed with a liquid-to-solid of 20 are shaken vigorously by hand for 5 minutes of every hour for the duration of the experiment (Hageman 2007). Comparison studies designed to isolate the relative importance of experimental parameters conclude that liquid-to-solid ratio has little to no effect on measured RCA leachate pH (Bestgen et al. 2016; Gupta et al. 2017); however, particle size variation, particularly an excess of fines fraction, may or may not affect leachate pH measurements in batch reactors (Bestgen et al. 2016; Coudray et al. 2017).

Results of batch reactor leaching investigations of leachate pH

Batch reactor leaching investigations of RCA leachate pH generally yield high pH measurements (Table 1.1). Existing batch reactor leaching studies, which differ in RCA source and degree of carbonation, measure RCA leachate pH ranging from pH 9.9 to 13.0 (Abbaspour et al. 2016; Bestgen et al. 2016; Butera et al. 2014; Chen et al. 2012, 2013; Coudray et al. 2017; Engelsen et al. 2009, 2010; Gupta et al. 2017; Madras Natarajan et al. 2019; Mulugeta et al. 2011; Sanchez et al. 2002), compared to pH 9 for leachate from limestone virgin aggregate (Gupta et al. 2017).

Much of the existing work compares RCA leachate pH from freshly-crushed RCA samples to leachate pH from carbonated RCA samples recovered from stockpiling facilities, recovered from field-deployed RCA base course, or are artificially-carbonated in the laboratory. Generally, the non-carbonated, freshly-crushed RCA samples exhibit leachate pH from 11.5 to 12.7 (Engelsen et al. 2009; Mulugeta et al. 2011), whereas the leachate pH of the carbonated samples ranged from 9.9 to 11.8 (Abbaspour et al. 2016; Engelsen et al. 2009; Madras Natarajan et al. 2019; Mulugeta et al. 2011; Sanchez et al. 2002). Batch reactor leaching investigations demonstrate that carbonation and the cement paste content of the RCA controls both pH and element leaching, such that leachate pH decreases with increased carbonation (Abbaspour et al. 2016; Bestgen et al. 2016; Engelsen et al. 2009; Mulugeta et al. 2011; Sanchez et al. 2002). Carbonation occurs with time, exposure to carbon dioxide, and intermittent wetting and drying cycles in RCA stockpiles, and carbonation conditions can be simulated in laboratory settings. Artificial carbonation in the laboratory using synthetic rainwater and intermittent wetting and drying cycles is faster than carbonation in a field stockpile because optimum conditions can be controlled and maintained (Abbaspour et al. 2016).

Limitations of batch reactor leaching investigations of leachate pH

Although batch reactor tests offer a straightforward, cost-effective basis for compliance testing, some characteristics of conventional batch reactor methodology tests do not reflect the leaching conditions in a percolation environment, such as RCA base course construction (Butera et al. 2015). Primarily, the use of an end-over-end tumbler to determine leachate pH likely causes particle abrasion and degradation of the protective surface coatings. Preservation of the protective carbonate surface layer is critical because particle surface chemistry, rather than the bulk mineral composition, governs leaching behavior and element release (Abbaspour et al. 2016; Bestgen et al. 2016; Engelsen et al. 2009; Ginder-Vogel et al. 2005; Loncnar et al. 2016; Mulugeta et al. 2011; Sanchez et al. 2002). Vigorous shaking and particle abrasion do not occur in the field applications of RCA base course, thus any carbonation that results from intermittent saturation and exposure to atmospheric carbon dioxide is assumed to remain intact.

Continuous saturation and contact times characteristic of conventional batch reactor methodology tests also do not reflect the percolation conditions relevant to RCA base course leaching (Delay et al. 2007). A primary function of the base course layer is to provide drainage for pavement systems, therefore the base course layer is designed to drain within hours of precipitation events (AASHTO 1993; FHWA 2017). Precipitation and base course drainage will cause the RCA base course layer to experience periods of intermittent wetting and drying, enhancing carbonation. Progressive carbonation with field-deployment of RCA is expected to reduce the leachate pH with time. Furthermore, after leachate drains from the RCA base course layer, there is no longer a source of hydroxide to the leachate to maintain a high pH, but exposure to carbon dioxide and soil acidity provide acid to neutralize the leachate pH (Gupta et al. 2017).

Column Leaching Tests

Methodology used in column leaching investigations of leachate pH

Column leaching tests offer a laboratory technique to measure RCA leachate pH that simulates percolation conditions relevant to RCA base course leaching. Column leaching tests are considered more environmentally relevant than batch reactors because column leaching experiments use representative liquid-to-solid ratios and preserve the carbonate surface coating by mitigating particle abrasion, (López

Meza et al. 2012). With lower liquid-to-solid ratios, column leaching tests equilibrate faster than batch reactors and, due to the short mass transfer distances, are often assumed to reach equilibrium conditions instantaneously (Grathwohl 2014).

Experimental design for column leaching tests generally follow the ASTM Standard Test Method for Leaching Solid Material in a Column Apparatus (ASTM 2014a). The conventional column leaching test utilizes an up-flow column, in which a peristaltic pump continuously moves leachate through a compacted RCA sample. Other column leaching tests may utilize a down-flow lysimeter column to allow the passive flow of leachate through the compacted RCA sample by gravitational force and hydraulic head. When comparing up-flow and down-flow column lysimeters, similar results are achieved with respect to cumulative element release from C&D waste materials (Butera et al. 2015). More important than flow direction of column lysimeter, then, is the saturation of the column apparatus: continuous saturation or intermittent wetting and drying cycles. Because intermittent wetting and drying cycles are crucial to carbonation of RCA, experiments designed to understand changes in RCA leachate chemistry over time are recommended to follow a schedule of intermittent wetting and drying periods (Gervais et al. 2004; Qin and Yang 2015).

Results of column leaching investigations of leachate pH

Existing column leaching investigations of RCA leachate pH also yield high pH measurements, pH 10 to 12.5 (Table 1.1) (Chen et al. 2012, 2013; Mulligan 2002; Qin and Yang 2015; Steffes et al. 1999). Much of the initial work to investigate RCA leachate was conducted by state departments of transportation concerned about the impeded vegetation growth, soil erosion, and crystalline deposits of tufa on the drain outlet wire mesh observed in field applications of RCA base course (Steffes et al. 1999). Both the Iowa Department of Transportation (IDOT) and Ohio Department of Transportation (ODOT) conducted a variation of column leaching test methodology called box tests. Box tests simulate a percolation environment using intermittently-saturated, down-flow lysimeter columns. ODOT box tests measured RCA leachate pH to be at least 10 (Mulligan 2002; ODOT 2002). IDOT employed intermittent wetting and drying cycles with box tests to measure RCA leachate pH over the course of a year, and found carbonation decreases the leachate pH from an initial pH 12.5 to pH 11.5 over the course of the year-long experiment (Steffes et al. 1999).

Other investigations of RCA leachate pH using column leaching tests illustrate the importance of intermittent wetting and drying and carbonation. When using continuously saturated columns, RCA leachate pH remained between pH 10.8 and 12.5 for 100 pore volumes of flow (PVF), with no observed pH decline (Chen et al. 2013). However, column leaching experiments that employ intermittent wetting and drying cycles result in carbonation of the RCA surfaces, and observe decreasing leachate pH over the course of the experiment (Qin and Yang 2015).

Limitations of column leaching investigations of leachate pH

Although column leaching tests use representative liquid-to-solid ratios and preserve the carbonate surface coating by mitigating particle abrasion, column leaching experiments that remain continuously saturated for the duration of the experiment fail to incorporate the intermittent wetting and drying cycles that carbonate RCA, similar to batch reactor leaching experiments (López Meza et al. 2012). The effectiveness of intermittent wetting and drying cycles in representing environmental conditions depends on the chosen length, duration, and relative humidity conditions of the cycles; experiments that employ intermittent wetting and drying cycles should consider precipitation intervals and intermittent relative humidity conditions representative to the climate of interest (Abbaspour et al. 2016; Galan et al. 2015).

Column leaching experiments are designed to simulate percolation conditions relevant to RCA base course leaching. The pH measured as the leachate leaves the column apparatus is analogous to the pH of leachate as it leaves the base course layer and drains to the subbase/subgrade pavement system or to edgedrains (Figure 1.3). After the leachate drains and is no longer in contact with RCA, there is no longer a source of strong base for the leachate. Instead, the leachate will interact with carbon dioxide and soil acidity from soil minerals, and the pH will decrease (Gupta et al. 2017). Therefore, the leachate pH measured in column leaching experiments represents the maximum pH of the leachate in the environment.

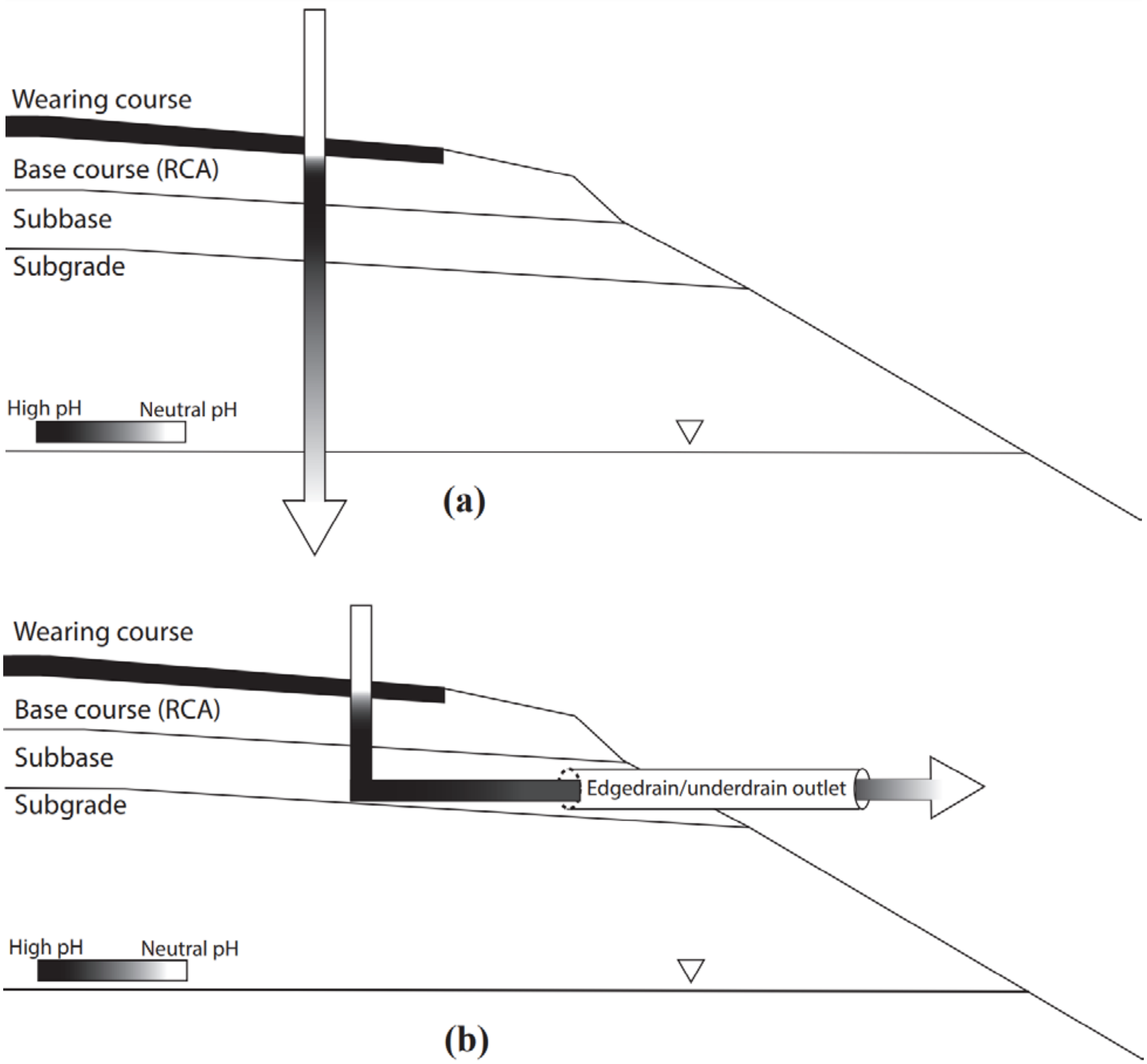

Figure 1.3. Additional processes that reduce leachate pH for different base course drainage designs (a) subbase drainage; (b) edgedrain/underdrain outlet.

Field-scale studies of leachate pH

Methodology used in field monitoring of leachate pH

Stockpiling RCA before construction is a common practice and offers a potential method to carbonate RCA before emplacement in base course construction applications; therefore, there is interest to characterize RCA carbonation in stockpiles, as well as the leachate generated from RCA stockpiles. Long-term field monitoring of RCA leachate from RCA stockpiles utilize an impermeable membrane and leachate collection system equipped with a sampling and data logging system (Sadecki et al. 1996). Similarly, long-term field monitoring of RCA leachate from pavement base course utilize full-depth pavement profiles sections (subbase, RCA base course, asphalt- or concrete-paved wearing course) with a leachate collection system installed beneath the RCA base course layer (Chen et al. 2012, 2013, Engelsen et al. 2006, 2012, 2017). HDPE impermeable membranes, sometimes called pan lysimeters, collect infiltrating leachate from the RCA base course and direct the flow to collection tanks (Chen et al. 2012, 2013, Engelsen et al. 2006, 2012, 2017). Engelsen et al. (2006, 2012, 2017) employ a data logger to monitor leachate pH immediately after leaving the base course layer, whereas Chen et al. (2012, 2013) sampled leachate from the collection tanks periodically.

Results of field monitoring investigations of leachate pH

Long-term field studies demonstrate that, after an initial phase of high pH, RCA leachate approaches neutral pH within one to two years of pavement base course construction or stockpiling (Table 1.1). Stockpiling RCA before construction is a common practice and offers a potential method to carbonate RCA before emplacement in base course construction applications. The Minnesota Department of Transportation (MnDOT) investigated and characterized leachate from RCA stockpiles by monitoring two outdoor RCA stockpiles for 13 months: one of coarse, gravel-sized RCA and the other of finer material (Sadecki et al. 1996). MnDOT found the coarse RCA to have pH between 8.5 and 10.9, median 9.8, while the leachate from the finer RCA was between 7.4 and 12.2, median 9.3 (Sadecki et al. 1996). Over the course of the experiment, the pH gradually decreased as the result of field carbonation (Sadecki et al. 1996).

Chen et al. (2012) and Chen et al. (2013) conducted a field investigation of RCA leachate in pavement base course applications at the Minnesota Road Research (MnROAD) facility in Minnesota. Leachate pH measured sampled from a collection tank seven months after construction was pH 6.5 and 8.0 (Chen et al. 2012, 2013). Field monitoring at the MnROAD site continued for eight years; before deconstruction, the final leachate pH measured as pH 7.2 to 7.4 (Madras Natarajan et al. 2019). In choosing to periodically sample the leachate from a collection tank, Chen et al. (2012, 2013) and Natarajan et al. (2018) left the leachate exposed to carbon dioxide without a source of hydroxide from the RCA layer for weeks or months. Although this study does not provide leachate pH as it leaves the base course layer, it provides evidence that leachate pH can decrease with time and exposure to carbon dioxide once it has drained from the RCA base course layer.

Engelsen et al. (2006) initialized a long-term field investigation and complementary laboratory analyses of RCA leachate in pavement base course on a section of highway near Oslo, Norway. Two full-depth pavement test sections were constructed using RCA or natural virgin aggregate, respectively, and another test section was constructed as uncovered (i.e., unpaved, exposed) RCA base course. Leachate from the asphalt-covered RCA section demonstrated a smaller decrease in pH, from 12.7 to 11.5, in the initial 14 months of the study compared to uncovered RCA, which decreased from 12.8 to 9.5. Leachate from the natural virgin aggregate road section remained between pH 8 and 9 throughout the monitoring period (Engelsen et al. 2006). Extended field investigations of RCA leachate chemistry monitor leachate pH, leachate volume, and leachate chemistry changes over time in field application. Engelsen et al. (2012) and Engelsen et al. (2017) continue to monitor inorganic constituent release and leachate pH at the same highway field site south of Oslo, Norway. Leachate from the uncovered RCA test section achieved a leachate pH below 10 within one year after construction, whereby the average pH of the asphalt-covered RCA section achieves a leachate pH below 10 within 2.5 years of field deployment. After more than ten years of field monitoring, the average pH of RCA leachate measured from asphalt-covered section is consistently between 7.3 and 8.7 (Engelsen et al. 2017).

Limitations of field monitoring investigations of leachate pH

Field experiments encompass many, if not all, of the variable parameters that are difficult to recreate in the laboratory. When measured with a data logger, leachate pH in the field is measured as leachate exits the RCA base course or stockpile (Engelsen et al. 2006, 2012, 2017; Sadecki et al. 1996). Leachate pH measured in field monitoring experiments with a data logger represents the maximum pH of the leachate in the environment because when the leachate drains from the RCA base course layer to the subbase/subgrade pavement system or through the edgedrain to the drainage ditch (Figure 1.3), it loses the source of strong base and is introduced to sources of acidity from carbon dioxide infiltration and soil minerals (Gupta et al. 2017). Conversely, when leachate is collected via a pan lysimeter and a collection tank, and is sampled later, the leachate has been exposed to carbon dioxide without a source of hydroxide from the RCA layer for weeks or months, resulting in a lower pH (Chen et al. 2012, 2013). Time-dependent leachate pH behavior after the leachate drains from the RCA base course layer has not been examined and is an opportunity for future research.

CONCLUSIONS AND RECOMMENDATIONS

The reviewed literature demonstrates the variability in results obtained from field and laboratory investigations of RCA leachate chemistry, even when comparing the same RCA material. Engelsen et al. (2006, 2009, 2010) and Natarajan et al. (2019) conducted simultaneous laboratory and field investigations of RCA leachate pH, and both studies measure significantly higher leachate pH in the laboratory than in field monitoring experiments (Table 1.1). The concurrent investigations by Engelsen et al. (2006, 2009, 2010) and Natarajan et al. (2019) illustrate a discrepancy between field and laboratory measurements of leachate pH, which indicates that the current laboratory methodology inadequately describes leachate conditions in the field. The many parameters that affect RCA in the field are difficult to encompass in laboratory methods and include pavement drainage design, frequency and duration of precipitation, degree of saturation, temperature, variation in subbase soil geology, and traffic loads, all of which vary in time and space. In designing laboratory investigations of RCA leachate chemistry and in providing guidance for the use of RCA as base course material, several factors must be considered: accurately modeling RCA carbonation, particle abrasion, contact time, and base course drainage.

Development of the protective carbonation layer on the surface of RCA is a result of intermittent wetting and drying cycles. This is a progressive process, such that carbonation depth increases with time and number of wetting and drying cycles of RCA. Utilization of an end-over-end tumbler to determine material pH causes particle abrasion and removal of the protective calcium carbonate layer, again exposing uncarbonated matrix with reactive portlandite. Such effects are illustrated in the simultaneous laboratory and field investigations presented by Engelsen et al. (2006, 2009, 2010) and Natarajan et al. (2019); these investigations employed batch reactor leaching experiments with end-over-end tumblers to characterize leachate pH in the laboratory. For experiments assessing leachate pH of stockpiled, aged, or otherwise carbonated RCA, particle abrasion should be limited to effectively represent the development and preservation of protective carbonate layers on the surface of RCA as a result of intermittent wetting and drying.

Depending on the drainage design of a base course layer, water may be in contact with the RCA for as little as one or two hours, or longer than several days (AASHTO 1993). Contact time is important in RCA leachate chemistry since longer contact times result in more mineral dissolution. Contact times employed in laboratory investigation of RCA leachate should be based on field drainage times, as this is the relevant amount of time for RCA and leachate phases to be in contact.

Different pavement drainage designs (e.g., subbase layers, subsurface drains, and daylighting) result in variations in leachate interactions with soil acidity, and atmospheric and soil vapor carbon dioxide. At the very least, the availability of carbon dioxide and soil acidity to neutralize high pH RCA leachate should be considered in the leachate fate and transport analysis. Gupta et al. (2017) investigate soil-RCA leachate interactions and found that soil acidity can neutralize small volumes of RCA leachate pH, such that 1 meter of subgrade soil has the capacity to neutralize RCA leachate for 20 years, disregarding the additional factors that reduce leachate pH (Figure 1.3) (Gupta et al. 2017). Additional subsurface processes that reduce leachate pH include carbonation, groundwater acidity from bicarbonate and other dissolved species, and soil vapor carbon dioxide (Gupta et al. 2017). Future research is required to evaluate the time-dependent leachate pH behavior after the leachate drains from the RCA base course layer.

The existing body of work regarding RCA leachate chemistry is extensive, and the contributing authors have developed foundational knowledge in understanding RCA solid phase chemistry, carbonation, pH-dependent trace element leaching, and pH of RCA in field applications. In order to make recommendations for implementation of RCA in pavement base course applications, future laboratory experiments should incorporate laboratory techniques relevant to field deployment of RCA, including contact times, carbon dioxide, and carbonation.

Table 1.1. Summary of existing field and laboratory determinations of RCA leachate pH.

Authors	Field pH	Batch pH	Column pH	Method	Sample Source
Abbaspour et al. 2016		10.4-11.3		ASTM D3987	Freshly-crushed
		9.9-10.3		ASTM D3987	Carbonated in laboratory
		11.2-11.4		USGS 5-D3	Stockpile
		10.1-10.6		USGS 5-D3	Carbonated in laboratory
Bestgen et al. 2016a		10.5-12.0		ASTM D5233	Freshly-crushed
Bestgen et al. 2016b		10.5-12.5		ASTM D4793	Freshly-crushed
Butera et al. 2014		11-13		CEN/TS 12457	Stockpile
Chen et al. 2012 Chen et al. 2013		11.3-12.1		SR002.1	RCA base course
	6.5-8.0			7 mos post-construction	RCA base course
			10.8-12.5	ASTM D4874	RCA base course
Coudray et al. 2017		11.0-12.5		CEN/TS 12457	Stockpile
Engelsen et al. 2006	9.5			1 yr post-construction (unpaved)	RCA base course
	11.5			1 yr post-construction (paved)	RCA base course
Engelsen et al. 2009, Engelsen et al. 2010		11.6-12.7		CEN/TS 14429	RCA base course
Engelsen et al. 2012	< 10			2.5 yrs post-construction (paved)	RCA base course
Engelsen et al. 2017	7.3 - 8.7			10 yrs post-construction (paved)	RCA base course
Gupta et al. 2017		10.5-12.3		EPA Method 1316	Stockpile
Mulligan et al. 2002			> 10	Box Test	NA
Madras Natarajan et al. 2019		11.2-11.4	7.2-7.4	SR002.1	RCA base course
Mulugeta et al. 2011		11.5-11.9		CEN/TS 14429	Stockpile
		12.4-12.5		CEN/TS 14429	Freshly-crushed
		10.3-11.8		CEN/TS 14429	Carbonated in laboratory
Sadecki et al. 1996	9.3-9.8			1 yr monitoring	Stockpile
Sanchez et al. 2002		11.0-11.8		SR002.2 (similar to SR002.1)	Carbonated in laboratory
Steffes et al. 1999			11.5-12.5	Box Test	Stockpile

2. INTEGRATING PHYSICOCHEMICAL PROPERTIES AND BATCH REACTOR LEACHING EXPERIMENTS TO PREDICT RECYCLED CONCRETE AGGREGATE LEACHATE CHEMISTRY

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Author contribution statement

Robin Ritchey and Gabrielle Campagnola assisted in the laboratory investigation of RCA leachate chemistry using batch reactor leaching experiments. Zoe Kanavas collected three RCA samples and conducted X-ray diffraction (XRD) on the samples. Bu Wang, Tuncer Edil, and Matthew Ginder-Vogel provided technical review of the manuscript. The authors would like to acknowledge the CEE/GLE 330 Soil Mechanics class of fall 2018 for their contributions in the physical property characterization of the RCA samples. .

ABSTRACT

Environmentally safe and responsible applications of recycled concrete aggregate (RCA) in pavement base course applications must consider the high alkalinity, high pH leachate and heavy metal leaching risks that are reported in literature. The purpose of the present study is to integrate the physical properties, solid phase composition, and RCA leachate chemistry to understand the physicochemical factors that affect RCA leachate pH and alkalinity. Ten RCA samples and one virgin limestone aggregate sample collected from various sites in Minnesota and Wisconsin were characterized using grain size distribution, Atterberg limits, specific gravity, absorption, X-ray diffraction, and thermogravimetric analysis. Laboratory investigations of RCA leachate pH and alkalinity were conducted using batch reactor leaching experiments constructed as open systems and continuously, gently agitated using a shaker plate to expose the system to atmospheric carbon dioxide and to mitigate particle abrasion. The physicochemical properties informed a geochemical model to describe the laboratory investigations of RCA leachate chemistry, described in Part II of this paper. Part II of this paper is a separate publication that is not included in this thesis.

INTRODUCTION

The use of recycled concrete aggregate (RCA) as a substitute for natural, virgin aggregate in pavement construction applications is well established and successful, particularly as granular or stabilized base course. RCA exhibits desirable mechanical proprieties for pavement base course applications including high resilient modulus, low compacted unit weight, and freeze-thaw resistance (Edil et al. 2012; "Recycling Concrete Pavements" 2009). Costs associated with the use of natural aggregates are largely incurred in transporting material from the quarry to the construction site. The use of RCA can be economically beneficial by eliminating costs related to mining and transporting materials (Robinson and Brown 2002). Similarly, the use of RCA exhibits life-cycle environmental benefits in conserving finite natural aggregate resources and reducing energy consumption, water usage, and carbon dioxide emissions associated with mining and transportation of aggregate material (Del Ponte et al. 2017).

RCA is a wise choice of engineering material in pavement construction, as it is recognized as a readily available, mechanically sufficient, construction and demolition waste product with life-cycle economic and environmental benefits. Environmentally safe and responsible applications of RCA must also consider the high alkalinity, high pH leachate as well as the heavy metal leaching risks (Abbaspour et al. 2016; Chen et al. 2013; Engelsen et al. 2006, 2009, 2010, 2012, 2017; Gomes et al. 2016). RCA leachate generation from stockpiles and road base is unavoidable, and therefore it is of great interest to understand the fate and transport of the leachate, and whether pre-treatment, prescribed aging, or remediation is necessary to limit the environmental impact of RCA.

Chapter I of this thesis presented a comprehensive literature review to critically evaluate field and laboratory investigations of RCA leachate chemistry (Sanger et al. 2019a). Long-term highway field studies of RCA leachate illustrate that, despite an initial elevated leachate pH ($pH > 10$), leachate pH approaches neutral pH approximately within a year of construction. Contrarily, laboratory investigations of RCA leachate chemistry measure persistently high leachate pH ($pH < 10$). It is likely that laboratory methods employed in the previous investigations may not be environmentally relevant for RCA application as pavement base course. While it is impractical and unnecessary to incorporate all field parameters into laboratory experiments, environmentally relevant laboratory experiments for RCA leachate should consider concrete-leachate contact times relevant to pavement drainage, the influence of atmospheric and soil vapor carbon dioxide, and the carbonation of RCA surfaces as a result of intermittent wetting and drying.

The purpose of the present study is to integrate the physical properties, solid phase composition, and chemistry of RCA leachate to understand the physicochemical factors that affect RCA leachate pH. By modifying existing laboratory techniques, the present study addresses the discrepancies between field and laboratory measurements of RCA 24-hour pH. The work presented in this study is the initial step to understand the generation, fate, and transport of RCA leachate, and whether pre-treatment, prescribed aging, or remediation is necessary to limit the environmental impact of RCA leachate. Understanding the physicochemical factors that control RCA leachate pH will inform the development of industry guidelines for prescribed aging or stockpiling criteria for the safe and responsible use of RCA as pavement base course.

RECYCLED CONCRETE AGGREGATE LEACHATE CHEMISTRY

Crushing concrete for use as RCA exposes fresh surfaces to atmospheric conditions, most notably carbon dioxide and rainwater infiltration. The fresh surfaces contain cement phases including ettringite (Afm), monosulfate (Aft), calcium hydroxide, also known as portlandite, ($Ca(OH)_2$), and calcium silicate hydrate (C-S-H), and may also contain trace amounts of unreacted cement phases (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Engelsen et al. 2009; Groves et al. 1990, 1991; Hidalgo et al. 2007; Hyun Nam et al. 2016; Matschei et al. 2007; Papadakis et al. 1989). The characteristic high pH and alkalinity (acid neutralization capacity) of RCA leachate is controlled by differences in solid phase composition of RCA, such that the dissolution of portlandite and calcium carbonate releases carbonate and hydroxide species, and the hydration of unreacted cement phases will produce additional portlandite for dissolution. Although AFm/Aft carbonation and dissolution may contribute leachate pH, dissolution of portlandite and the release of hydroxide ions are required to achieve the high pH observed in RCA leachate chemistry.

In completely hydrated cement, calcium hydroxide initially accounts for approximately 15%-25% of the hardened cement paste and is present in macrocrystalline, microcrystalline, slightly crystalized, or amorphous forms (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Hidalgo et al. 2007). Through the process of carbonation, cement hydrate phases in hardened cement pastes are converted to calcium carbonate ($CaCO_3$) in vaterite and calcite forms (Arandigoyen et al. 2006; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006; Groves et al. 1991; Papadakis et al. 1989, 1992; Šavija and Luković 2016; Silva et al. 2015). Carbonation begins at the surface and progresses inward, creating zonation within the monolith or aggregate: a carbonated outer zone, a partially-carbonated transition zone, and an uncarbonated inner matrix (Van Gerven et al. 2006; Groves et al. 1990). Carbonation requires diffusion of carbon dioxide into the water, where the reaction takes place in the aqueous phase. Carbonation rate and depth depends on carbon dioxide diffusion, relative humidity, and intermittent wetting and drying cycles (García-González et al. 2006; Van Gerven et al. 2006). Optimal conditions for conversion of calcium hydroxide to calcium carbonate occur at 20 degrees Celsius and 40-80% relative humidity (Abbaspour et al. 2016; Galan et al. 2015).

During the process of carbonation, calcium carbonate nucleates on the surface of portlandite crystals and forms masses around small amounts of calcium hydroxide (Galan et al. 2015; Groves et al. 1990, 1991). Carbonation limits the mass transport and dissolution of calcium hydroxide, therefore the relative amounts of unreacted calcium hydroxide and calcium carbonate control the alkalinity and pH of RCA leachate (Galan et al. 2015; Garrabrants et al. 2004; Gervais et al. 2004; Van Gerven et al. 2006). The influence of carbonation on RCA leachate chemistry makes it an important consideration in RCA leachate investigations and in RCA construction applications. With time, intermittent saturation, and exposure to atmospheric carbon dioxide, a calcium carbonate surface coating precipitates on the surface of RCA, called carbonation, which prevents dissolution of minerals contributing to high pH leachate (Papadakis et al. 1989). This is a progressive process, such that carbonation depth increases with intermittent wetting and drying cycles.

A critical evaluation of the existing investigations of RCA leachate pH, presented in Chapter I, determined that the abrasive, closed system conventional laboratory methodology is not representative of RCA field applications (Sanger et al. 2019a). In designing laboratory investigations of RCA leachate chemistry, particle abrasion should be limited to effectively represent the development and preservation of protective carbonate layers on the surface of RCA. Particle abrasion from vigorous agitation (e.g., and end-over-end tumbler) results in degradation of the protective carbonate surface coating and again exposes the uncarbonated inner matrix and reactive portlandite. (Ginder-Vogel et al. 2005; Loncnar et al. 2016). Additionally, the availability of atmospheric carbon should be considered throughout the duration of the leaching experiment and in considerations of the fate of the leachate after base course drainage. The availability of atmospheric and soil vapor carbon dioxide to neutralize high pH RCA leachate should be considered in the leachate fate and transport analysis (Chen et al. 2019).

MATERIALS AND METHODS

RCA samples

Ten RCA samples and one virgin limestone aggregate sample were collected from various sites in Minnesota and Wisconsin with the intent to collect a variety of RCA samples for characterization and analysis. Samples were obtained from active highway construction sites around Madison, WI (ML18, WS18, PR18), recycling facilities in Madison, WI (CT18, CT17) and stockpiles in West Allis and Oconomowoc, WI (WA17, OC17, respectively). Additionally, recovered RCA samples from the MnROAD test facility near Minneapolis, MN were used in this study (16C, 16D, 16P); the MnROAD samples were field-deployed for eight years as RCA base course, and significant work has been done to characterize the physical and chemical properties of this material (Chen et al. 2012; Madras Natarajan et al. 2019). RCA samples were given a four-character sample name, with two letters that correspond to the sample source and two numbers that correspond to the year the sample was obtained. The MnROAD samples (16C, 16D, 16P) have been previously studied and the previously-used sample names were upheld avoid confusion (Chen et al. 2013; Madras Natarajan et al. 2019). For the sake of comparison, virgin limestone aggregate was obtained from Yahara Materials Quarry in Madison, WI. Details regarding the RCA sources are provided in Table 2.1. The laboratory work presented in this paper was conducted in the summer and fall of 2018.

Table 2.1. Sample source information.

Sample Symbol	Sample Provider	Storage Conditions	Approximate Crush Date
16C	MnROAD	RCA base course	Summer 2007
16D	MnROAD	RCA base course	Summer 2007
16P	MnROAD	RCA base course	Summer 2007
CT18	Raymond P. Cattell, Inc.	Recycling facility	Summer 2018
PR18	Parisi Construction	Stockpile	Summer 2018
ML18	Corre, Inc.	Stockpile	Summer 2018
WS18	Corre, Inc.	Stockpile	Summer 2018
CT17	Raymond P. Cattell, Inc.	Recycling facility	Summer 2017
OC17	--	Stockpile	May 2016
WA17	--	Stockpile	May 2016
VA	Yahara Materials, Inc.	Quarry	Summer 2018

Methods

Physical property characterization

The physical properties of the samples were characterized using grain size distribution (GSD), Atterberg limits, specific gravity, and absorption (ASTM 2014b, 2015, 2017c). Table 2.2 summarizes the physical properties of the sample suite. Guidance for testing methodology and acceptance criteria were provided by the Construction and Materials Manual and the Standard Specifications of the Wisconsin Department of Transportation (WisDOT) because the most of base course samples examined were to be used for construction in the state of Wisconsin (WisDOT 2017, 2019a; b). Figure 2.1 illustrates the GSD curves of the sample suite with respect to the upper and lower gradation requirements for base course aggregate

(WisDOT 2019b). With the exception of samples CT17 and WA17, the base course samples fell within the desired gradation bounds. The base course materials all classify as well-graded gravels (GW) or poorly-graded graves (GP) by the Unified Soil Classification System (USCS) (Table 2.2, Table A.3). Atterberg limits of the base course samples were within reason of the desired liquid limit and plasticity margins, such that liquid limit is less than or equal to 25 and plasticity index less than or equal to 6 (Table 2.2, Table A.1) (WisDOT 2019a). Specific gravity and absorption values were consistent with other comprehensive investigations of the geotechnical properties of RCA (Table 2.2, Table A.2) (Edil et al. 2012).

Table 2.2. Physical properties of sample suite.

	CT18	**PR18**	**ML18**	**WS18**	**OC17**	**CT17**	**WA17**	**16C**	**16D**	**16P**	**VA**
Liquid limit	28.3	21.9	23.5	27.4	27.8	27.4	31.6	36.7	36.7	40.2	19.7
Plasticity index	6.1	NP	7.8	3.3	NP	NP	NP	2.2	NP	NP	4.2
Absorption (%)	6.9	6.5	5.7	5.3	6.2	3.8	5.2	8.0	6.3	7.6	3.6
Porosity (%)	15.3	18.8	12.9	12.1	14.1	15.0	12.3	16.9	15.7	17.2	9.3
Specific gravity	2.23	2.88	2.24	2.27	2.27	3.99	2.34	2.13	2.50	2.26	2.56
Fines content (%)	1.28	4.80	1.98	3.27	1.12	1.95	0.92	1.12	1.16	1.20	2.58
USCS classification	GW	GW	GW	GW	GW	GW	GP	GP	GP	GP	GW
Surface area (mm^2)	221.8	772.6	304.5	372.7	126.34	223.4	130.2	119.2	139.6	126.3	142.8

Additional physical properties of the RCA sample suite were characterized by the CEE/GLE 330 Soil Mechanics class in the fall of 2018. Student groups were provided with an RCA sample and VA sample and were instructed to evaluate the materials based on two mechanical properties relevant to base course material. Students chose to investigate the friction angle via direct shear (Table A.4), the maximum dry unit weight and optimum water content via Proctor compaction (Table A.5), the compression index and swelling index via one-dimensional compression (Table A.6), and the hydraulic conductivity using constant and falling head tests (Table A.7).

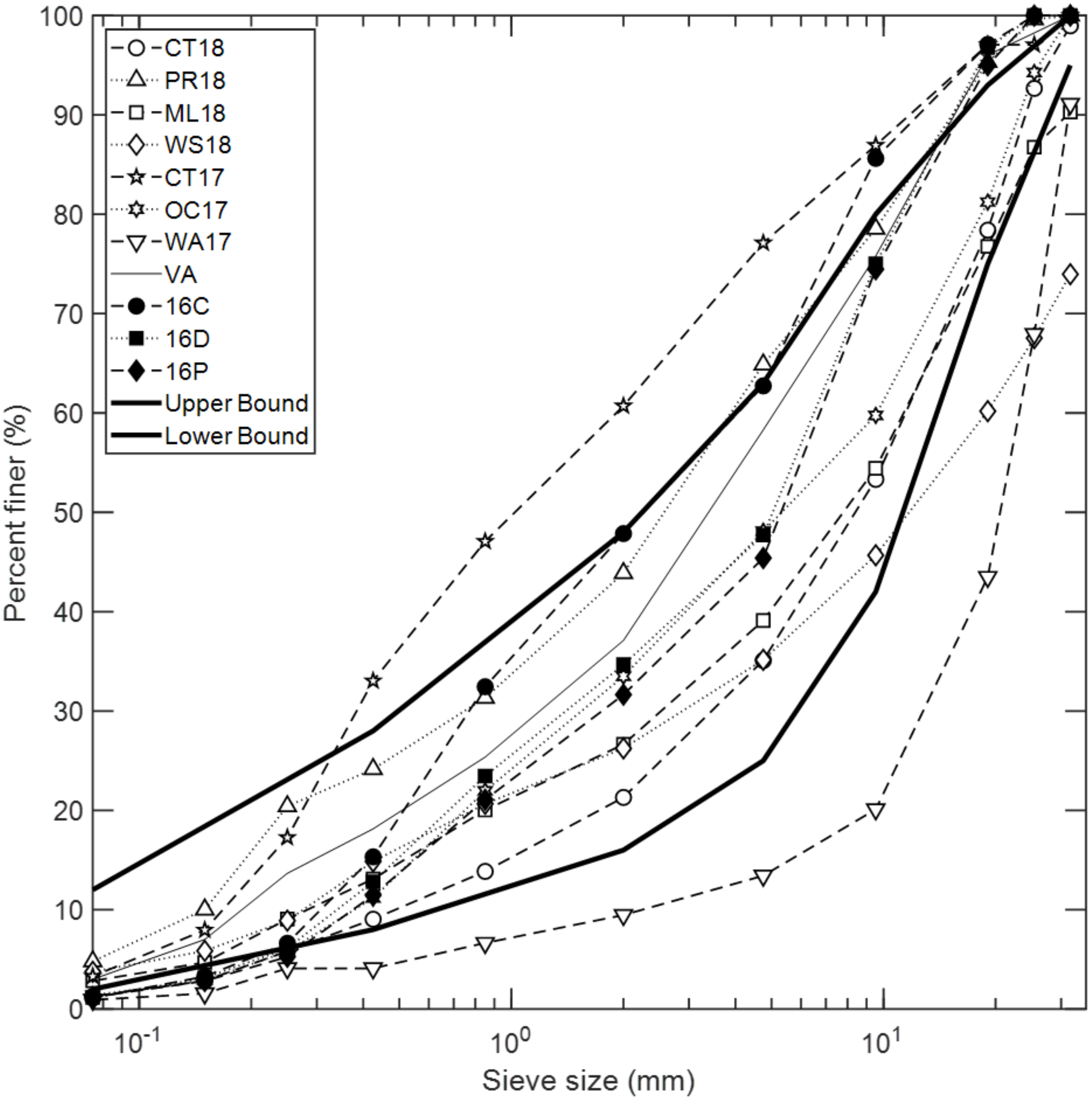

Figure 2.1. Grain size distribution for sample suite (Table A.8). Samples 16C, and 16D, and 16P from (Madras Natarajan et al. 2019).

Solid phase characterization

Solid phase composition was determined using X-ray diffraction (XRD) and thermogravimetric analysis (TGA) (Table A.9, Table A.10). Table 2.3 summarizes the mineralogical composition for each sample obtained from XRD analysis (ASTM 2018). TGA was used to compare carbonate mineral percentage (Table 2.4) (ASTM 2014c). XRD traces for each samples are provided as Figure A.2 through Figure A.13 in Appendix A. TGA traces for the tested samples are provided as Figure A.14through Figure A.20 in Appendix A.

Table 2.3. Mineral percentages from XRD (Figure A.1).

		CT18	**PR18**	**ML18**	**WS18**	**OC17**	**CT17**	**WA17**	**16C**	**16D**	**16P**	**VA**
Calcite	$CaCO_3$	11.4	3.6	14.6	13.1	5.9	5.6	16.5	16.1	14.0	21.6	1.6
Dolomite	$CaMgC_2O_6$	55.1	70.7	40.7	64.3	66.8	26.4	46.9	12.0	15.9	15.7	88.9
Anorthite	$CaSiAlO_4$	18.0	6.1	6.7	7.0	5.8	2.9	16.9	18.5	38.3	23.5	ND
Magnetite	Fe_3O_4	ND	0.8	0.4	0.5	0.2	0.7	0.3	0.7	ND	0.4	ND
Ilmenite	$FeTiO_3$	0.8	0.6	0.5	0.4	0.5	ND	0.2	0.9	1.0	1.2	ND
Afwillite	$Ca_3Si_2O_{10}H_6$	ND	1.2	2.7	2.1	ND	1.6	2.3	2.2	2.0	3.9	ND
Ettringite	$Ca_6Al_2(SO_4)_3 (OH)_2 6H_2O$	2.0	1.1	2.5	0.7	9.9	7.5	0.7	1.5	0.3	ND	ND
Quartz	SiO_2	12.8	15.9	31.8	12.0	10.9	55.2	16.2	48.0	28.5	33.7	9.5
Portlandite	$Ca(OH)_2$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 2.4. Carbonate mineral percentages from XRD and TGA (Table A.9, Table A.10).

		CT18	**PR18**	**ML18**	**WS18**	**OC17**	**CT17**	**WA17**	**16C**	**16D**	**16P**	**VA**
XRD	$(Ca,Mg)CO_3$	66.5	74.3	55.3	77.4	72.7	32.0	63.4	28.1	29.9	37.3	90.5
TGA	$(Ca,Mg)CO_3$	62.5	73.8	51.1	68.9	–	–	–	19.0	20.6	19.7	–

Batch reactor leaching experiments

Base course samples were homogenized by hand mixing and oven-dried overnight. Each base course sample was tested in triplicate using batch reactors prepared with an initial liquid to solid ratio of 10 mL/g: 50 g of base course in 500 mL Milli-Q Integral Ultrapure Water (MQ) (18.2 MΩ·cm). Leachate pH was measured using a Thermo Scientific Orion Combination pH Electrode. To determine alkalinity, a 6-mL leachate sample from the batch reactor was filtered using Millipore 0.2-μm Isopore Membrane Filters and diluted with 34 mL of MQ, then titrated in a Mettler Toledo Compact Titrator to pH 4.5 with 0.01 N H_2SO_4. To ensure homogeneity while minimizing abrasion between particles, the present study modified batch reactor leaching experiments to exclude the use of an end-over-end tumbler and instead use a shaker plate to continuously, gently shake the batch reactor for 24 hours. The construction of the modified batch reactors as open system, continuous-shaken beaker reactors enabled periodic pH and alkalinity throughout the duration of the 24-hour experiment.

Geochemical modelling

A geochemical model developed to describe time-dependent leachate chemistry for each RCA sample is summarized here and is described in greater detail a separate publication not included as a part of this thesis. Using Geochemist's Workbench (GWB), the physical properties and solid phase composition of each RCA sample informed a basic model, and the goal was to fit the observed in the batch reactor experiments (Table B.1, Figure B.1). In order for the basic model to simulate the time-dependent pH behavior observed in the laboratory experiments, trace amounts of portlandite had to be included in the mineral assemblage (0.07% to 0.26% portlandite) (Table B.2). This trace amount of portlandite was not detected in the XRD or TGA solid phase characterization experiments because it is below the detection limit of both methods. Similarly, for the basic model to simulate the pH decrease observed in the laboratory experiments, carbon dioxide availability (Table B.2). As such, portlandite content and the availability of carbon dioxide were model fitting parameters, and the controlling parameters of the observed RCA leachate chemistry.

RESULTS AND DISCUSSION

Modifying existing batch reactor methodology

A comprehensive literature review of existing investigations of RCA leachate chemistry, presented in Chapter I, revealed clear discrepancies between field and laboratory leachate pH measurements. Practices in conventional batch reactor leaching experiments, such as abrasive stirring methods and closed system batch reactors, may contribute to the observed field and laboratory inconsistencies (Sanger et al. 2019a). In the conventional batch reactor leaching experiments, the use of an end-over-end tumbler to determine 24-hour pH likely causes particle abrasion and removal of the protective calcium carbonate surface coating that would otherwise limit the leachate pH by reducing mineral dissolution. Vigorous shaking and particle abrasion are not relevant to RCA base course in the field, thus any surface coating that forms as a result of time, intermittent saturation, and exposure to atmospheric carbon dioxide is assumed to remain intact. Additionally, RCA leachate in field applications is exposed to carbon dioxide, and conventional batch reactor leaching experiments maintain a closed system for the duration of the leaching period.

The present study compared the modified, non-abrasive, open system batch reactor leaching procedure developed and described herein to a field investigation and conventional, abrasive, closed system batch reactor leaching experiment conducted on the same RCA material by Madras Natarajan et al (2019). In 2008, a field investigation of RCA base course was initiated at the Minnesota Road Research test facility (MnROAD) mainline westbound of I-94 between St. Cloud and Minneapolis, Minnesota (Chen et al. 2012, 2013). A full-depth pavement profile was constructed with asphalt pavement surface overlaying RCA base course aggregate to investigate the effects of RCA as base course on leachate pH and alkalinity (Madras Natarajan et al. 2019). Pan lysimeters were installed beneath the pavement profile to collect percolating leachate and direct it to a collection tank for storage and sampling. Additional site construction details are described by Chen et al. (2013). Leachate pH was sampled periodically throughout the duration of the field investigation; leachate pH measured between 7.2 and 7.4 in samples collected from April 2016 to July 2016, approximately eight years after construction (Table 2.5) (Madras Natarajan et al. 2019). The test sections were deconstructed in July 2016 and RCA samples were collected from the RCA base course layer below the passing lane, driving lane, and centerline of the MnROAD research facility: samples 16P, 16D, and 16C, respectively (Madras Natarajan et al. 2019).

During the eight-year field deployment, calcium carbonate content of the RCA material increased from 13.3% before construction to 18.6-20.3% after deconstruction, indicating carbonation of the RCA in the base course layer (Madras Natarajan et al. 2019). Madras Natarajan et al. (2019) conducted batch reactor leaching experiments were for base course samples 16C, 16D, and 16P using the conventional procedure, such that RCA samples were tested in batch reactors with an initial liquid to solid ratio of 10 mL/g and were agitated throughout the duration of the experiment in an end-over-end tumbler at 30 rpm (±2 rpm) (Kosson et al. 2002; Madras Natarajan et al. 2019). Leachate pH was measured using a Thermo Scientific Orion Combination pH Electrode. More information regarding MnROAD RCA characterization and conventional batch reactor leaching experiments can be found in Madras Natarajan et al (2018).

Despite near-neutral field pH measurements and significant surface carbonation during field deployment, Madras Natarajan et al. (2019) measured 24-hour leachate pH of the recovered RCA material to be greater than pH 11 (Table 2.5). In the present study, non-abrasive, open system batch reactor leaching experiments conducted on the same MnROAD RCA base course material (samples 16C, 16D, and 16P) yielded 24-hour pH measurements 1.3 to 1.6 pH lower than the 24-hour pH determined by Madras Natarajan et al. (2018) for the same material (Table 2.5). By using a shaker plate instead of an end-over-end tumbler, particle abrasion is limited, and the protective calcium carbonate surface coating is preserved, thereby limiting the dissolution of cement hydrate phases (portlandite) that cause high leachate pH. Reducing particle abrasion and including exposure to atmospheric carbon dioxide, more effectively simulates the field conditions of RCA base course applications.

Table 2.5. Comparison of field-measured leachate pH, conventional batch reactor leaching experiments, and batch reactor leaching experiments of the MnROAD RCA samples (Chen et al. 2012, 2013; Madras Natarajan et al. 2019).

	16 P	16 D	16 C
24-hour pH – Conventional Method [a]	11.3	11.4	11.1
24-hour pH – Modified Method	9.9	10.1	9.5
Field leachate pH [a]		7.2 - 7.4	

[a] (Madras Natarajan et al. 2019)

Based on the comparison of batch reactor procedure using the MnROAD RCA, time-dependent leachate pH and alkalinity of the sample suite were monitored using the non-abrasive, open system batch reactor leaching experiments. Using open system batch reactors allowed for continuous monitoring of leachate pH for 48 hours (24 hours for the MnROAD samples) (Figure 2.2). Similarly, alkalinity was sampled periodically throughout the 48-hour experiment (Figure 2.3).

The time-dependent leachate pH behavior illustrates the expected pattern based on RCA leachate chemistry for each of RCA sample: a steep initial increase in leachate pH over the first few hours of the experiment, followed by a gradual, linear decrease in leachate pH (Figure 2.2). The steep initial increase in leachate pH and alkalinity is the result of mineral dissolution from the RCA surfaces, namely calcium carbonate ($CaCO_3$) and portlandite/calcium hydroxide ($Ca(OH)_2$). Portlandite was not detected in XRD or TGA analyses for any of the base course samples; however, geochemical modelling of the observed RCA physical properties and solid phase chemistry indicate that a trace percentage of portlandite was present in each of the samples, undetectable at the resolution of XRD and TGA analyses (Table B.2, Figure B.1). The decline in leachate pH is the result of carbon dioxide dissolution into the leachate which acts like a titrating acid, neutralizing the leachate pH.

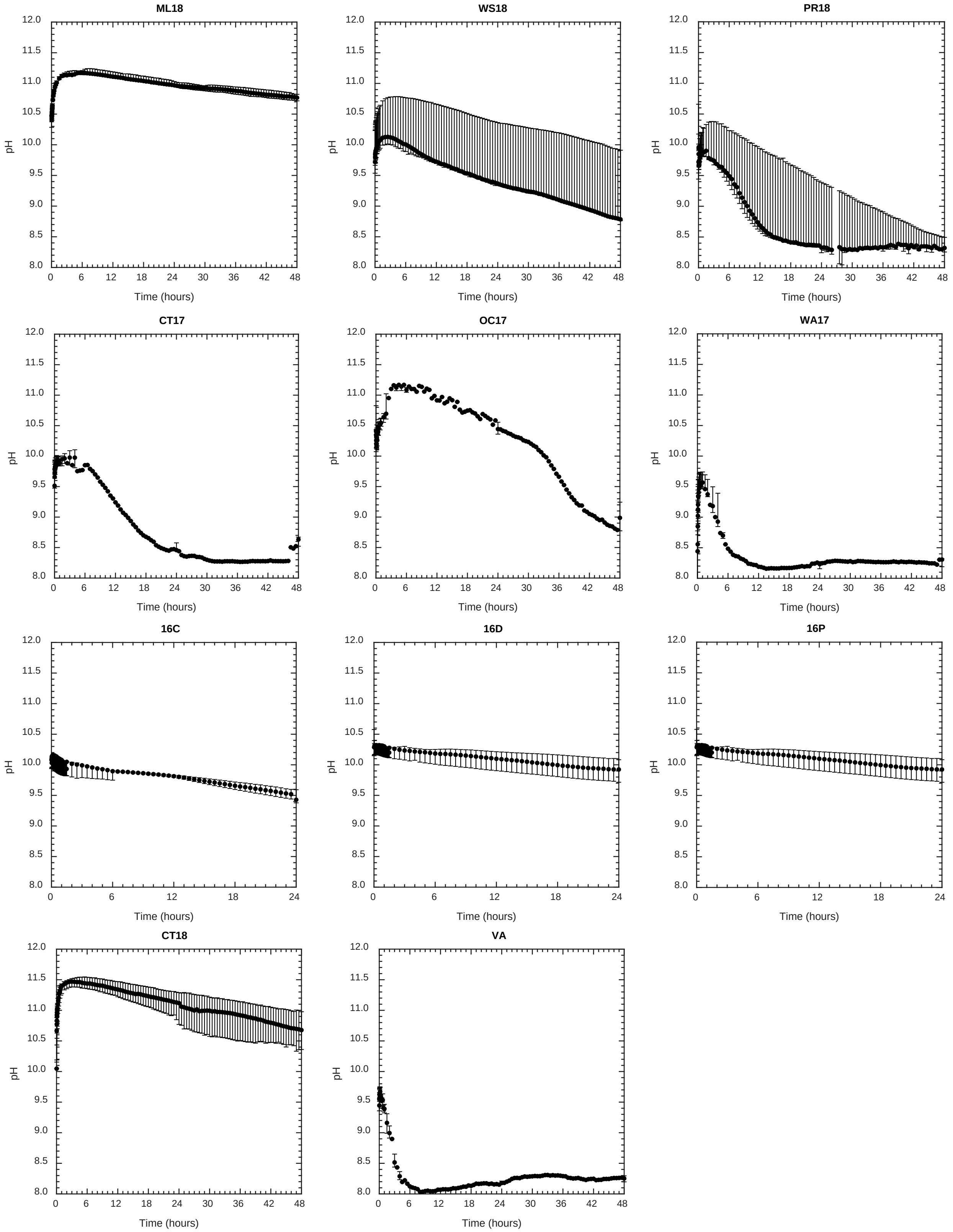

Figure 2.2. pH of sample suite from continuous monitoring batch reactor leaching experiments. Results reported as median of three trials with range bars to illustrate the minimum and maximum measured leachate pH.

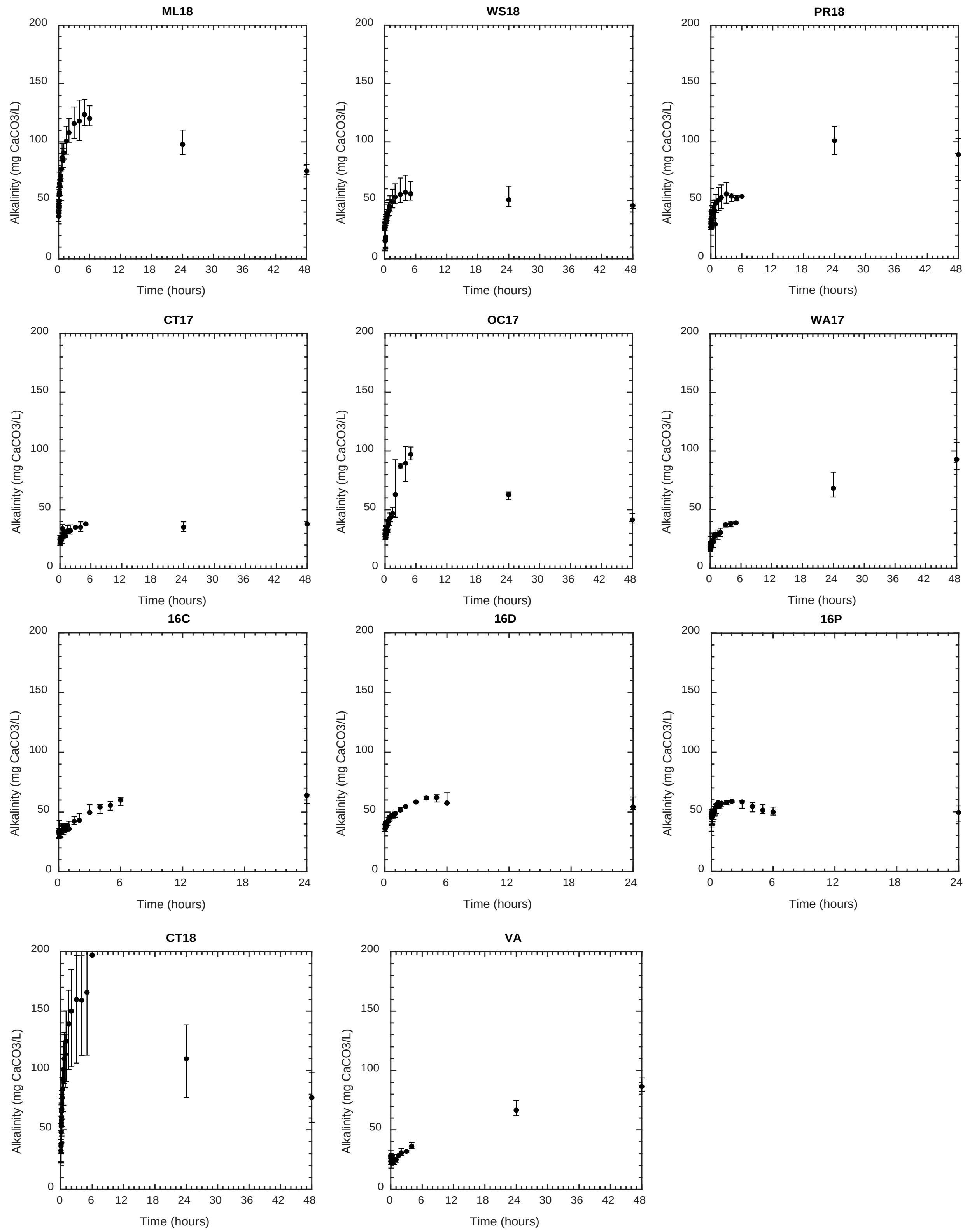

Figure 2.3. Alkalinity of sample suite from continuous monitoring batch reactor leaching experiments. Results reported as median of three trials with range bars to illustrate the minimum and maximum measured leachate pH.

The peak pH of the virgin aggregate (VA) sample is 9.75 and the peak is observed at 8 minutes of contact time. The alkalinity of the VA sample ranges from 17.9 to 93.8 mg $CaCO_3$/L. The peak pH of the RCA samples ranges from 9.74, comparable to the peak pH of VA, to very high pH, pH 11.55 (Figure 2.2, Table 2.6). Alkalinity of the RCA samples range from 6.6 to 202.9 mg $CaCO_3$/L (Figure 2.3). Variability within the RCA samples shows moderate correlation with sample crush date and storage conditions. For example, CT17 and WA17, both crushed in 2017, produce 24-hour leachate pH near that of VA (Table 2.6). Similarly, sample CT18 and sample ML18, both crushed in summer 2018, produce the highest 24-hour leachate pH (Table 2.6). Samples with higher peak pH tend to exhibit peak pH at later times, e.g., CT18, ML18, and OC17 (Table 2.6). The MnROAD samples (16C, 16D, and 16P), which have experienced nearly identical crushing and storage conditions, exhibit very similar time-dependent pH and alkalinity behavior (Figure 2.2, Figure 2.3). Field applications of RCA may not be afforded the opportunity to know monolith age, crush date, or RCA storage conditions. For this reason, the details of RCA sourcing were not emphasized in the present study, but rather emphasis was given to the measurable physicochemical properties that affect RCA leachate chemistry.

Table 2.6. Leachate pH and alkalinity of RCA leachate for sample suite, as determined by modified batch reactor leaching experiments. Reported as median of three trials.

	24 hours		**48 hours**		**Peak**	
	pH	**Alkalinity (mg $CaCO_3$/L)**	**pH**	**Alkalinity (mg $CaCO_3$/L)**	**pH**	**Time of peak pH (minutes)**
CT18	11.12	113.86	10.68	76.83	11.55	330
PR18	8.33	101.02	8.32	97.74	10.38	150
ML18	10.97	94.54	10.77	72.57	11.24	450
WS18	9.37	44.71	8.78	46.64	10.79	270
OC17	10.44	62.06	8.99	38.96	11.17	240
CT17	8.46	64.81	8.63	73.14	10.10	240
WA17	8.23	62.00	8.31	87.50	9.74	60
16C	9.40	60.39	-	-	10.16	10
16D	10.19	49.36	-	-	10.53	30
16P	9.92	54.26	-	-	10.58	9
VA	8.17	63.24	8.26	83.41	9.75	8

Physicochemical properties affecting RCA leachate pH and alkalinity

Using the physical properties, solid phase chemistry, time-dependent leachate chemistry, and a geochemical model of ten RCA samples, the physicochemical properties that control RCA leachate chemistry can be described by two parameters: portlandite content from RCA surfaces and the availability of carbon dioxide. These two parameters counteract one another, such that portlandite content controls the peak pH risk associated with RCA leachate, and the availability of carbon dioxide controls the neutralization of leachate pH.

Portlandite content

Geochemical modelling of the time-dependent RCA pH demonstrates the magnitude of the peak pH is controlled by the portlandite content readily-available for dissolution from the RCA surface (Figure B.1). 24-hour pH is also directly related to portlandite content of the RCA, although with a weaker correlation, corroborating the usefulness of 24-hour pH in evaluating the peak pH risk associated with the RCA material. Portlandite content cannot be determined by XRD nor TGA, because the portlandite in RCA is in trace amounts, below the detection limit of both methods. Using a non-abrasive, open system batch reactor as described in the present study, one can estimate the portlandite content of any given RCA sample using the measured peak pH or 24-hour pH and the corresponding relationship (Figure B.2).

The magnitude of the peak pH is controlled by the portlandite content readily-available for dissolution from the RCA surface. Portlandite content cannot be determined by XRD nor TGA because the portlandite in RCA is in trace amounts, below the detection limit of both methods.

Surface passivation of RCA material can be achieved using carbonation of portlandite to calcium carbonate and understanding the role of solid phase surface chemistry has implications on RCA storage before construction. Carbonation can be achieved by “naturally” by stockpiling RCA before construction, a common practice that exposes RCA to intermittent wetting and drying cycles, or RCA can be carbonated "artificially" in a laboratory setting using synthetic rainwater (Abbaspour et al. 2016).

Availability of atmospheric carbon dioxide

Geochemical modelling of the time-dependent RCA pH demonstrates that the decrease in leachate pH of the RCA samples following peak pH is directly related to availability of atmospheric carbon dioxide (Figure B.3). Within the 48-hour experiment, samples PR18, CT17, and WA17, as well as the VA sample, reach a minimum pH value (less than pH 8.5) and maintain that final pH for the remainder of the experiment (Figure 2.2). This is the neutralized pH and represents the minimum, equilibrium pH value that the leachate will achieve while in the batch reactor with the RCA material. These materials equilibrated with atmospheric carbon dioxide during the 48-hour experiment. The leachate pH of the other RCA samples will continue to decrease linearly until an equilibrium pH is reached (pH < 8.5), as demonstrated in Chapter III. The availability of carbon dioxide and/or soil acidity, the parameter that controls RCA leachate pH neutralization, can be controlled by base course drainage design.

24-hour pH characterization

In order to advise the safe use of RCA in field applications, it is valuable to define a physicochemical parameter that is easy to determine in the field that quantifies the leachate pH risk associated with any given RCA material. Peak pH provides the maximum pH risk associated with the given material, but the time at which peak pH is observed is not consistent (Table 2.6). It is impractical to suggest that field engineers monitor the time-dependent leachate pH behavior of the RCA material in order to find the peak pH. Instead, the present study illustrates that the leachate pH measured at 24 hours is directly related to peak pH and the pH at 48 hours (Figure 2.4). 24-hour pH is also directly related to the portlandite content of a given RCA sample, and it is directly related the peak pH of RCA leachate from the sample (Figure B.2). Therefore, 24-hour pH is a practical proxy for characterizing maximum leachate pH associated with a given RCA material.

Field engineers can evaluate the RCA material onsite using to determine if the RCA is ready for use or if additional carbonation (artificial or natural) is required. Field engineers can prepare a beaker with RCA and water at a liquid-to-solid ratio of 10, leave the beaker open to the ambient air overnight, measure the leachate pH after 24 hours using a pH-indicator or probe, and use the 24-hour pH to evaluate the peak risk associated with the RCA material.

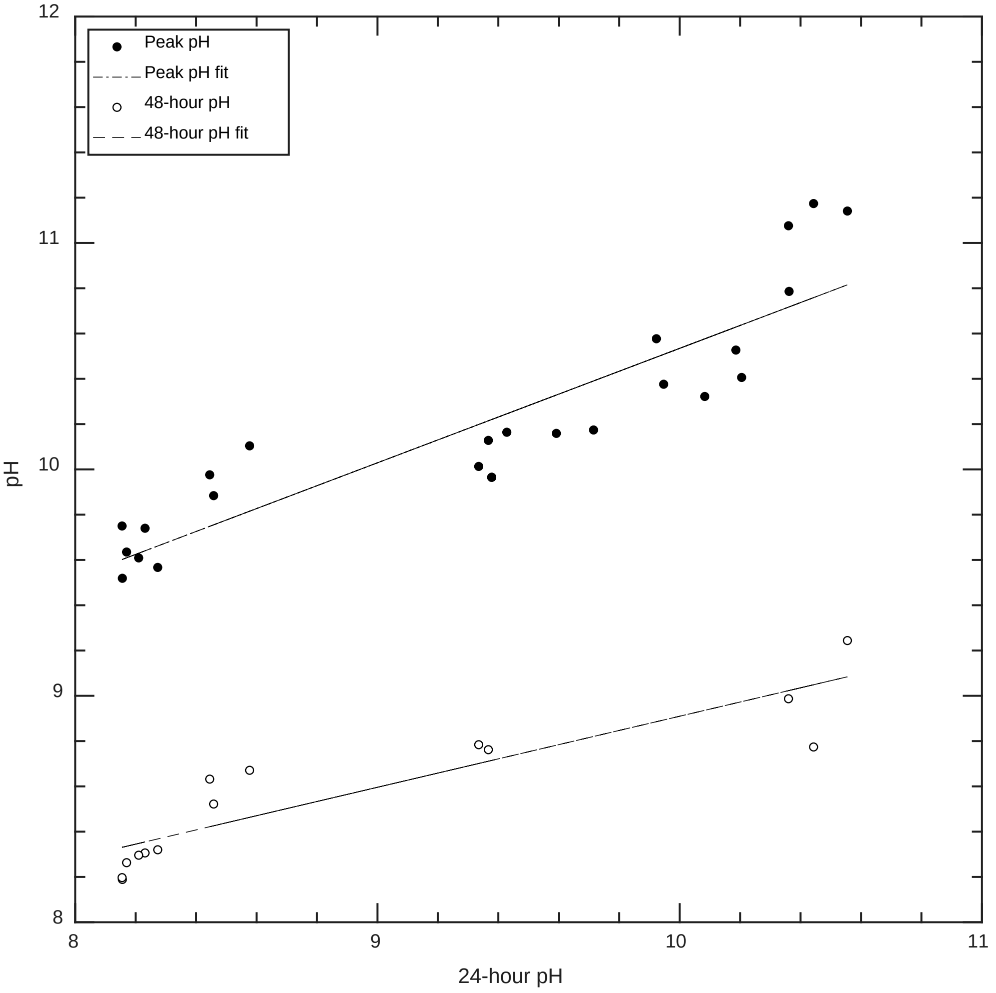

Figure 2.4. Relationship between 24-hour leachate pH, peak pH, and 48-hour pH. Peak pH fit: y = 0.5055x + 5.4795 (R^2 = 0.8158); 48-hour pH fit: y = 0.4057x + 5.0031 (R^2 = 0.7091).

CONCLUSIONS

The work presented in this study is the initial step to understand the generation, fate and transport of RCA leachate, and whether pre-treatment, prescribed aging, or remediation is necessary to limit the environmental impact of RCA leachate. Particle abrasion and equilibration with atmospheric carbon dioxide are important factors in simulating field conditions of RCA leachate pH that must be considered in experimental design for RCA leachate chemistry. RCA leachate pH behavior is controlled by two regimes: portlandite dissolution from RCA surface and availability of carbon dioxide. Understanding these two regimes has implications for stockpiling or artificial carbonation of RCA and base course drainage design, respectively. Portlandite content, the physicochemical parameter that controls peak pH from RCA leachate, can be controlled by carbonating RCA prior to construction, thereby reducing RCA leachate peak pH risk. Similarly, the availability of carbon dioxide and/or soil acidity, the parameter that controls RCA leachate pH neutralization, can be controlled by base course drainage design.

Stockpiling RCA before construction is a common practice and offers a potential method to carbonate RCA before emplacement in base course applications. In order to advise the safe use of RCA in field applications, it is useful to define a physicochemical parameter that is easy to determine in the field that quantifies the leachate pH risk associated with any given RCA material. 24-hour pH is a practical proxy to be used to evaluate the peak risk associated with the RCA material. Understanding the pivotal role of carbon dioxide in managing RCA leachate pH has implications of pavement drainage design. Different pavement drainage designs (i.e., subbase layers, subsurface drains, and daylighting) are different in their interactions with soil acidity, and atmospheric and soil vapor carbon dioxide. The availability of carbon dioxide and soil acidity to neutralize high pH RCA leachate should be considered in the leachate fate and transport analysis (Gupta et al. 2017). Additional work is required to monitor leachate chemistry after phase separation to simulate drainage from the base course layer into the subgrade and hydrogeologic system.

3. THE INFLUENCE OF CONTACT TIME AND BASE COURSE DRAINAGE ON RECYCLED CONCRETE AGGREGATE LEACHATE CHEMISTRY

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Author contribution statement

Robin Ritchey and Gabrielle Campagnola assisted in the laboratory investigation of RCA leachate chemistry using batch reactor leaching experiments. Bu Wang, Tuncer Edil, and Matthew Ginder-Vogel provided technical review of the manuscript.

ABSTRACT

The widespread use recycled concrete aggregate (RCA) as a substitute for virgin aggregate in pavement base course applications is limited due to the high pH, high alkalinity RCA leachate. Different pavement drainage designs are different in their drainage quality and interactions with the environment. As leachate drains from the base course layer, the liquid phase is no longer in contact with the RCA, and the source of hydroxide is removed. Instead, acid for neutralizing the RCA leachate pH is now is available as atmospheric carbon dioxide and/or neutralization by soil acidity. The existing literature regarding RCA leachate chemistry does not consider the time-dependent behavior of RCA leachate chemistry relevant to pavement drainage design. The purpose of the present study is to evaluate the influence of contact time on RCA leachate as well as the potential to neutralize pH after RCA leachate drains from the base course layer. This study demonstrates that increasing contact times does not increase risk associated with RCA leachate pH, as pH decreases to pH 7.7 and pH 8.5 within two to six hours after phase separation, regardless of sample or contact time. RCA base course applications, the 24-hour pH can be used to characterize the RCA material, and can be established as a design parameter that considers the environmental sensitivity, subgrade soil, and drainage design system of the site to establish a threshold, or maximum, 24-hour pH for the RCA to be used construction.

INTRODUCTION

Recycled concrete aggregate (RCA) is a readily-available construction and demolition waste product that has demonstrated mechanical and economic viability as substitute for virgin aggregate in pavement base course applications (Sanger et al. 2019a). Implementation of RCA as pavement base course is limited, in part, by uncertainty regarding the high pH, high alkalinity leachate generated by water in contact with RCA in stockpiles and/or pavement systems. Sanger et al. (2019a) review the existing literature regarding RCA leachate chemistry and conclude that future laboratory experiments should incorporate laboratory techniques relevant to field deployment of RCA. In order to make recommendations for implementation of RCA in base course applications, laboratory investigations should consider concrete-leachate contact times relevant to pavement drainage design and the persistence of high pH, high alkalinity leachate in the environment, after the RCA leachate drains from the base course layer.

Base course systems are designed to provide structural support, stiffness, and drainage to the pavement using a well-graded gravel of durable, freely draining material (FHWA 2017). RCA used in base course applications is often recycled from the existing roadway or from a nearby demolition site, where the concrete monolith is crushed to form a well-graded RCA gravel. Portland cement concrete is a mixture of coarse and fine aggregate in Portland cement paste; Portland cement paste consists of calcium carbonate ($CaCO_3$), ettringite (Afm), monosulfate (Aft), calcium hydroxide, also known as portlandite ($Ca(OH)_2$), calcium-silicate hydrate (C-S-H) ($1.7CaO \cdot SiO_2 \cdot xH_2O$), and trace amounts of unreacted cement (e.g., $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$) (Bache, H. H., Idorn, G. M., Nepper-Christensen, P., and Nielsen 1966; Brunauer and Copeland 1964; Engelsen et al. 2009; Groves et al. 1990, 1991; Hidalgo et al. 2007; Hyun Nam et al. 2016; Matschei et al. 2007; Papadakis et al. 1989; Richardson and Groves 1993).

Crushing concrete to create RCA exposes fresh, reactive surface area of the concrete. Saturation of the fresh surfaces facilitates portlandite and calcium carbonate dissolution from the RCA surface, releasing carbonate and hydroxide species, and possibly hydration of unreacted cement to form additional portlandite (Ritchey et al. 2019; Sanger et al. 2019b; Taylor 1997). Therefore, the characteristic high pH, high alkalinity RCA leachate is controlled by differences in solid phase composition of RCA (Ritchey et al. 2019; Sanger et al. 2019b). Depending on the drainage quality of the base course, water may be in contact with the RCA for as little as one or two hours, or more than a week (Table 3.1) (AASHTO 1993). Contact time is important in RCA leachate chemistry because longer contact times result in more mineral dissolution. Contact times employed in laboratory investigations of RCA leachate chemistry should be based on field drainage times, as this is the relevant amount of time for RCA and leachate phases to be in contact.

Different pavement drainage designs (i.e., subbase layers, subsurface drains, and daylighting) vary in their interactions with the environment. In field construction of RCA base course, leachate drains from the base course layer into a drainage ditch via edge drains or into the subsurface via hydraulic flow. Once leachate drains from the base course layer, the liquid phase is no longer in contact with the RCA, and the source of high pH bases is removed. Upon draining from RCA base course layer, the leachate no longer has a source of hydroxide base, but is not exposed to soil acidity and/or the atmospheric and soil vapor carbon dioxide.

The purpose of this study is to evaluate the influence of contact time on RCA leachate as well as the potential to neutralize pH after RCA leachate drains from the base course layer. The present study uses exposure times that correspond with the AASHTO classifications of pavement drainage quality to evaluate the time-dependent behavior of RCA leachate pH and alkalinity (Table 3.1) (AASHTO 1993). Additionally, phase separation experiments are used to simulate base course drainage in the laboratory. Ultimately, understanding the time-dependent behavior of leachate chemistry and the persistence of high pH leachate in the environment will inform the safe and responsible use of RCA as base course.

Table 3.1. AASHTO classifications of pavement drainage quality for use in pavement drainage design. Adapted from (AASHTO 1993).

Quality of Drainage	Time-to-drain (50%)
Excellent	2 hours
Good	1 day
Fair	1 week
Poor	1 month
Very Poor	Does not Drain

MATERIAL AND METHODS

Materials

Four RCA samples were obtained from various sites in Minnesota and Wisconsin, including active highway construction sites around Madison, WI (ML18, WS18, PR18), recycling facilities in Madison, WI (CT18). The samples are named with a four-character code such that the initial two letters symbolize the sample source and the two numbers indicate the year the RCA was crushed. Additional information regarding sample source, crushing, and storage history are not available. Therefore, it is more useful to focus on the measurable physicochemical and leachate chemistry properties of RCA.

The physical properties and solid phase chemistry of the sample suite were previously evaluated by the authors as part of a study of the physicochemical properties that control RCA leachate chemistry (Table 3.2) (Sanger et al. 2019b). The samples used in the present study are all well-graded gravels (GW) with less than 5% fines content (Table 3.2) (Sanger et al. 2019b). Dolomite, calcite, and quartz comprise the bulk of the RCA mineralogical composition, as determined by X-ray diffraction (Table 3.2) (Sanger et al. 2019b). Geochemical modelling was used to determine portlandite content of the samples, which at percent mass between 0.08 to 0.26%, is well below the detection limits of X-ray diffraction (Table 3.2) (Ritchey et al. 2019; Sanger et al. 2019b). For more information regarding the physicochemical properties of the sample suite, refer to Sanger et al. (2019b). For more information regarding the geochemical model of RCA leachate chemistry, refer to Ritchey et al. (2019).

Table 3.2. Summary of physicochemical properties of RCA samples ((Sanger et al. 2019c).

	CT18	PR18	ML18	WS18
Specific gravity	2.23	2.88	2.24	2.27
Fines content (%)	1.28	4.8	1.98	3.27
USCS classification	GW	GW	GW	GW
Calcite (%)[1]	11.4	3.6	14.6	13.1
Dolomite (%)[1]	55.1	70.7	40.7	64.3
Quartz (%)[1]	12.8	15.9	31.8	12
Portlandite (%)[2]	0.26	0.08	0.18	0.09

[1] XRD

[2] Geochemical model

Methods

Contact time experiments

Base course samples were homogenized by hand mixing, oven-dried overnight, and tested in batch reactors prepared with a liquid to solid ratio of 10 mL/g: 50 g of base course in 500 mL Milli-Q Integral Ultrapure Water (MQ) (18.2 MΩ·cm) that had equilibrated with atmospheric carbon dioxide. Batch reactors were constructed as open-system beaker reactors to allow infiltration of atmospheric carbon dioxide for the duration of the experiment. Batch reactors were not shaken or agitated but were gently stirred once daily for the duration of the experiment. Leachate pH was measured using a Thermo Scientific Orion Combination pH Electrode. To determine alkalinity, a 6-mL leachate sample from the batch reactor was filtered using Millipore 0.2-μm Isopore Membrane Filters and diluted with 34 mL of MQ, then titrated in a Mettler Toledo Compact Titrator to pH 4.5 with 0.01 N H_2SO_4. Triplicate batch reactors were prepared for each sample, and for each of the Excellent, Good, Fair, and Poor drainage scenarios presented in Table 3.1 (i.e., 12 batch reactors prepared per sample) (AASHTO 1993). Leachate pH and alkalinity were monitored periodically according to each contact time.

Phase separation experiments

The batch reactors previously described were deconstructed at the completion of time-dependent batch reactor leaching experiments, such that 250 mL of the remaining leachate was poured into a new beaker to separate the liquid-phase leachate from the solid-phase RCA. These new batch reactors were again constructed as open-system beaker reactors and were continuously shaken on a shaker plate. The time-dependent pH and alkalinity of the stand-alone liquid leachate was monitored for 24 hours following phase separation. Leachate pH was measured using a Thermo Scientific Orion Combination pH Electrode. To determine alkalinity, a 6-mL leachate sample from the batch reactor was filtered using Millipore 0.2-µm Isopore Membrane Filters and diluted with 34 mL of MQ, then titrated in a Mettler Toledo Compact Titrator to pH 4.5 with 0.01 N H_2SO_4.

RESULTS AND DISCUSSION

The influence of contact time on RCA leachate chemistry

Within the first minute of the experiments for all four samples, the pH increases from 5.5, the pH of the MQ equilibrated with atmospheric carbon dioxide, to greater than 9.5 (Figure 3.1). In the 2-hour contact time experiments, pH continues to increase gradually for the duration of the experiment for all four RCA samples (Figure 3.1). In the 1-day contact time experiments, pH increases rapidly in the initial hours of the experiments to a peak pH and maintains a similar pH for the duration of the experiment for all four RCA samples (Figure 3.1). In the 1-week and 1-month contact time experiments, pH reaches a maximum value in the initial 24 hours of the experiment for each RCA sample (Figure 3.1). Following the peak pH in the 1-week and 1-month contact time experiments, pH decreases linearly with time for the duration of the experiment (Figure 3.1). The pH behavior with time follow similar trends for each sample (Figure 3.3). Sample CT18 consistently exhibits the highest pH, followed by ML18, PR18, and WS18 (Figure 3.3). Like pH, alkalinity of RCA leachate increases from less than 5 mg $CaCO_3$/L, the alkalinity of the MQ equilibrated with atmospheric carbon dioxide, to greater than 20 mg $CaCO_3$/L within the first minute of the experiments for all four samples (Figure 3.3). Alkalinity continues to increase gradually during the initial hours of the experiment for all four RCA samples (Figure 3.3). Unlike pH, alkalinity does not exhibit as clear of a decrease with time as pH, but rather it maintains a relatively constant value, irrespective of contact time.

The low observed calcium ion concentrations meant that the precision of the measurement was often a limiting factor in observed calcium ion behavior. There is potential for interference from other ions, so the calcium ion concentrations will not be used in further calculations, but rather can be used to illustrate dissolution behavior. Initial saturation of RCA dissolves calcium hydroxide, calcium portlandite, and other soluble species on the RCA surfaces. As saturation is approached, calcium ion concentration stabilizes (Figure 3.4).

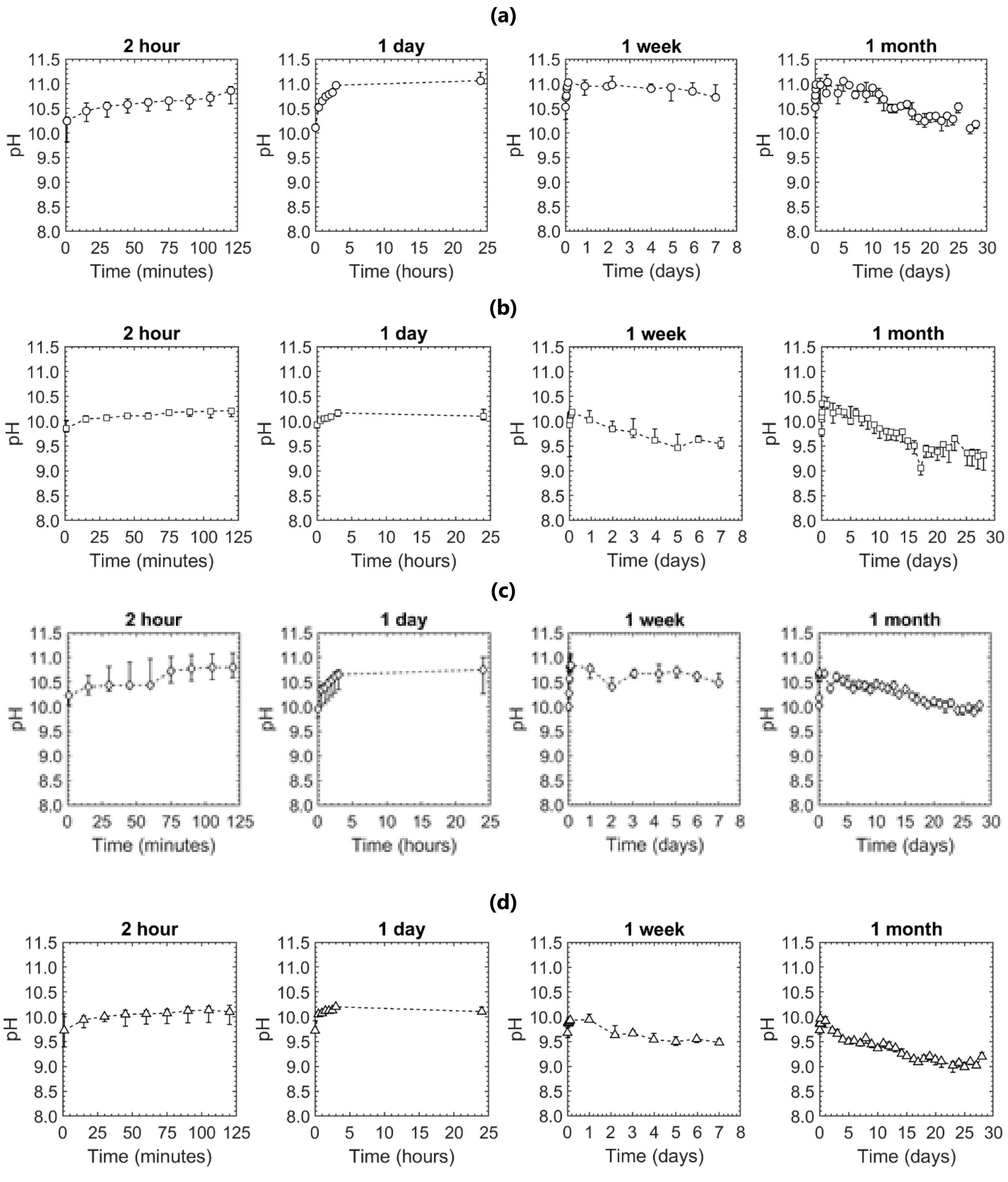

Figure 3.1. pH vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured pH values.

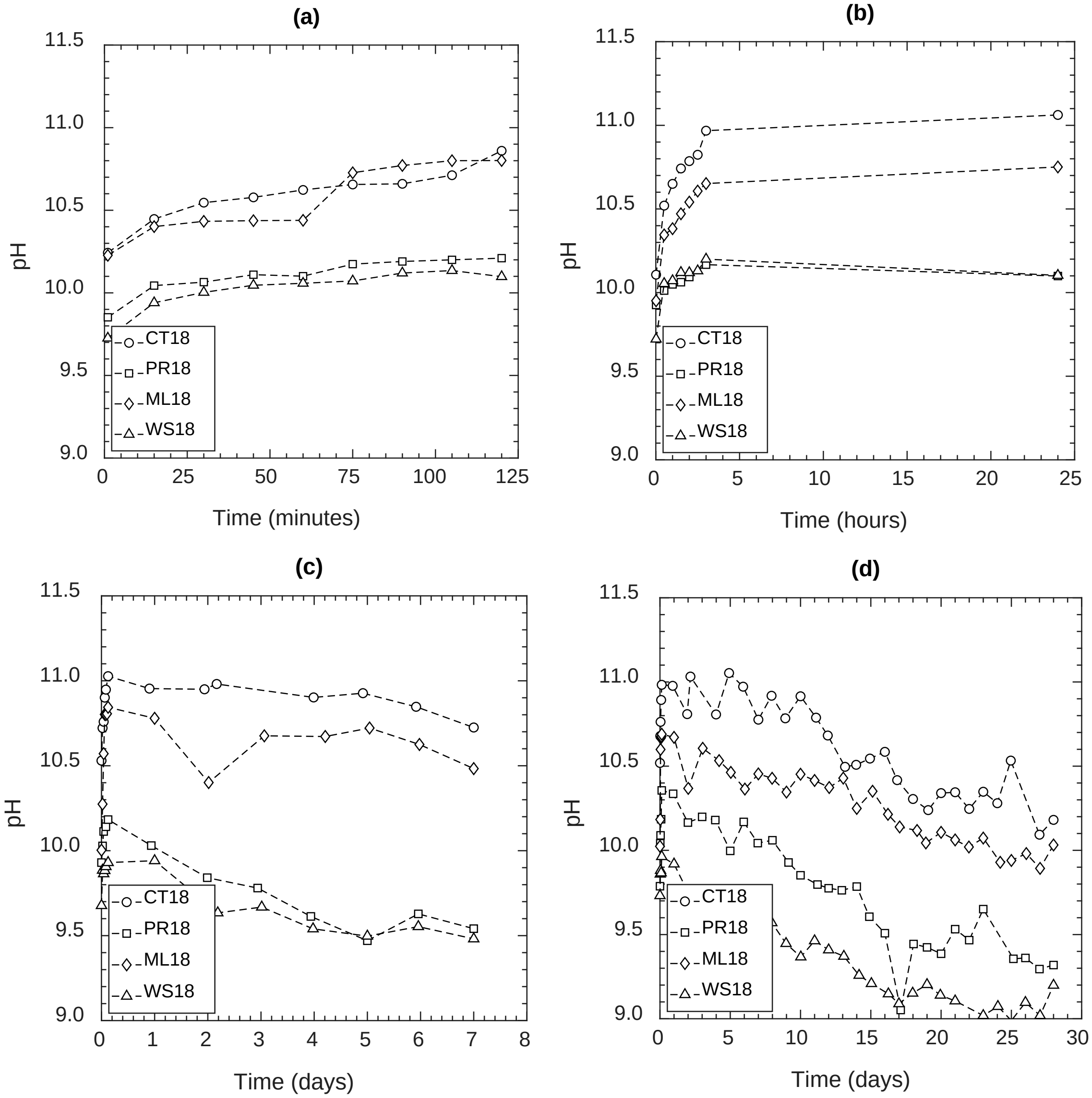

Figure 3.2. pH vs. contact time for all samples, subplots for each time (a) 2 hour (b) 1 day (c) 1 week (d) 1 month. Results reported as the median of three trials.

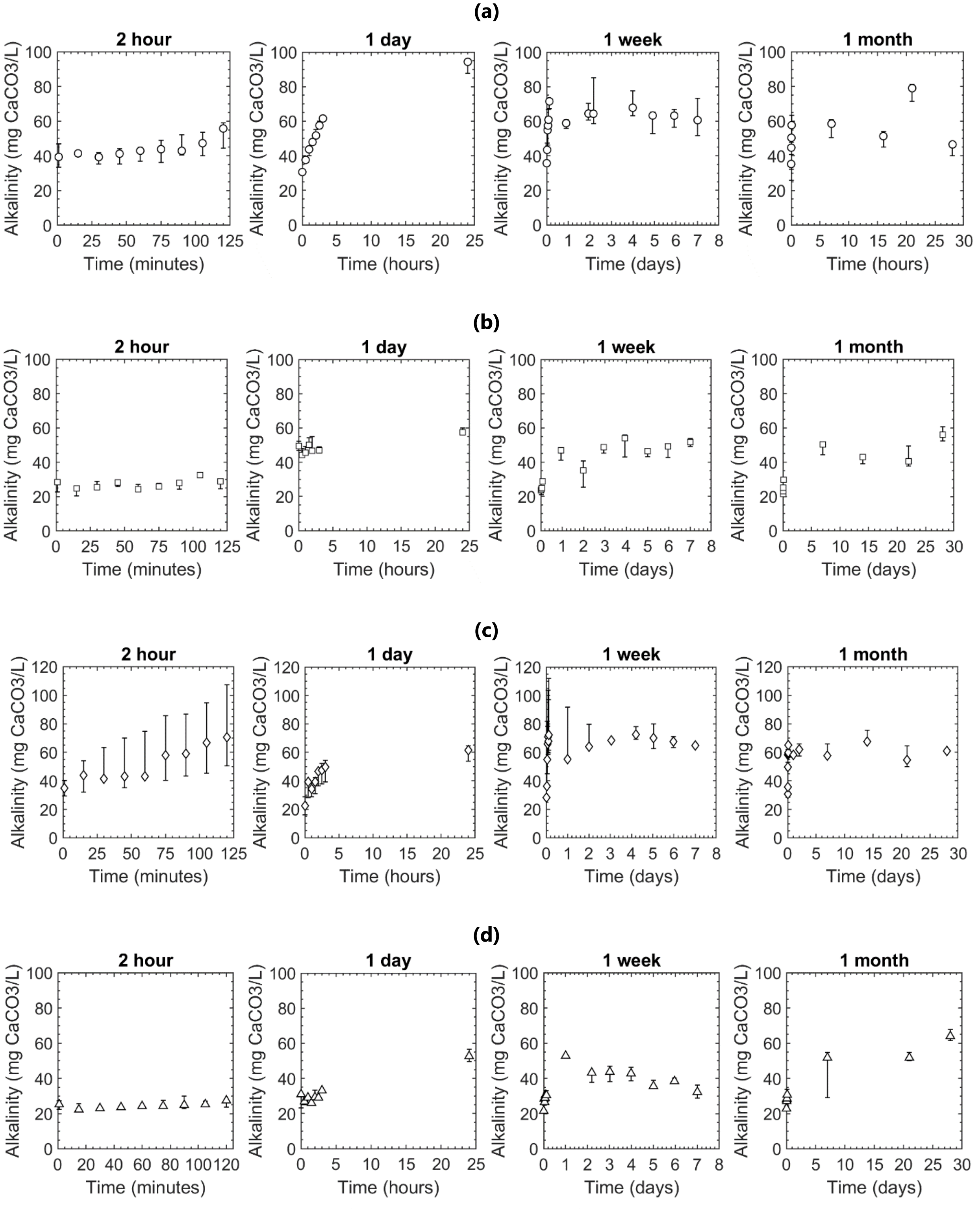

Figure 3.3. Alkalinity vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured alkalinity values.

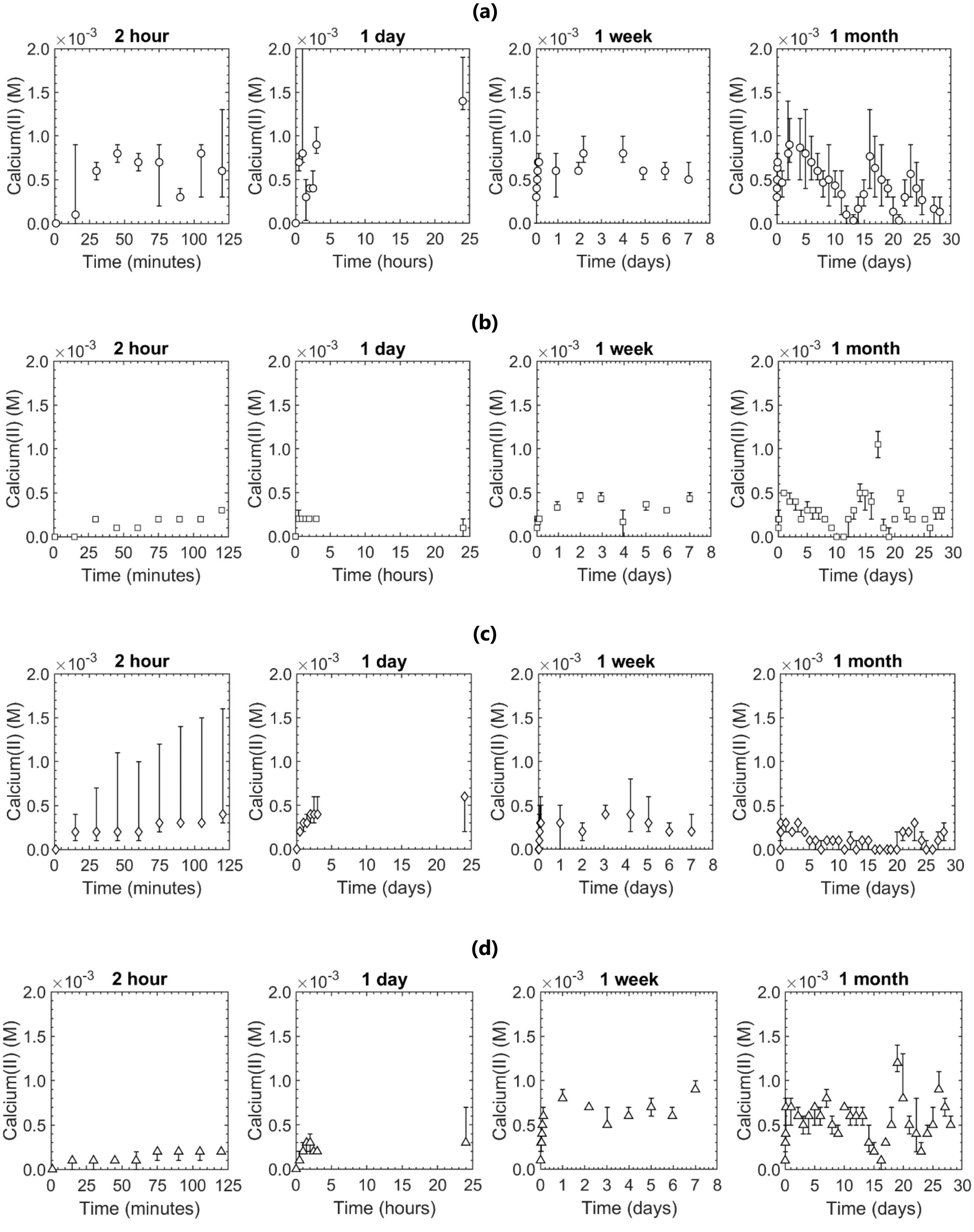

Figure 3.4. Calcium ion concentration vs. contact time for all samples, subplots for each time (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials with error bars to illustrate the minimum and maximum measured calcium ion concentration.

The time-dependent RCA leachate chemistry observed in the contact time experiments fits the expected behavior as modelled previously by the authors, such that RCA leachate chemistry can be described simply by two regimes: (1) mineral dissolution and (2) carbon dioxide infiltration (Ritchey et al. 2019; Sanger et al. 2019b). The first regime, mineral dissolution, governs the peak pH of the leachate, and is directly related to the portlandite content of the RCA sample (Ritchey et al. 2019; Sanger et al. 2019b). The peak pH observed at each contact time corresponds to the portlandite content of each sample, such that the increasing order of portlandite content and peak pH is WS18, PR18, ML18, CT18 (Figure 3.2, Table 3.2) (Ritchey et al. 2019; Sanger et al. 2019b). The second regime, carbon dioxide infiltration, governs the linear decrease in leachate pH following peak pH, and is directly related to availability of atmospheric carbon dioxide (Ritchey et al. 2019; Sanger et al. 2019b). The alkalinity of each sample results from the hydroxide and carbonate species released into solution upon saturation of RCA. The addition of these bases increases the pH and alkalinity of the leachate simultaneously, but the dissolution of carbon dioxide in the system, which forms $H_2CO_3^*$ to react quickly with hydroxide and produces bicarbonate and/or carbonate, depending on the system pH. The consumption of hydroxide reduces the leachate pH, but the products are still weak bases, such that bicarbonate and carbonate still contribute to the alkalinity of the system. Therefore, it fits expected leachate behavior that alkalinity would remain the same as leachate pH decreases (Figure 3.1, Figure 3.3).

The RCA sample suite used in this work was previously investigated by the authors in order to isolate the physicochemical properties that control RCA leachate chemistry using batch reactors and geochemical modelling (Ritchey et al. 2019; Sanger et al. 2019b). In the previous experiments, RCA batch reactors were continuously agitated on a shaker plate for the duration of the 48-hour experiments (Sanger et al. 2019b). In conducting the present experiments, shaker plates were not used; instead, batch reactors were left stationary for leachate chemistry measurement and were gently agitated by hand once daily. The overlap in time-dependent pH measurements for the same samples was thereby inadvertently distinguished the leachate pH of continuously-shaken and unshaken RCA samples (Figure 3.5). The unshaken samples exhibit lower peak pH values and have slower pH declines than the previously-monitored, continuously-shaken experiments, indicating that even gentle agitation using a shaker plate increases dissolution and increases carbon dioxide infiltration into the system (Figure 3.5). It is inferred that the unshaken samples provide a better representation of field conditions with respect to the time-dependent leaching behavior in an RCA base course layer.

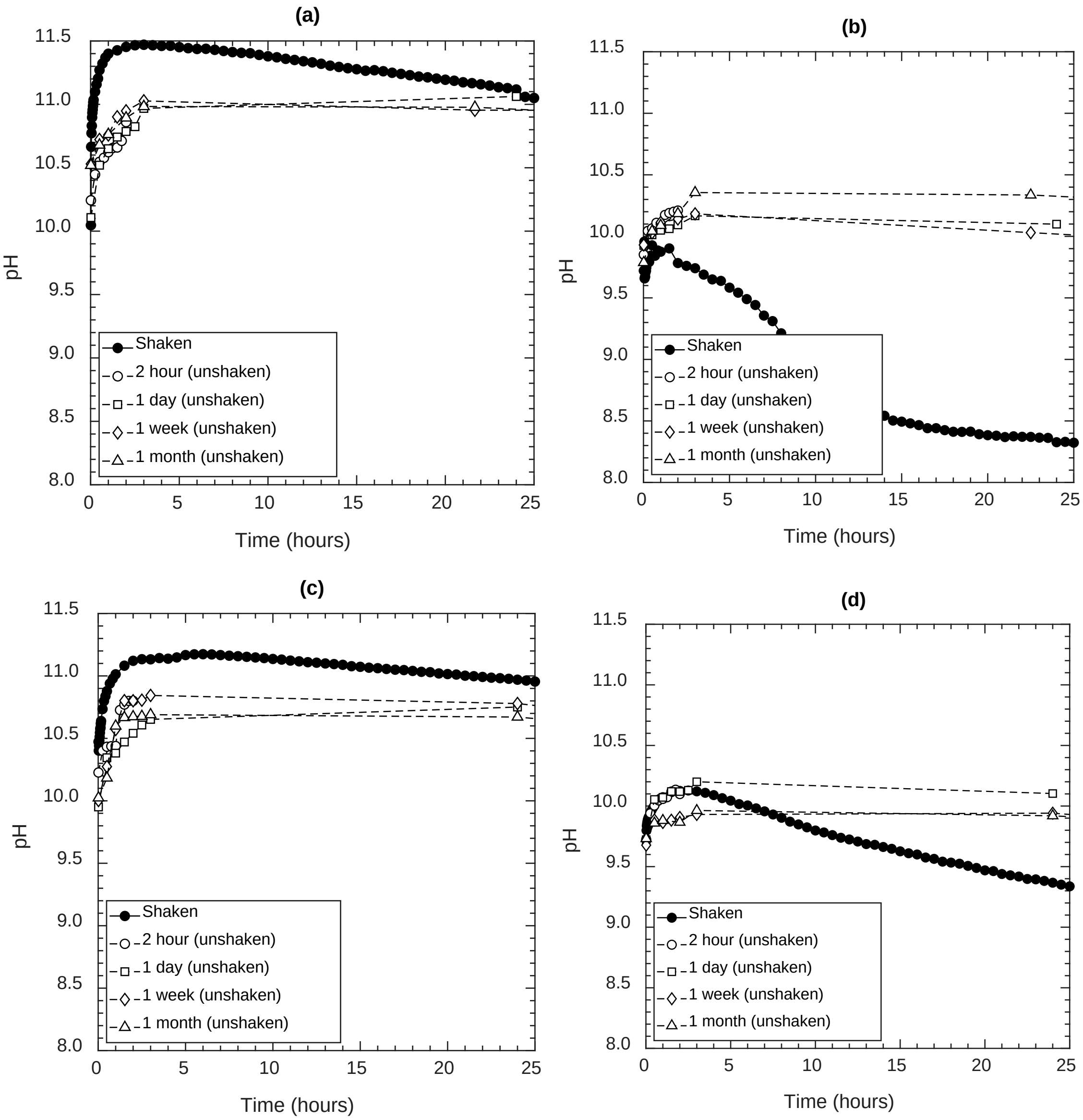

Figure 3.5. Effects of stirring (pH vs. contact time for all samples) (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as the median of three trials.

The influence of RCA-leachate phase separation on leachate chemistry

After each of the contact time experiments, the liquid leachate phase was separated from the solid RCA phase to simulate drainage from the RCA base course layer. Leachate pH and alkalinity were monitored in the 24 hours that followed phase separation in order to evaluate the time-dependent leachate chemistry following drainage from the RCA base course layer. Regardless of contact time prior to phase separation, pH decreases rapidly for each sample following phase separation (Figure 3.6). Leachate pH continues to decrease linearly until a consistent, near-neutral value between pH 7.7 and pH 8.5 is reached, within two to three hours following phase separation (Table 3.3, Figure 3.6). Regardless of sample or contact time, pH decreases at a similar rate following phase separation; as the slopes of pH decline are nearly all parallel (Figure 3.8). The near-neutral, equilibrium pH is not correlated to the contact time nor any physicochemical parameters of the RCA sample. Unlike pH, alkalinity does not change drastically in the 24 hours following RCA-leachate phase separation; instead, alkalinity remains consistent with that measured before phase separation, and alkalinity is maintained for the duration of the 24-hour monitoring (Figure 3.8).

Upon phase separation, i.e. base course drainage, the leachate is no longer in contact with RCA, there is no longer a source of hydroxide from portlandite, and the mineral dissolution regime no longer influences the leachate chemistry. Instead, only the second regime remains to equilibrate the RCA leachate. Regardless of sample properties or contact time, the rate of carbon dioxide infiltration and pH decrease is the same for all RCA samples (Figure 3.8). Leachate pH for each sample equilibrates to a near-neutral value between pH 7.7 and pH 8.5 within two to three hours after phase separation (Figure 3.8, Table 3.2). pH 7.7 to 8.5 is consistent with leachate pH measured from limestone virgin aggregate, and therefore RCA leachate pH is not a risk given sufficient acid to neutralize leachate pH (Sanger et al. 2019b).

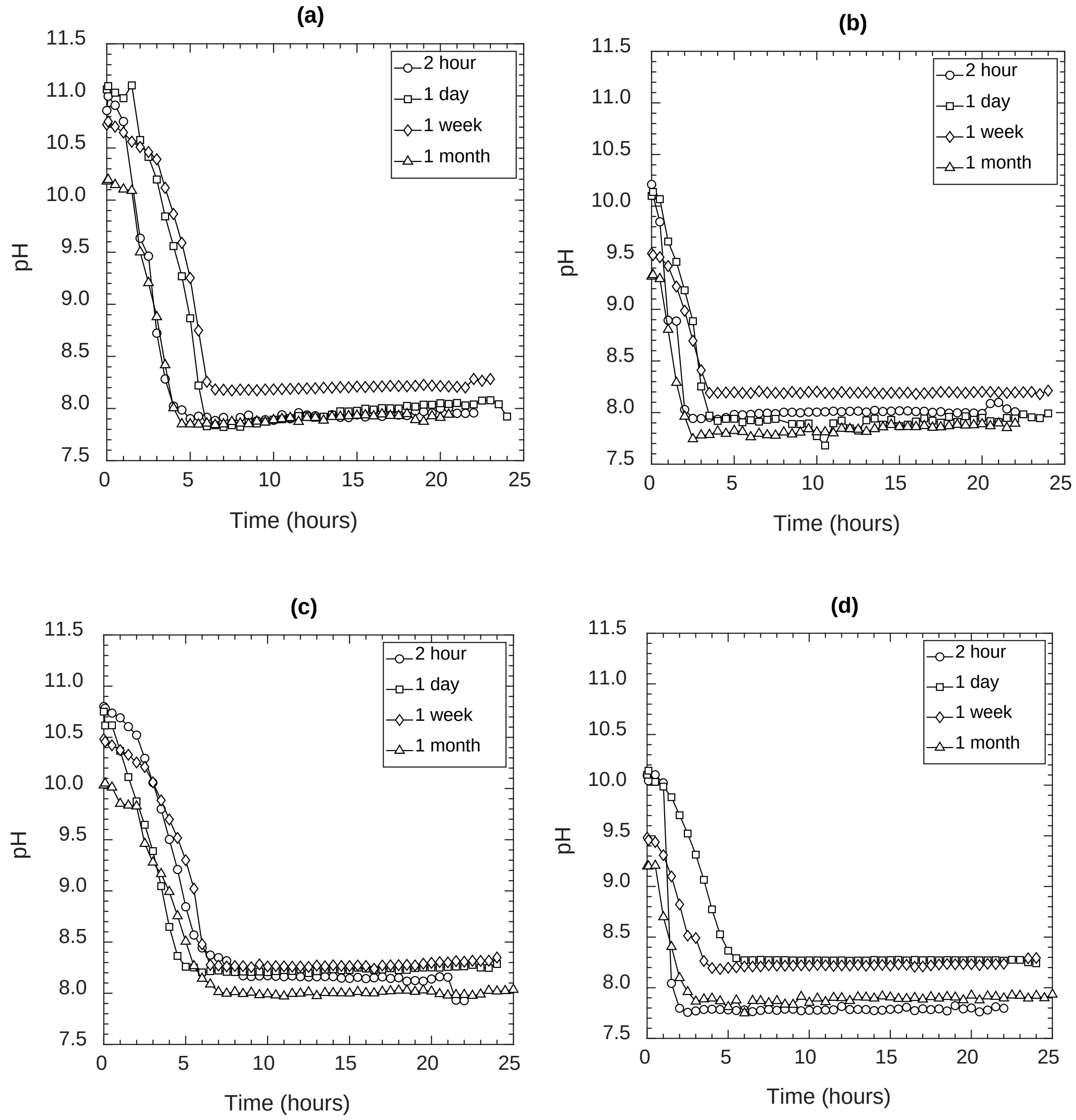

Figure 3.6. Post-drainage pH vs. time for all samples, all times on each plot (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials.

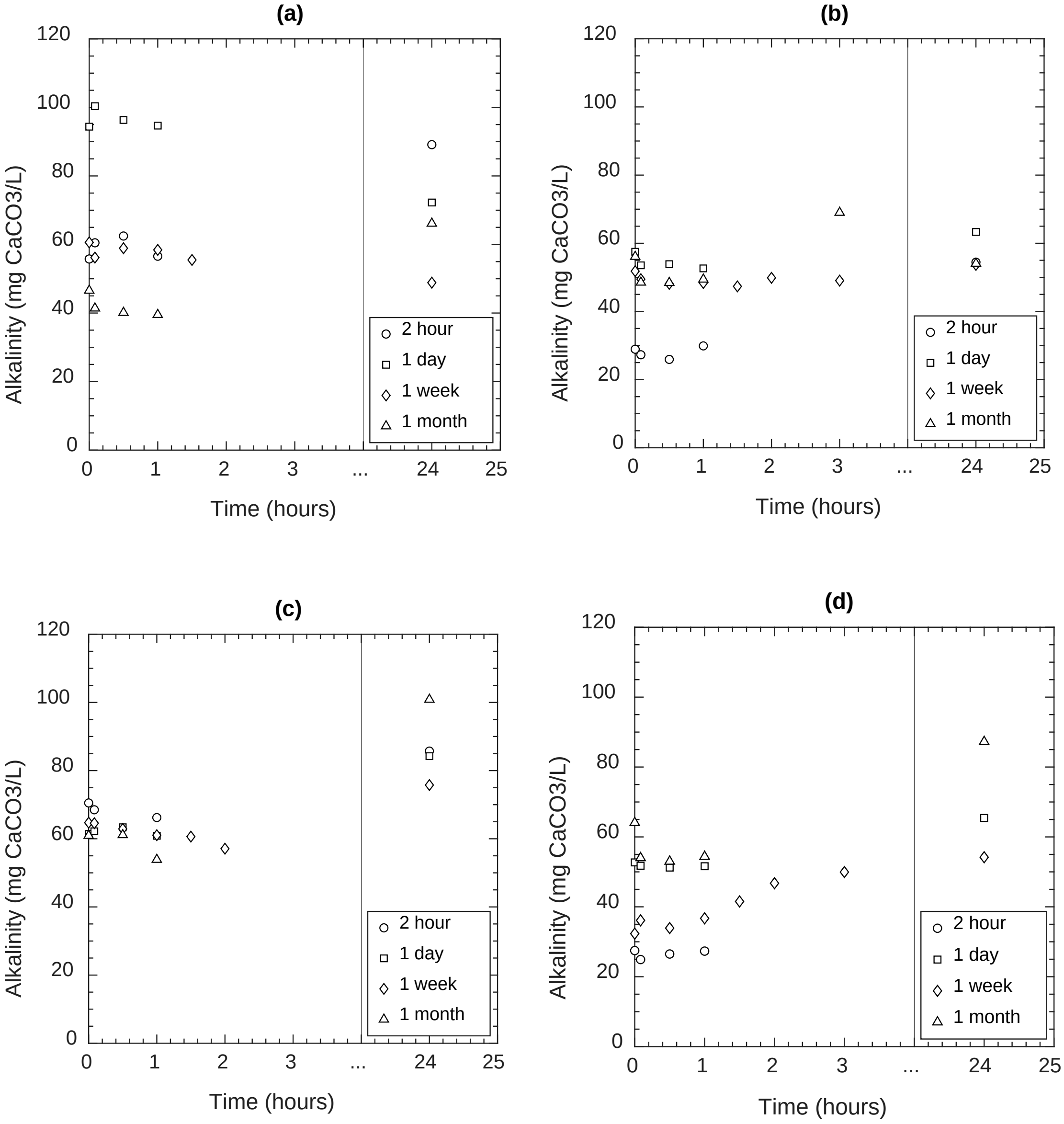

Figure 3.7. Post-drainage alkalinity vs. time for all samples, all times on each plot (a) CT18 (b) PR18 (c) ML18 (d) WS18. Results reported as median of three trials.

Table 3.3. Neutralization pH of leachate after phase separation and the time to reach neutralization pH.

Sample	Contact time trial	Neutralized pH	Time to neutralization (hours)
CT18	2 hour	7.96	3.5
	1 day	7.92	5.5
	1 week	8.27	6.0
	1 month	8.23	3.5
PR18	2 hour	8.01	2.0
	1 day	7.99	3.0
	1 week	8.21	2.5
	1 month	8.29	2.0
ML18	2 hour	8.17	6.0
	1 day	8.24	4.5
	1 week	8.29	5.3
	1 month	8.48	5.5
WS18	2 hour	7.79	1.5
	1 day	8.25	4.8
	1 week	8.29	3.0
	1 month	8.42	1.5

RCA leachate neutralization in the environment

Using the pH and alkalinity at the time of peak pH, as well as the final, post-separation pH and alkalinity, the amount of acidity required to equilibrate RCA leachate pH was determined. The amount of acidity required to neutralize the pH increases linearly with 24-hour pH (Figure 3.8). The 24-hour pH is a suitable proxy for characterizing a given RCA sample because it is related to the peak pH risk as well as the portlandite content of the RCA (Sanger et al. 2019b). Acid for neutralizing RCA leachate pH is available in the environment in the form of atmospheric carbon dioxide infiltration, as demonstrated in the experiments herein, and/or neutralization by soil acidity (Chen et al. 2019). In general, subgrade soils with low hydraulic conductivity and higher clay mineral content will be more successful in neutralizing high pH leachate from RCA base course layers (Chen et al. 2019).

Ultimately, understanding the time-dependent behavior of leachate chemistry and the persistence of high pH leachate in the environment will inform the safe and responsible use of RCA as base course. In field applications of RCA base course, the 24-hour pH can be used as the material parameter to characterize the RCA material. The 24-hour pH indicates the peak pH risk associated with the RCA, the amount of portlandite in the RCA sample, and the amount of acid required to neutralize the leachate pH (Ritchey et al. 2019; Sanger et al. 2019b). As such, 24-hour pH can be included as a design parameter for base course systems that considers the environmental sensitivity, subgrade soil, and drainage design system of the site to establish a threshold, or maximum, 24-hour pH for the RCA to be used construction. The 24-hour pH of RCA material onsite can then be determined relative to the established threshold pH for the design to determine if the RCA material is ready for construction or if it requires additional carbonation.

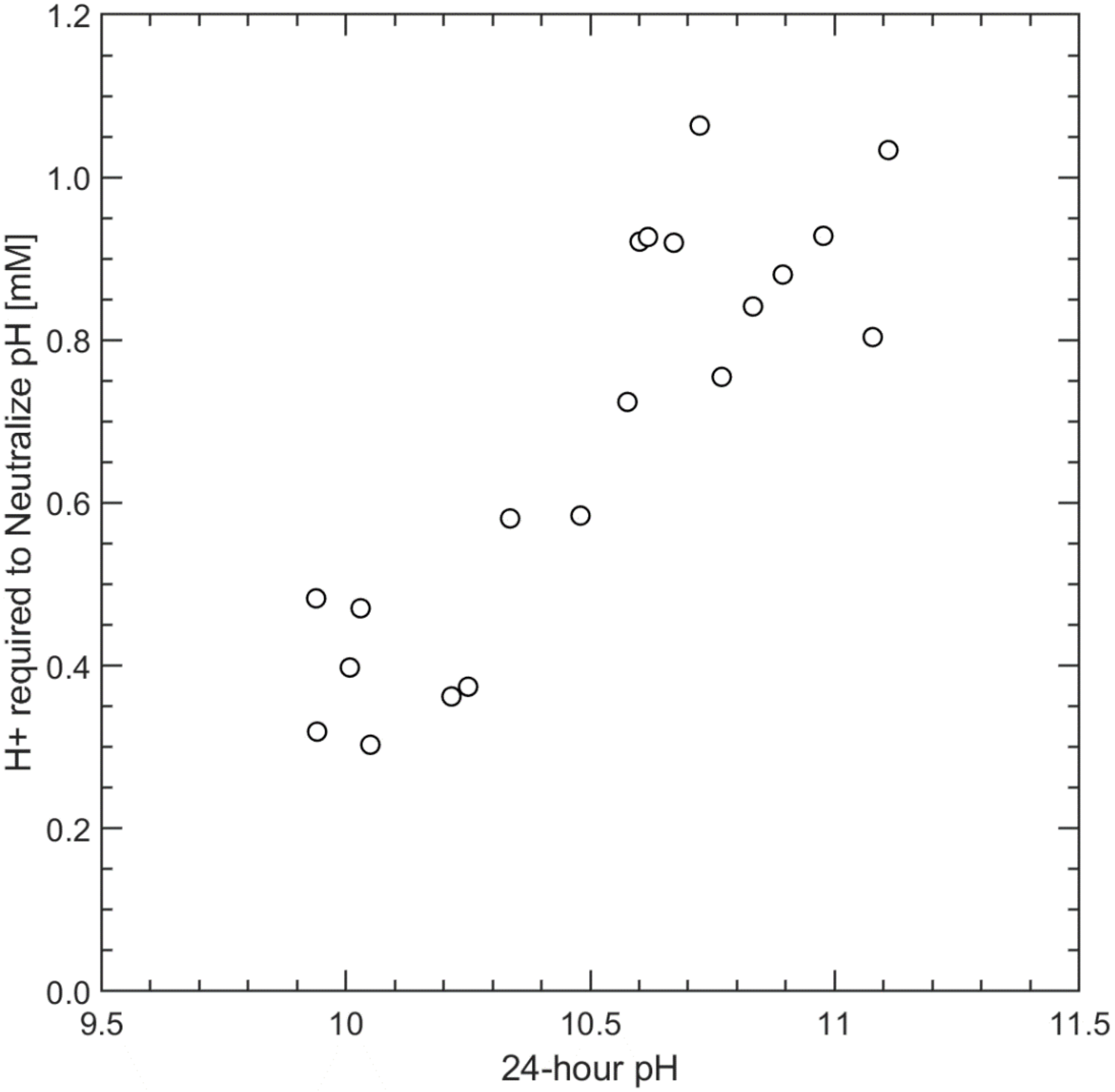

Figure 3.8. Acidity required to neutralize RCA leachate pH. Curve fit: H+ [M] = 0.0006x - 0.0052 R^2 = 0.7453.

CONCLUSIONS

The purpose of the present study is to evaluate the influence of contact time and base course drainage on RCA leachate chemistry in base course applications. Using time points that correspond with the AASHTO classifications of pavement drainage quality, the present study evaluates the time-dependent behavior of RCA leachate pH and alkalinity. Additionally, phase separation experiments are used to simulate base course drainage in the laboratory.

Time-dependent leachate pH behavior is directly related to portlandite content of the RCA and availability of carbon dioxide, or other sources of acidity. Longer contact times do not increase risk associated with RCA leachate pH, such that using RCA in base course applications poses no additional concern regarding drainage quality.

In practical applications of RCA base course, 24-hour pH is a suitable proxy for characterizing RCA materials and assessing the associated pH risk. 24-hour pH is a straightforward parameter that can be used to assess readiness of the RCA for construction and whether stockpiling, artificial carbonation of the material are required before construction. RCA leachate pH will equilibrate to a safe, near-neutral value regardless of the portlandite content of the RCA given sufficient exposure to atmospheric carbon dioxide or soil acidity.

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this thesis is to understand the time-dependent behavior of leachate chemistry from recycled concrete aggregate (RCA) in pavement base course applications, and the persistence of high pH leachate in the environment through the following objectives: 1) identify and address the discrepancies in previous laboratory and field investigations of RCA leachate chemistry; 2) isolate the physicochemical parameters that control RCA leachate chemistry; 3) determine the influence of contact time and base course drainage on RCA leachate chemistry.

A state-of-the-art review of the existing laboratory and field investigations of RCA leachate chemistry, provided in Chapter I, identified and addressed the discrepancies in previous laboratory and field investigations of RCA leachate chemistry. Critical evaluation of the existing laboratory and field measurements of RCA leachate pH determined that the conventional laboratory methodology, which employs abrasive, closed system laboratory techniques, is not representative of RCA leachate chemistry in field applications. In designing laboratory investigations of RCA leachate chemistry, particle abrasion should be limited to effectively represent the development and preservation of protective carbonate layers on the surface of RCA. Additionally, RCA-leachate contact times should be based on field drainage times, as this is the relevant amount of time for RCA and leachate phases to be in contact, and the availability of atmospheric carbon should be considered throughout the duration of the leaching experiment and in considerations of the fate of the leachate after base course drainage.

Using the physical properties, solid phase chemistry, time-dependent leachate chemistry, and a geochemical model of ten RCA samples, presented in Chapter II, the physicochemical properties that control RCA leachate chemistry can be described by two parameters: portlandite content from RCA surfaces and the availability of carbon dioxide. These two parameters counteract one another, such that portlandite content controls the peak pH risk associated with RCA leachate, and the availability of carbon dioxide controls the neutralization of leachate pH. 24-hour pH is directly related to the portlandite content of a given RCA sample, and it is directly related the peak pH of RCA leachate from the sample. For that reason, 24-hour pH is isolated as a defining parameter that can be used a proxy to characterize an RCA sample and assess the pH risk associated with a given RCA sample. The 24-hour pH can be used in practical applications of RCA base course as a straightforward parameter to assess readiness of the RCA for construction and whether stockpiling, artificial carbonation of the material are required before construction.

Contact time and phase separation experiments, presented in Chapter III, illustrate that longer contact times do not increase risk associated with RCA leachate pH, such that using RCA in base course applications poses no additional concern regarding drainage quality. Ultimately, RCA leachate pH will eventually equilibrate to a safe, near-neutral value regardless of the physicochemical properties and portlandite content of the initial RCA sample, given sufficient exposure to atmospheric carbon dioxide or soil acidity. Therefore, drainage system designs for RCA base course should consider the availability of carbon dioxide and/or soil acidity, especially in sensitive areas.

The findings of this thesis can be used to provide guidelines for practice to ensure safe and wise use of RCA base course. 24-hour pH can be included as a design parameter for base course systems that considers the environmental sensitivity, subgrade soil, and drainage design system of the site to establish a threshold, or maximum, 24-hour pH for the RCA to be used construction. The 24-hour pH of RCA material onsite can then be determined relative to the established threshold pH for the design to determine if the RCA material is ready for construction or if it requires additional carbonation.

FUTURE RESEARCH OPPORTUNITIES

The non-abrasive, open system batch reactors employed in the presented investigations of recycled concrete aggregate (RCA) leachate chemistry represent the conditions of RCA in base course applications. However, RCA base course construction involves compaction, which likely produces additional fines and abrades the carbonate surface coating. It would be useful to quantity the change in RCA leachate chemistry caused by compaction by conducting non-abrasive, open system batch reactor leaching experiments, presented in Chapter II, on RCA samples both before and after simulated compaction. Fly ash is a coal by-product commonly-used substitute to Portland cement in concrete mix design; in order to recycle concrete monoliths constructed with fly ash as RCA base course, it would be useful to determine the time-dependent leachate pH and alkalinity from RCA base course with varying fly ash content.

Portlandite content, the physicochemical parameter that controls peak pH from RCA leachate, can itself be controlled by carbonating RCA prior to construction, thereby reducing RCA leachate peak pH risk. A single sample experiment was conducted to investigate the influence of wetting and drying cycles on RCA leachate pH and alkalinity (Figure A.21). Future research may review the existing evaluations of intermittent wetting and drying on RCA carbonation and expand on the sample experiment conducted herein and work to develop standard methodology for artificially carbonating RCA in the field. Similarly, the availability of carbon dioxide and/or soil acidity, the parameter that controls RCA leachate pH neutralization, can itself be controlled by base course drainage design. It would be useful to expand the existing geochemical model of RCA leachate chemistry, introduced in Chapter II and Appendix B, to evaluate the neutralization of RCA leachate pH given different drainage designs. Additionally, a field investigation of RCA leachate chemistry would be useful to corroborate the conclusions made in this thesis regarding RCA leachate neutralization via atmospheric carbon dioxide and/or soil acidity. Some base course drainage systems utilize geosynthetic fabrics; it would be useful to quantify the availability of calcium ions for precipitation of calcium carbonate on the geosynthetic.

The 24-hour pH is a can serve as a proxy to characterize RCA material, and can be used to inform guidelines for practice to ensure safe and wise use of RCA base course in pavement base course construction. In order to establish the 24-hour pH as a design parameter for base course systems, future work should define acceptable RCA leachate pH values given construction sites of varying environmental sensitivity, subgrade soil, and drainage design. Additionally, future work should look to develop methodology for determining the 24-hour pH of the RCA material in the field, beyond the pH indicators presented in Appendix C of this thesis.

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A. APPENDIX A

Physicochemical properties

Table A.1. Atterberg limits for base course sample suite.

Sample	Liquid Limit	Plastic Limit	Plasticity Index
CT18	28%	22%	6%
PR18	22%	29%	NP
ML18	24%	16%	8%
WS18	27%	24%	3%
CT17	27%	33%	NP
OC17	28%	41%	NP
WA17	32%	30%	2%
16C	37%	39%	NP
16D	37%	33%	3%
16P	40%	37%	3%
VA	20%	16%	4%

Table A.2. Specific gravity (G_s) and absorption for base course sample suite.

Sample	Bulk G_s	Bulk G_s (SSD)	Apparent G_s	Absorption	Porosity
CT18	2.23	2.38	2.64	7%	15%
PR18	2.88	3.07	3.55	7%	19%
ML18	2.24	2.37	2.57	6%	13%
WS18	2.27	2.39	2.58	5%	12%
CT17	3.99	4.14	4.70	4%	15%
OC17	2.27	2.41	2.64	6%	14%
WA17	2.34	2.46	2.67	5%	12%
16C	2.13	2.30	2.56	8%	17%
16D	2.50	2.65	2.96	6%	16%
16P	2.26	2.43	2.72	8%	17%
VA	2.56	2.65	2.82	4%	9%

Table A.3. Grain size properties.

Sample	USCS Classification	Percent fines	C_U	C_C	Surface Area (mm^2)
CT18	GW	1.28%	24.1	2.5	221.77
PR18	GW	4.80%	25.2	1.0	772.62
MI18	GW	1.98%	32.1	2.2	304.50
WS18	GW	3.27%	69.6	1.6	372.69
CT17	GW	1.95%	19.9	2.0	223.35
OC17	GW	1.12%	18.4	1.1	126.34
WA17	GW	0.92%	11.3	3.9	130.18
16C	GP	1.12%	13.3	0.5	119.18
16D	GP	1.16%	23.7	0.8	139.56
16P	GP	1.20%	22.8	1.0	126.29
VA	GW	2.58%	22.5	1.1	142.85

Table A.4. Friction angle from direct shear. Courtesy of Soil Mechanics.

Sample	φ
CT18	28.4
PR18	--
ML18	44.8
WS18	--
CT17	--
OC17	--
WA17	--
16C	--
16D	--
16P	--
VA	44.1

Table A.5. Optimum water content and maximum dry unit wright from modified Proctor compaction.

Sample	w_{opt} (%)	γ_{dry} (kN/m^3)
CT18	8.8	19.4
PR18	9.8	20.9
ML18	15.3	17.8
WS18	--	--
CT17	8.1	19.6
OC17	12.1	19.0
WA17	--	--
16C	--	--
16D	--	--
16P	--	--
VA	9.1	22.1

Table A.6. Compression indices from one-dimensional compression.

Sample	Compression Index, C_C	Swelling Index, C_S
CT18	0.2340	0.0140
PR18	0.0063	0.0001
ML18	0.0332	0.0011
WS18	0.0430	0.0023
CT17	--	--
OC17	--	--
WA17	--	--
16C	--	--
16D	--	--
16P	--	--
VA	0.1029	0.0015

Table A.7. Hydraulic conductivity from falling head and constant head rigid wall permeameters.

Sample	Falling Head, k (cm/s)	Constant Head, k (cm/s)
CT18	0.1164	0.0014
PR18	--	0.0043
ML18	0.0488	--
WS18	0.0184	0.0460
CT17	0.0029	0.0019
OC17	--	0.0568
WA17	--	--
16C	--	--
16D	--	--
16P	--	--
VA	0.0081	0.0086

Table A.8. Grain size distribution data.

Sieve	Percent Finer										
	CT18	**PR18**	**ML18**	**WS18**	**CT17**	**OC17**	**WA17**	**VA**	**16C**	**16D**	**16P**
1.25 in	99%	100%	90%	74%	100%	100%	91%	100%	100%	100%	100%
1 in	93%	100%	87%	68%	97%	94%	68%	98%	100%	100%	100%
0.75 in	78%	95%	77%	60%	97%	81%	43%	96%	97%	97%	95%
3/8 in	53%	79%	54%	46%	87%	60%	20%	76%	86%	75%	74%
No. 4	35%	65%	39%	35%	77%	48%	13%	58%	63%	48%	45%
No. 10	21%	44%	27%	26%	61%	33%	9%	37%	48%	35%	32%
No. 20	14%	31%	20%	21%	47%	22%	7%	25%	32%	23%	21%
No. 40	9%	24%	13%	15%	33%	11%	4%	18%	15%	13%	11%
No. 60	6%	20%	9%	9%	17%	6%	4%	14%	7%	6%	5%
No. 100	3%	10%	5%	6%	8%	3%	2%	7%	3%	3%	3%
No. 200	1%	5%	3%	4%	3%	1%	1%	3%	1%	1%	1%
Pan	0%	0%	1%	0%	0%	0%	0%	0%	0%	0%	0%

Table A.9. Mineral percentages from XRD.

		CT18	**PR18**	**ML18**	**WS18**	**OC17**	**CT17**	**WA17**	**16C**	**16D**	**16P**	**VA**
Calcite	$CaCO_3$	11.4	3.6	14.6	13.1	5.9	5.6	16.5	16.1	14.0	21.6	1.6
Dolomite	$CaMgC_2O_6$	55.1	70.7	40.7	64.3	66.8	26.4	46.9	12.0	15.9	15.7	88.9
Anorthite	$CaSiAlO_4$	18.0	6.1	6.7	7.0	5.8	2.9	16.9	18.5	38.3	23.5	ND
Magnetite	Fe_3O_4	ND	0.8	0.4	0.5	0.2	0.7	0.3	0.7	ND	0.4	ND
Ilmenite	$FeTiO_3$	0.8	0.6	0.5	0.4	0.5	ND	0.2	0.9	1.0	1.2	ND
Afwillite	$Ca_3Si_2O_{10}H_6$	ND	1.2	2.7	2.1	ND	1.6	2.3	2.2	2.0	3.9	ND
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_26H_2O$	2.0	1.1	2.5	0.7	9.9	7.5	0.7	1.5	0.3	ND	ND
Quartz	SiO_2	12.8	15.9	31.8	12.0	10.9	55.2	16.2	48.0	28.5	33.7	9.5
Portlandite	$Ca(OH)_2$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table A.10. Carbonate mineral percentages from XRD and TGA, and portlandite percentage from geochemical model.

		CT18	**PR18**	**ML18**	**WS18**	**OC17**	**CT17**	**WA17**	**16C**	**16D**	**16P**	**VA**
XRD	$(Ca,Mg)CO_3$	66.5	74.3	55.3	77.4	72.7	32.0	63.4	28.1	29.9	37.3	90.5
TGA	$(Ca,Mg)CO_3$	62.5	73.8	51.1	68.9	–	–	–	19.0	20.6	19.7	–
Model	$Ca(OH)_2$	0.32	0.11	0.11	0.23	–	–	–	0.11	0.11	0.11	0.0

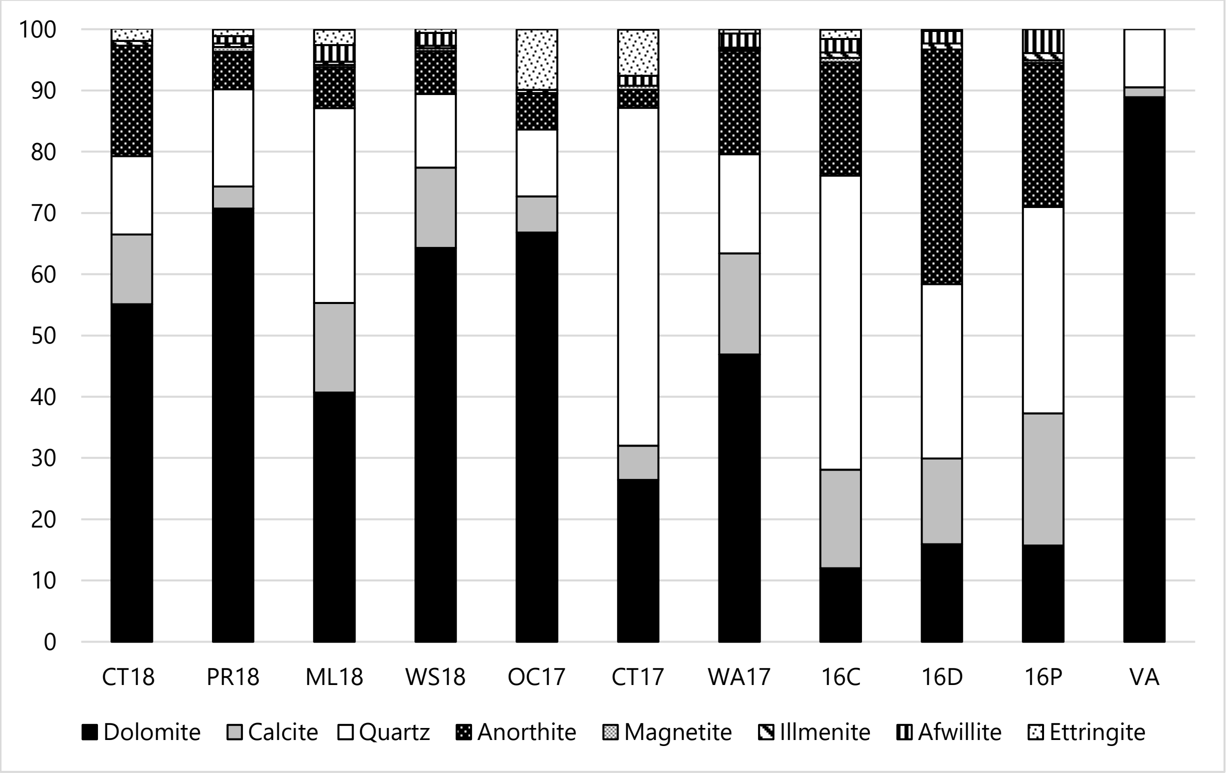

Figure A.1. Relative mineral percentages.

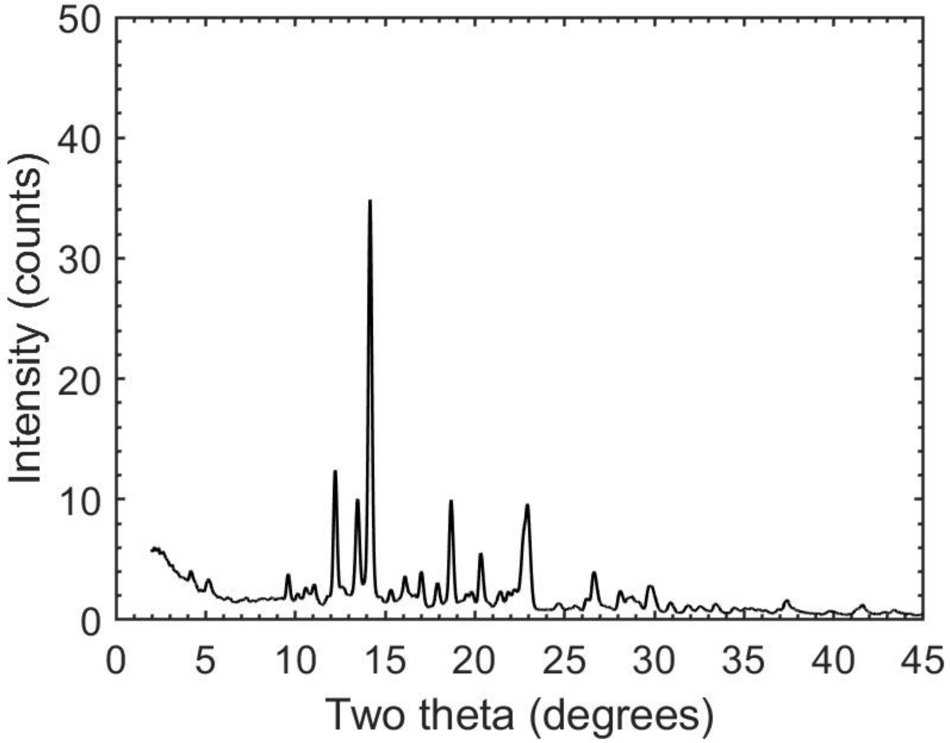

Figure A.2. CT18 XRD Trace.

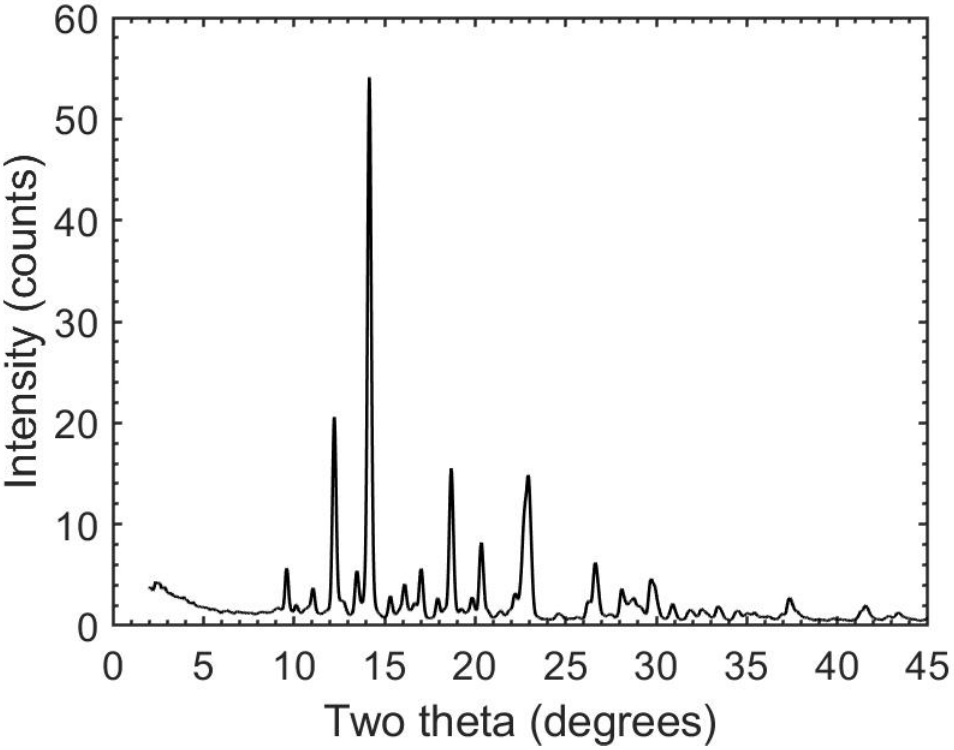

Figure A.3. PR18 XRD Trace.

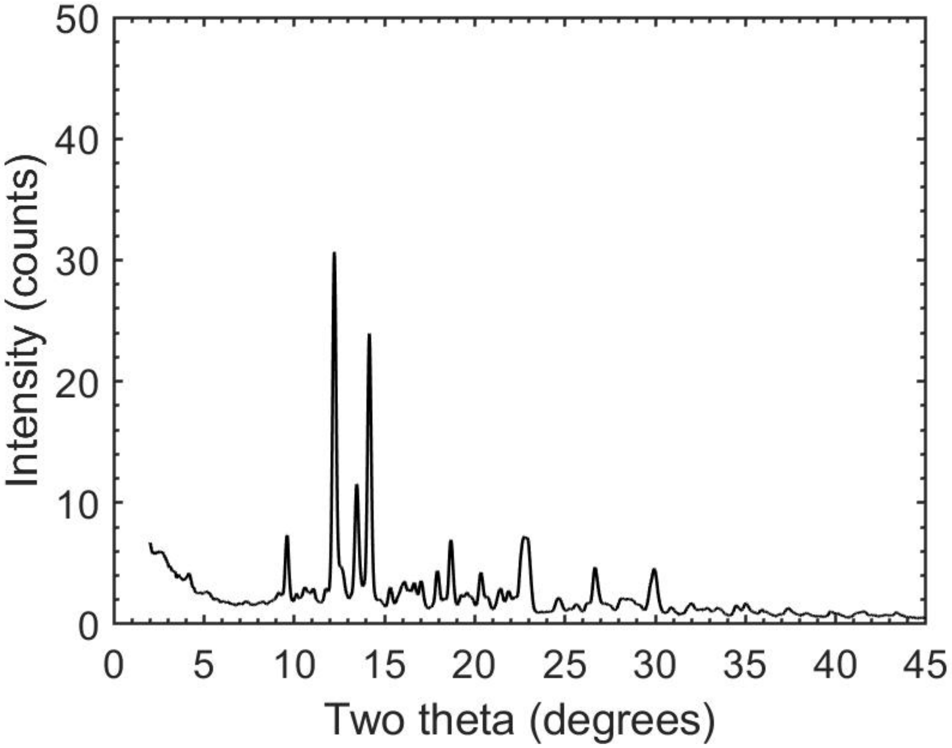

Figure A.4. ML18 XRD Trace

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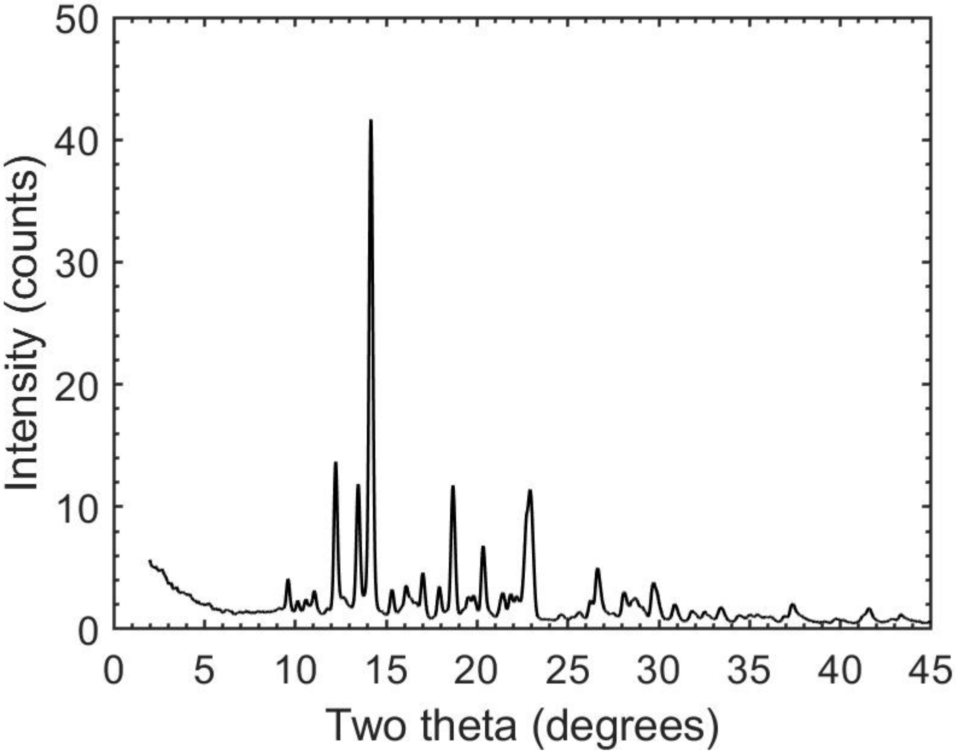


Figure A.5. WS18 XRD Trace.

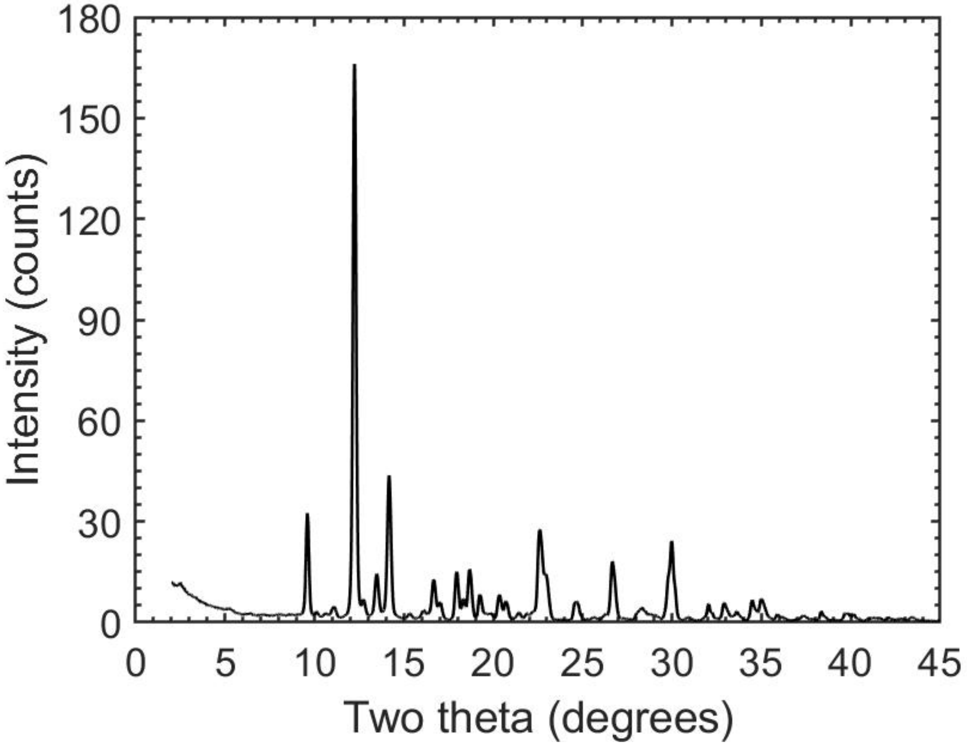


Figure A.6. CT17 XRD Trace.

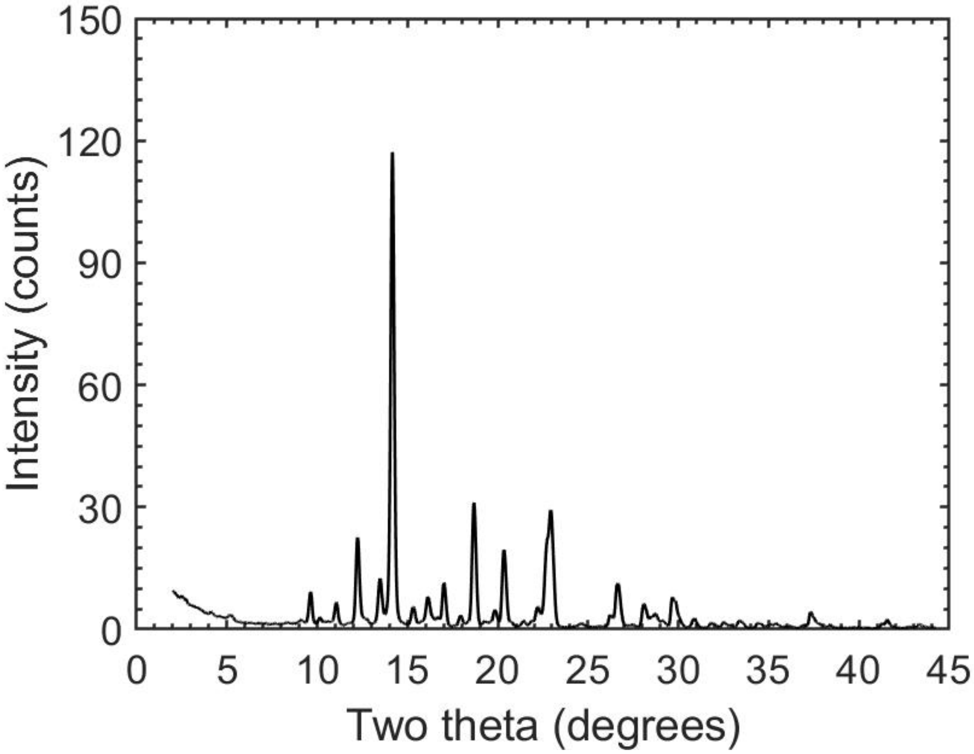


Figure A.7. OC17 XRD Trace.

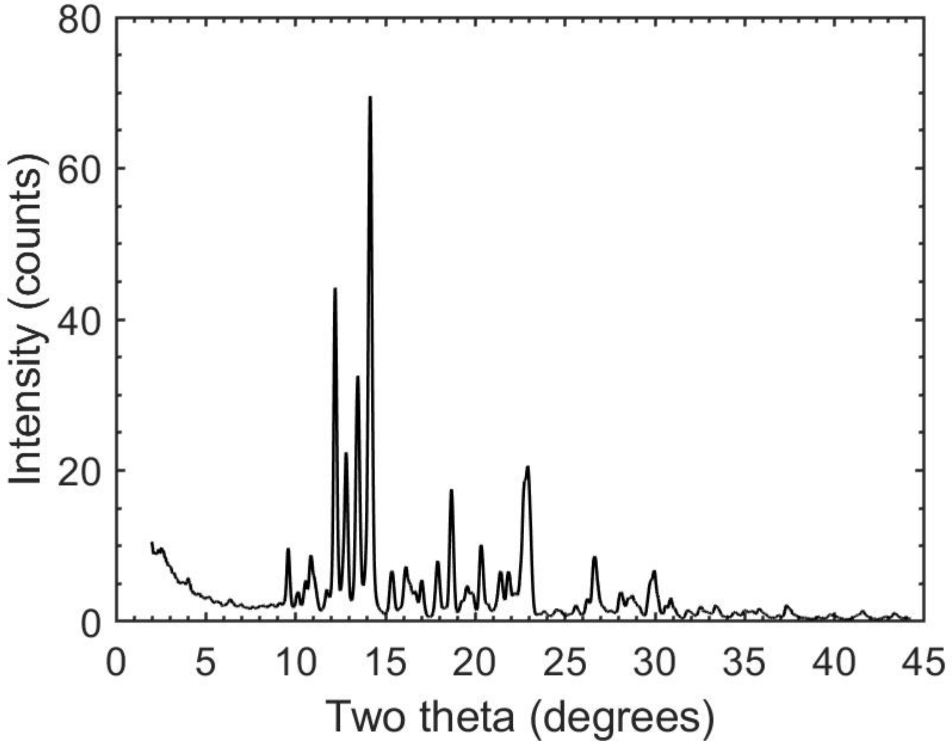


Figure A.8. WA17 XRD Trace.

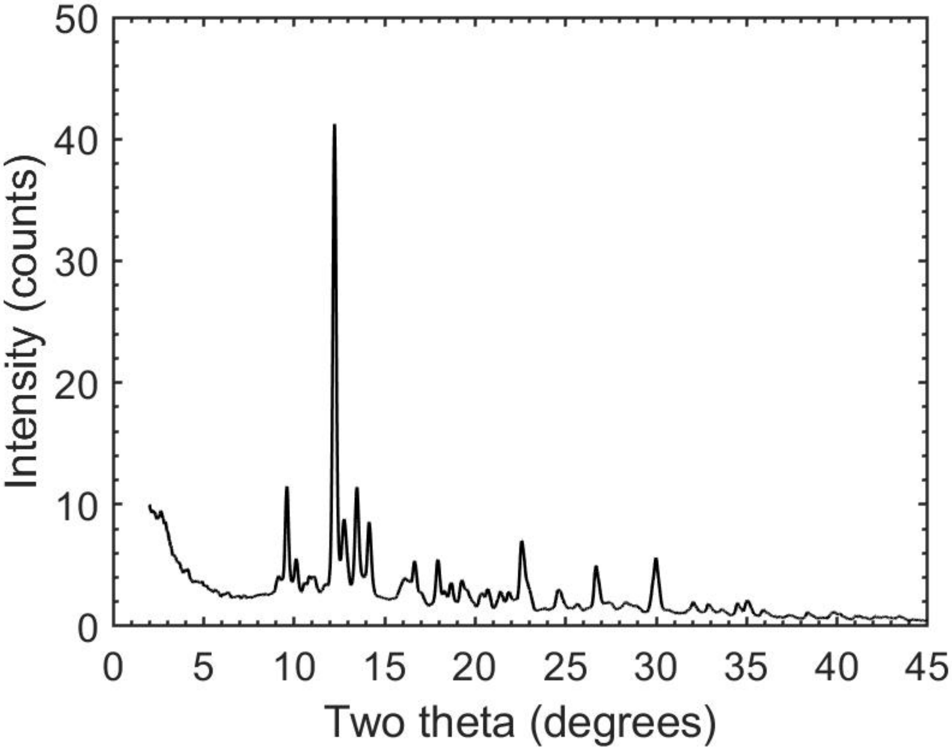


Figure A.9. 16C XRD Trace.

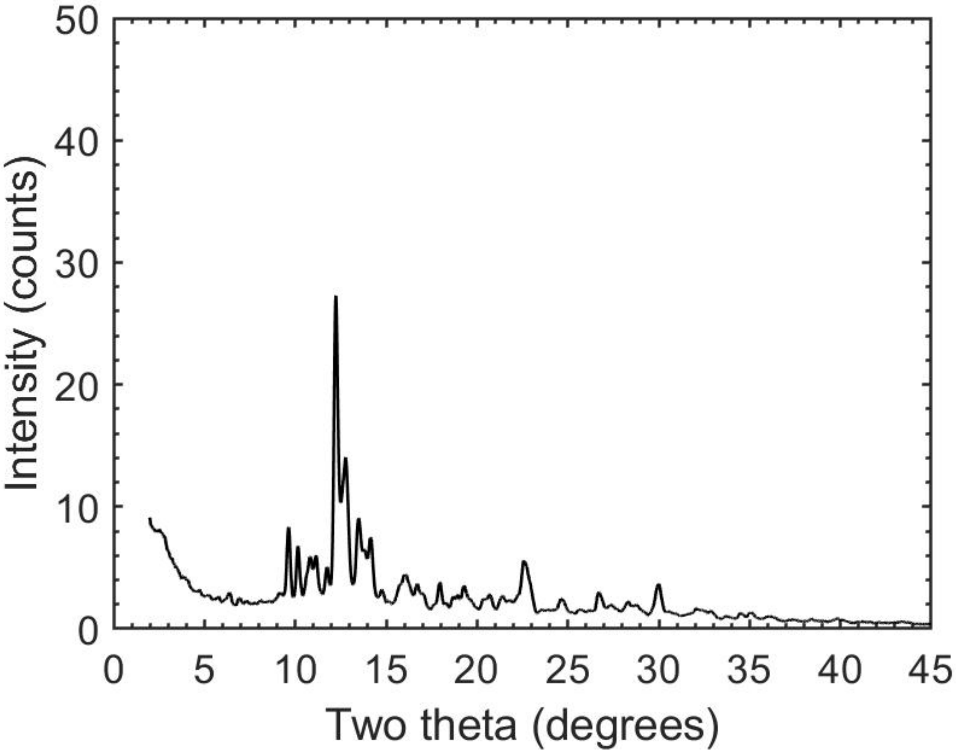


Figure A.10. 16D XRD Trace.

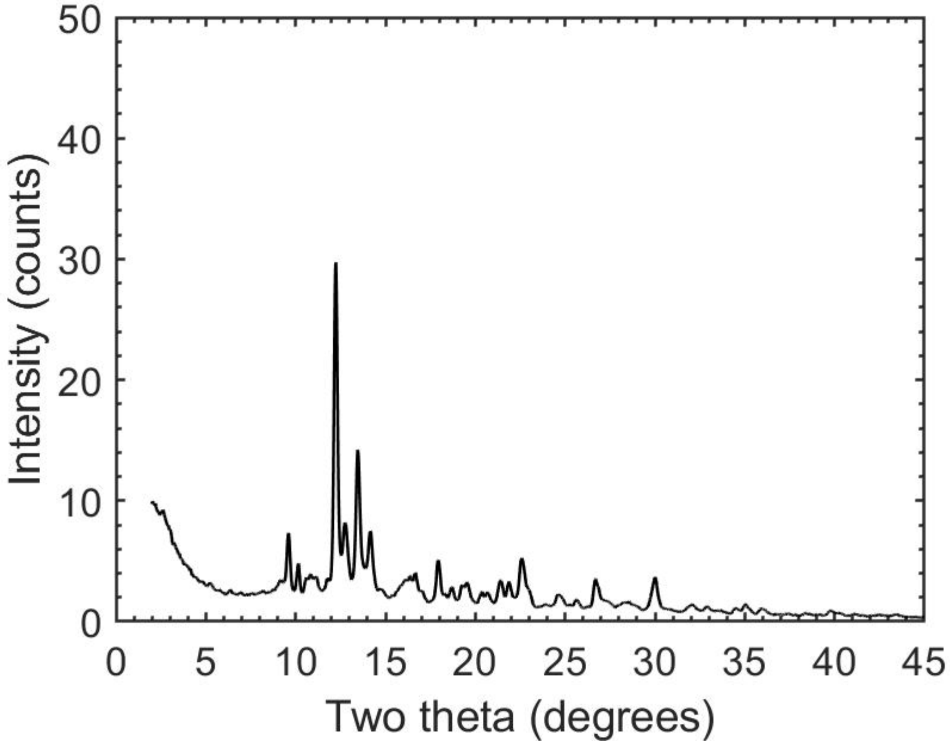


Figure A.11. 16P XRD Trace.

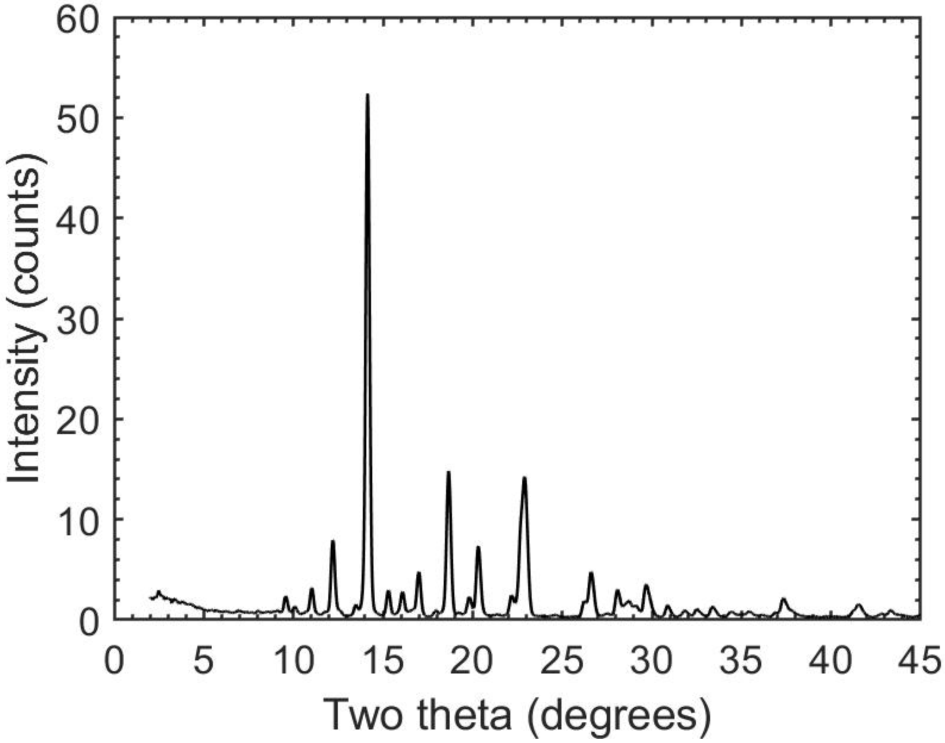


Figure A.12. VA XRD Trace.

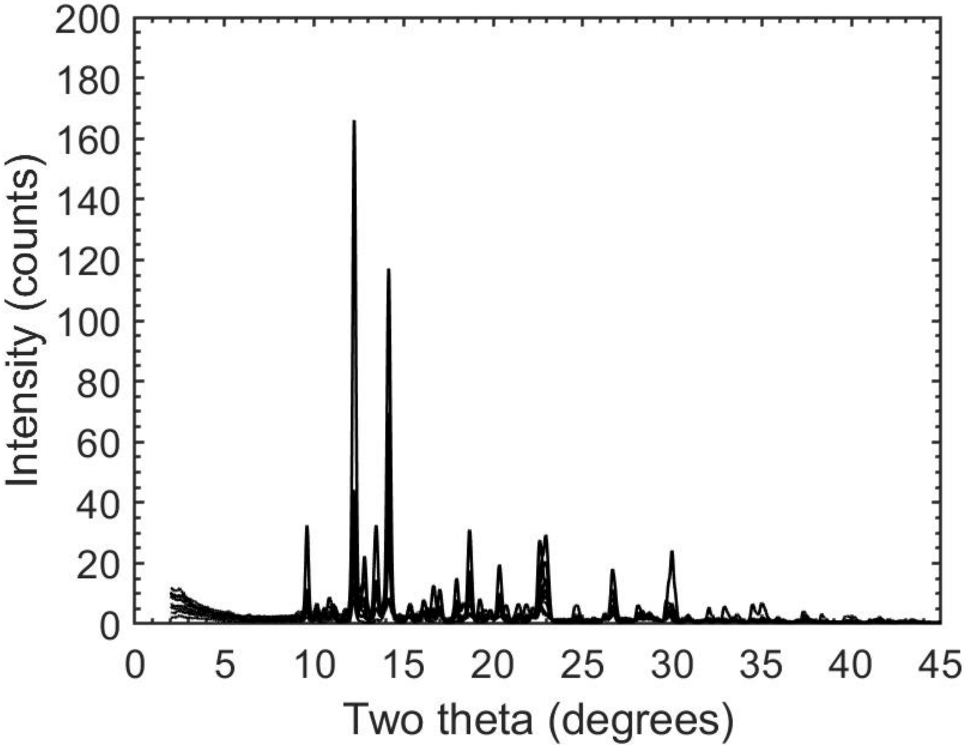


Figure A.13. All XRD Traces.

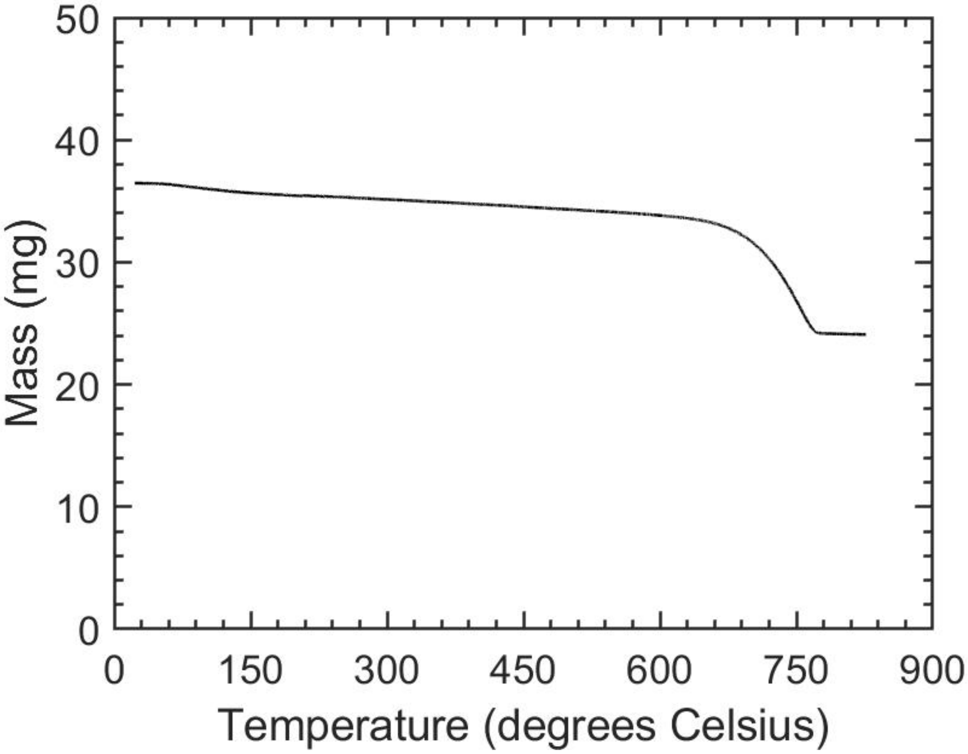


Figure A.14. CT18 TGA Trace.

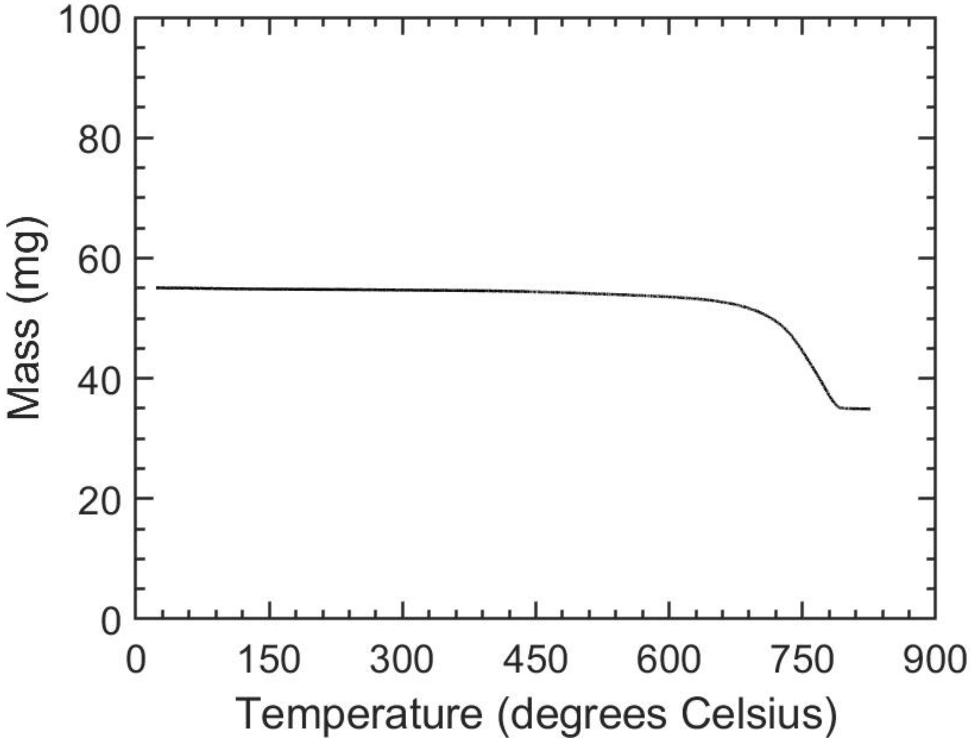


Figure A.15. PR18 TGA Trace.

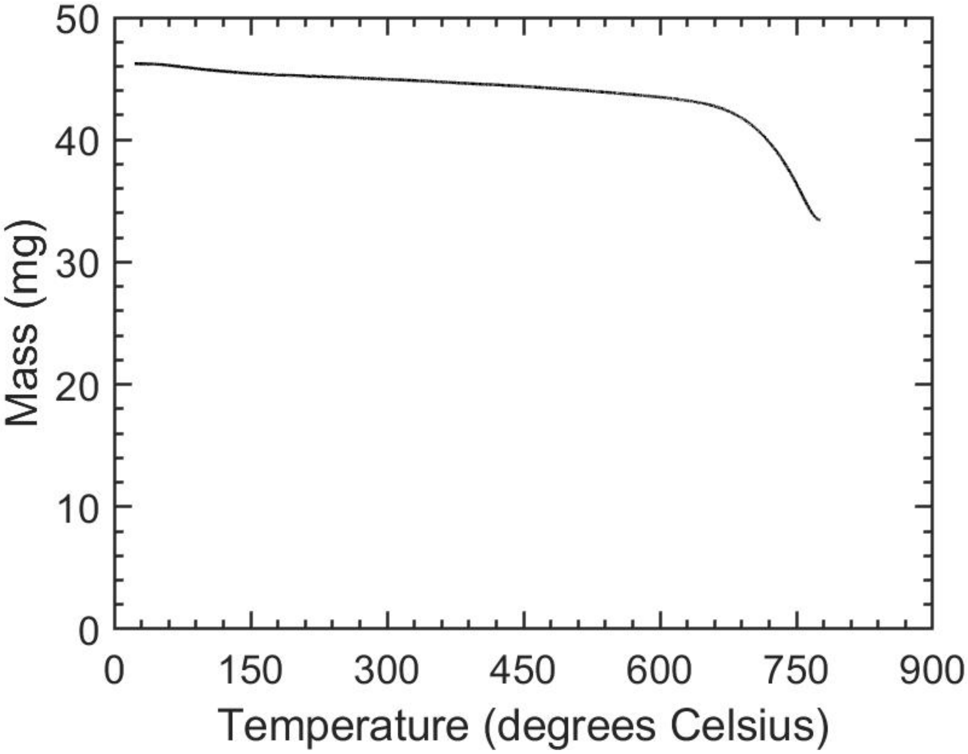


Figure A.16. ML18 TGA Trace.

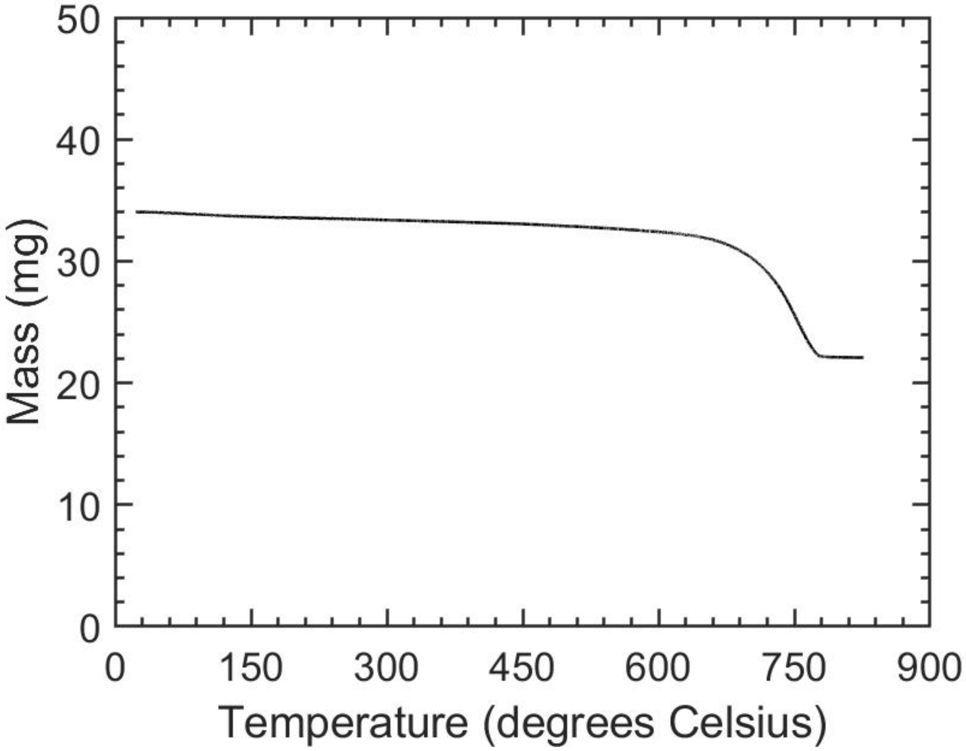


Figure A.17. WS18 TGA Trace.

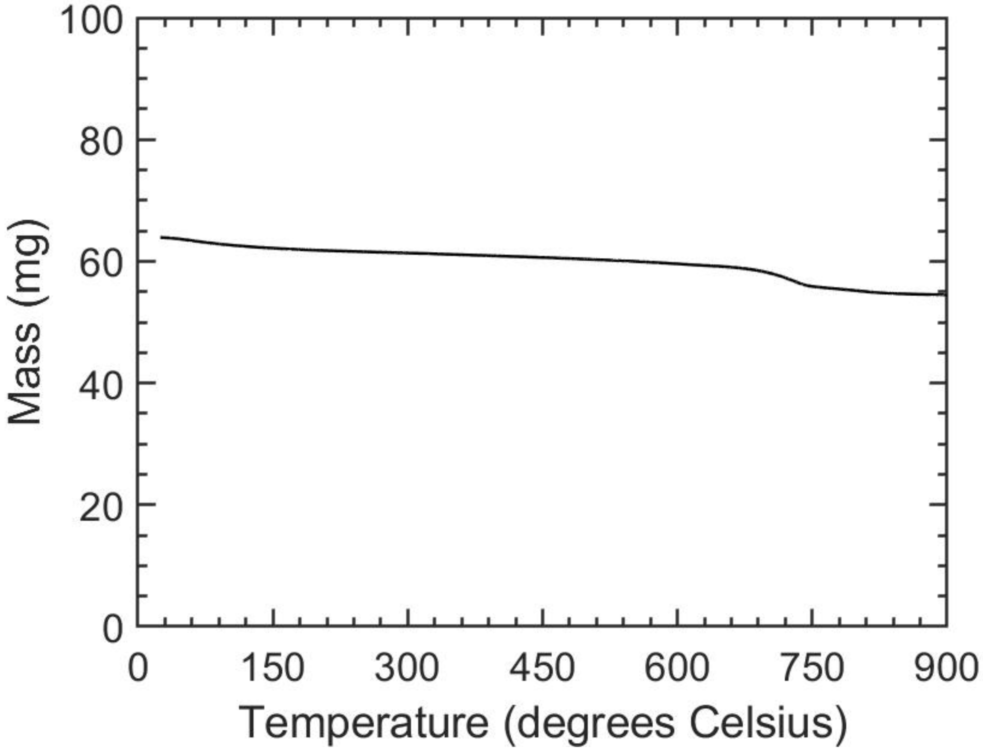


Figure A.18. 16C TGA Trace.

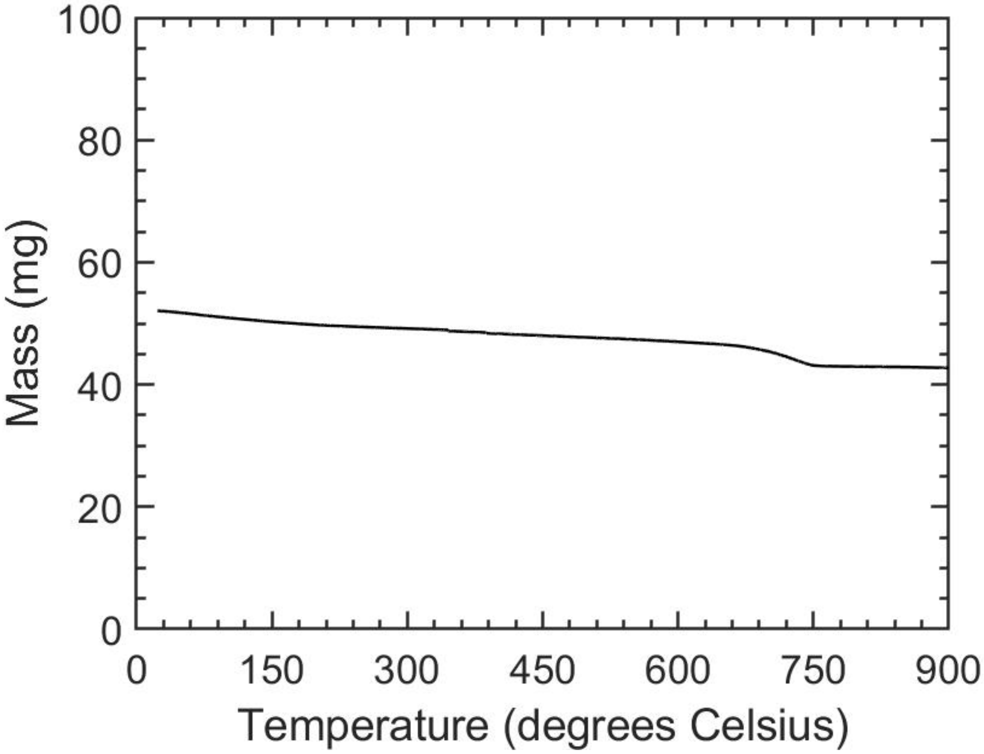


Figure A.19. 16D TGA Trace.

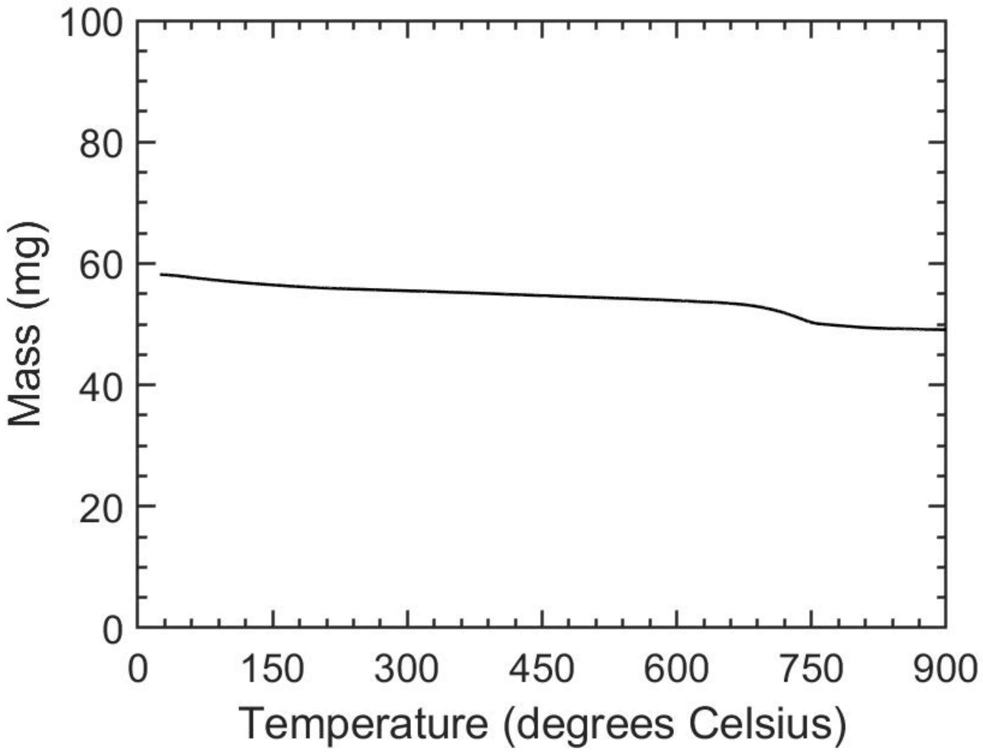


Figure A.20. 16P TGA Trace.

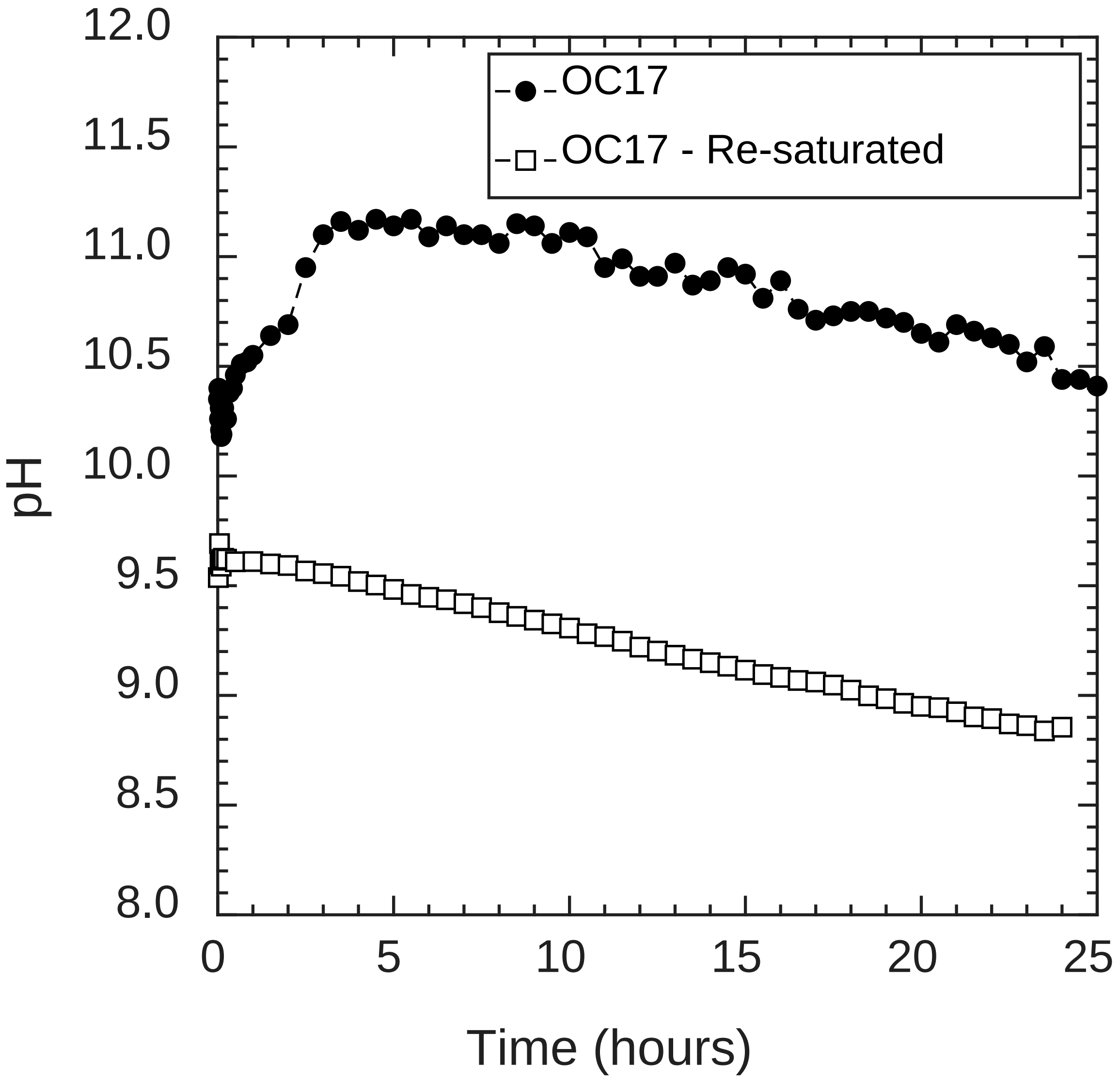


Figure A.21. Monitoring time-dependent pH of sample OC17 in a non-abrasive, open system batch reactor (Chapter II), then allowing that sample to air-dry in the laboratory and conducting a second time-dependent batch reactor leaching experiment. Singular experiment conducted on sample OC17. Demonstrates carbonation.

B. APPENDIX B

Geochemical modelling

Table B.1. Kinetic rate laws and masses used in the model for each RCA sample tested.

Mineral	k_+ ^{a} (mol/cm^2s)	ML18 (g)	WS18 (g)	CT18 (g)	PR18 (g)	OC17 (g)	CT17 (g)	WA17 (g)	16C (g)	16D (g)	16P (g)
Afwillite	2.24E-14	1.352	0	0	0.603	0	0	1.159	1.103	1.003	1.953
Anorthite	1.00E-15	3.355	9.047	9.043	3.065	2.923	1.454	8.517	9.272	19.2	11.77
Calcite	1.55E-18	7.23	5.695	5.607	1.796	2.893	2.777	8.289	8.04	6.98	10.782
Dolomite	2.57E-25	20.382	27.695	27.681	35.509	33.664	13.234	23.636	6.014	7.971	7.863
Ettringite	2.24E-14	1.252	1.001	1.005	0.553	4.989	3.76	0.353	0.752	0.15	0
Ilmenite	2.00E-24	0.25	0.402	0.402	0.301	0.252	0	0.101	0.451	0.501	0.601
Magnetite	2.57E-13	0.2	0	0	0.402	0.101	0.351	0.151	0.351	0	0.2
Portlandite	1.55E-08	0.08	0.035	0.12	0.025	0.08	0.03	0.027	0.029	0.038	0.035
Quartz	5.13E-29	15.925	6.434	6.43	9.989	5.493	27.671	8.164	24.056	14.287	16.878

(a) Anorthite, Calcite (Chen et al. 2013), Dolomite (Chen et al. 2013), Ettringite (Baur et al. 2004), Magnetite (Palandri and Kharaka 2004), Portlandite (Chen et al. 2013), Quartz (Chen et al. 2013).

Table B.2. Percent portlandite, carbon dioxide contact area, neutralization time, and neutralization pH as calculated by the GWB model which would not have been available with only the experimental data. Peak pH, 24-hour pH, and neutralization pH serve as the boundaries of the two regions of the time-dependent pH curve for the leachate.

Sample	Peak pH	Portlandite content (%)	24-hour pH	CO_2 contact area (cm^2/kg)	Equilibration Time (hr)	Equilibration pH
ML18	11.2	0.18	11.0	300	261	8.8
WS18	10.3	0.09	9.7	400	80	8.4
CT18	11.5	0.26	11.2	750	146	9.0
PR18	10.1	0.08	8.8	700	33	8.4
OC17	11.2	0.19	10.1	3500	64	8.8
CT17	10.0	0.08	8.3	1250	21	8.4
WA17	9.6	0.07	8.3	3500	11	8.3
16C	10.0	0.08	9.5	400	58	8.2
16D	10.4	0.10	10.0	300	111	8.5
16P	10.2	0.09	9.8	300	93	8.4

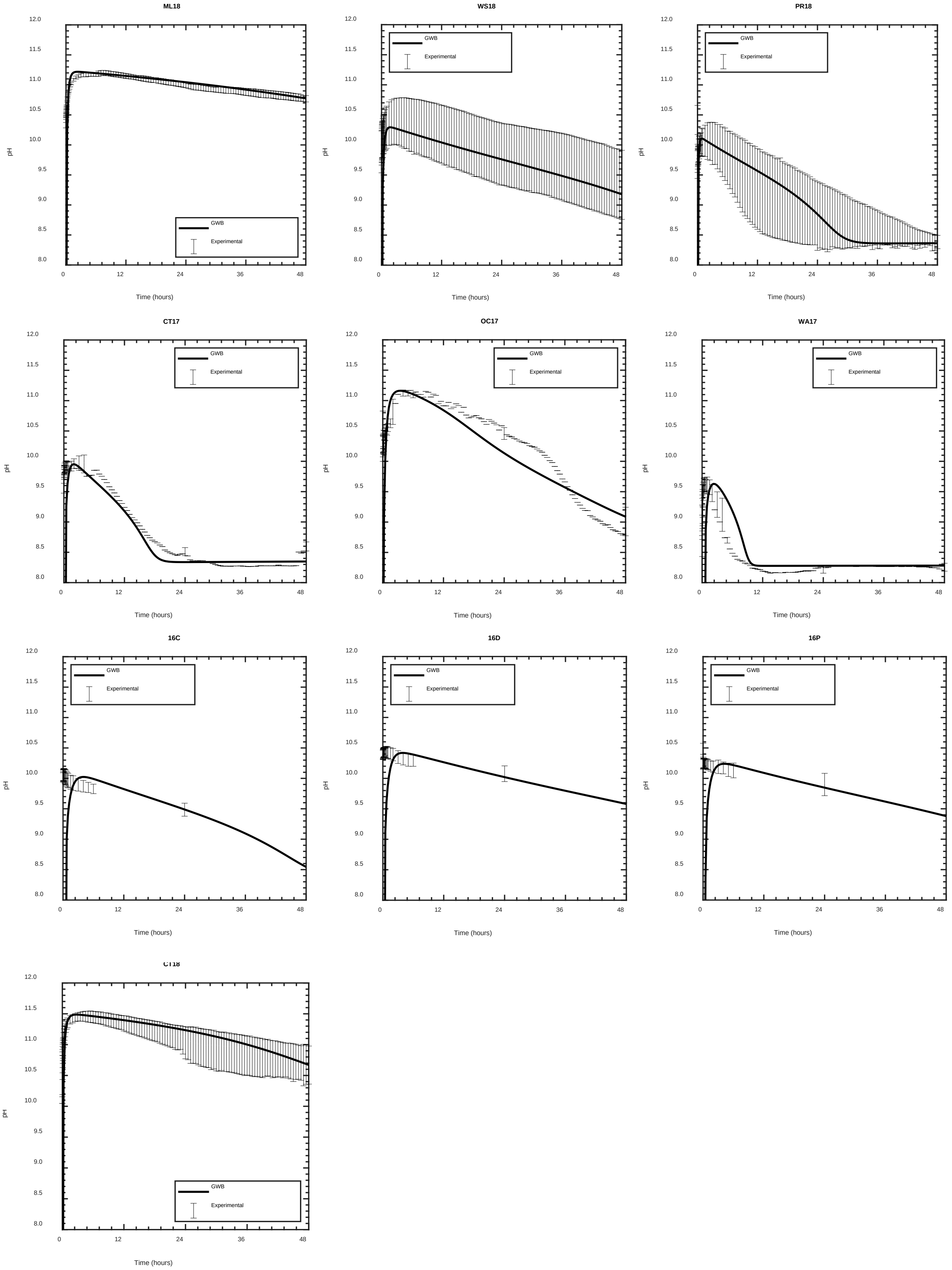


Figure B.1. Laboratory data compared to model outputs for the ten RCA samples used.

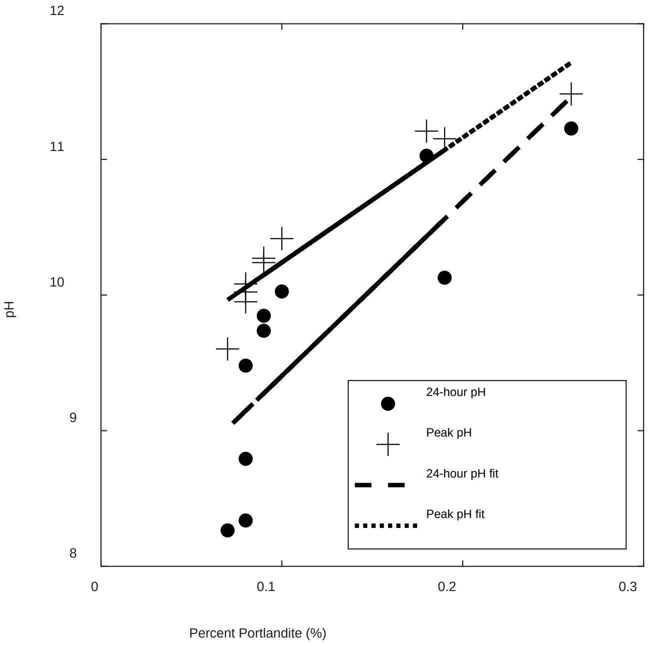


Figure B.2. Relationship between percent portlandite to the 24-hour pH and peak pH, peak pH fit: y = 9.21x+9.3 (R^2=0.91), 24-hour pH fit: y = 12.86x+8.1 (R^2 = 0.68)

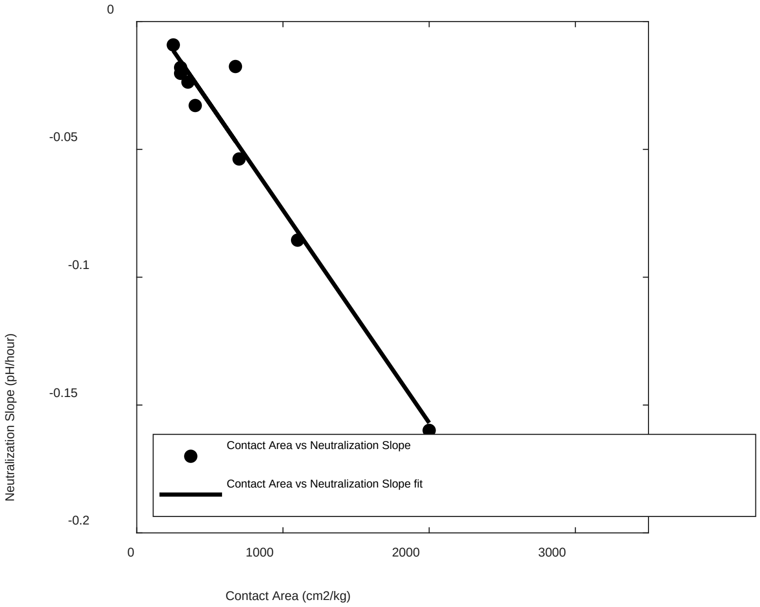


Figure B.3. Linear relationship between carbon dioxide contact area and the rate of pH, fit: y = -11,928x + 91.5 (R^2 = 0.95)

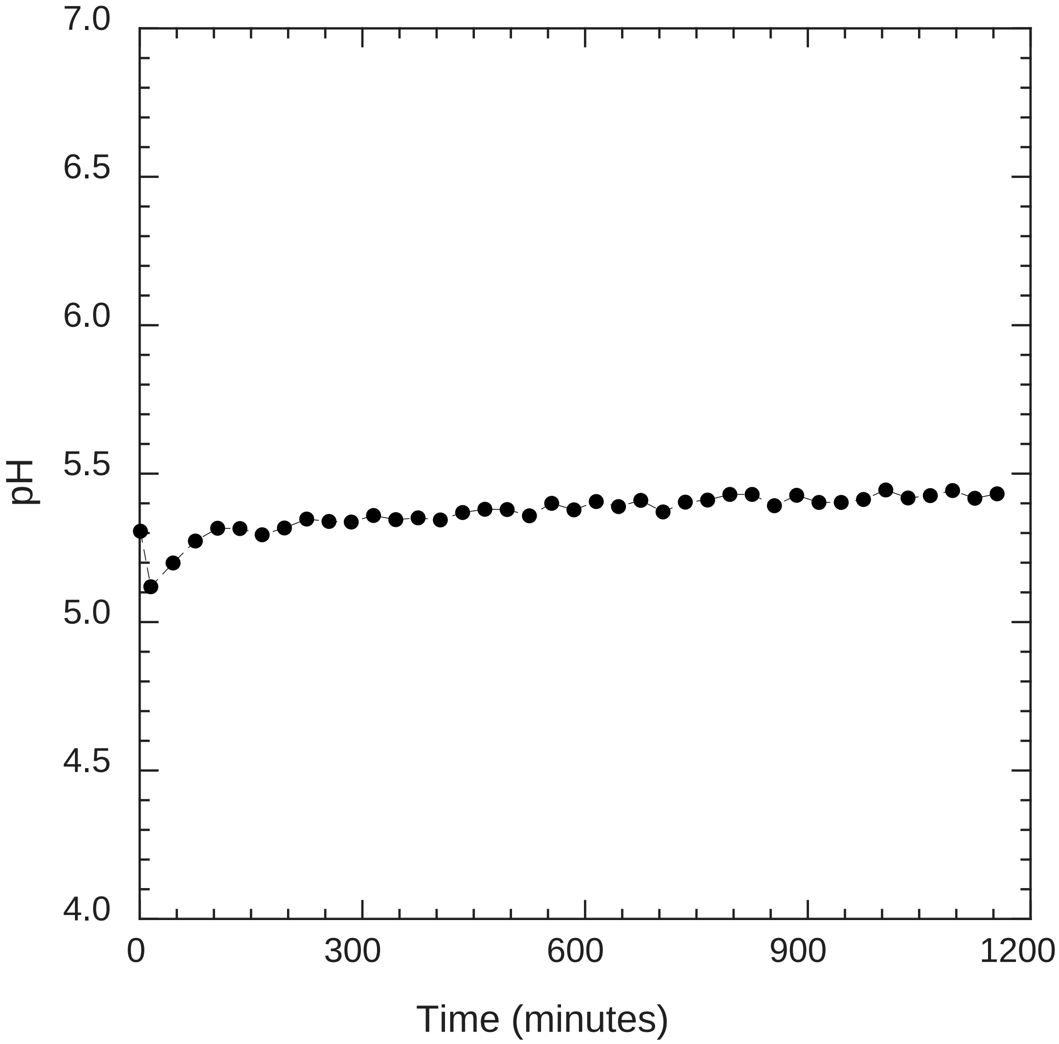


Figure B.4. Monitoring pH of Ultrapure MQ equilibrated with atmospheric carbon dioxide in an open system batch reactor.

Table B.3. Alkalinity measurements of Ultrapure MQ equilibrated with atmospheric carbon dioxide in an open system batch reactor.

Alkalinity (mg $CaCO_3$/L)
2.7
2.2
2.3

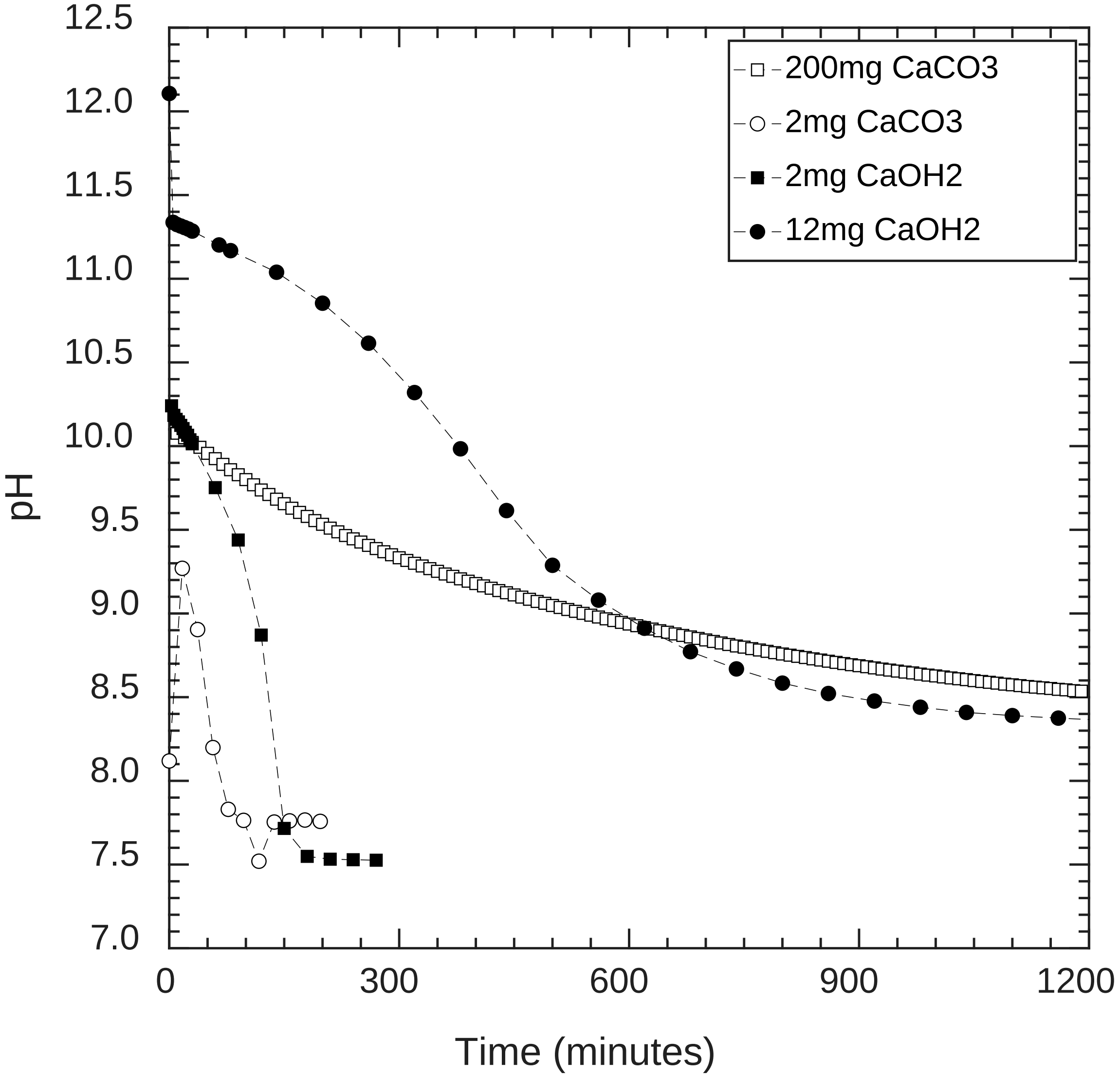


Figure B.5. Monitoring time-dependent pH of calcium carbonate powder and calcium hydroxide powder in an open system batch reactor.

C. APPENDIX C

Field determination of leachate pH

FIELD DETERMINATION OF LEACHATE PH

Morgan Sanger

Introduction

Uncertainty regarding the environmental implications of the characteristic high pH, high alkalinity leachate from recycled concrete aggregate (RCA) leachate limits the widespread use of RCA as a substitute for virgin aggregate in pavement base course applications. The 24-hour pH is a can serve as a proxy to characterize RCA material, and can be used to inform guidelines for practice to ensure safe and wise use of RCA base course in pavement base course construction. In order to implement the 24-hour pH as a design parameter for base course systems given construction sites of varying environmental sensitivity, subgrade soil, and drainage design, there is need determine 24-hour pH in the field. The use of pH indicators presents a straightforward, inexpensive method for determining RCA leachate pH in the field, and characterizing the RCA material. In this report, ten RCA samples and one virgin limestone aggregate sample were evaluated using four pH indicators (phenolphthalein, thymolphthalein, thymol blue, and Litmus paper) along with a pH probe to qualitatively evaluate the usefulness of pH indicators in characterizing RCA leachate pH in the field.

Materials

Ten RCA samples and one virgin limestone aggregate sample were collected from various sites in Minnesota and Wisconsin with the intent to collect a variety of RCA samples for characterization and analysis. Samples were obtained from active highway construction sites around Madison, WI (ML18, WS18, PR18), recycling facilities in Madison, WI (CT18, CT17) and stockpiles in West Allis and Oconomowoc, WI (WA17, OC17, respectively). Additionally, recovered RCA samples from the MnROAD test facility near Minneapolis, MN were used in this study (16C, 16D, 16P); the MnROAD samples were field-deployed for eight years as RCA base course, and significant work has been done to characterize the physical and chemical properties of this material (Chen et al. 2012; Madras Natarajan et al. 2019). RCA samples were given a four-character sample name, with two letters that correspond to the sample source and two numbers that correspond to the year the sample was obtained. The MnROAD samples (16C, 16D, 16P) have been previously studied and the previously-used sample names were upheld avoid confusion (Chen et al. 2013; Madras Natarajan et al. 2019). For the sake of comparison, virgin limestone aggregate was obtained from Yahara Materials Quarry in Madison, WI.

Methods

Base course samples were homogenized by hand mixing and oven-dried overnight. Each base course sample was tested using batch reactors prepared with an initial liquid to solid ratio of 10 mL/g: 50 g of base course in 500 mL Milli-Q Integral Ultrapure Water (MQ) (18.2 MΩ·cm). Leachate was tested at specified contact times: 1 minute, 10 minutes, 30 minutes, 120 minutes, and 24 hours, leachate pH.

At each time point, leachate pH was measured using a Thermo Scientific Orion Combination pH Electrode, and four leachate samples were extracted from the batch reactor for pH indicator analysis. One of the four leachate extractions was used to saturate Fisherbrand Litmus paper and was promptly photographed (Figure C.2). The remaining three extracted leachate samples were mixed with three drops of a pH indicator and photographed. The pH indicators used were phenolphthalein, thymolphthalein, thymol blue, and these indicators were selected to change colors in high pH ranges (**Error! Reference source not found.**). In addition to mixing with time-varied leachate extractions, phenolphthalein, thymolphthalein, and thymol blue were also applied directly to RCA samples in spray form and in concentrated application.

Figure C.1. Fisherbrand Litmus paper ("Fisherbrand^{TM} pH Test Paper Rolls" 2019).

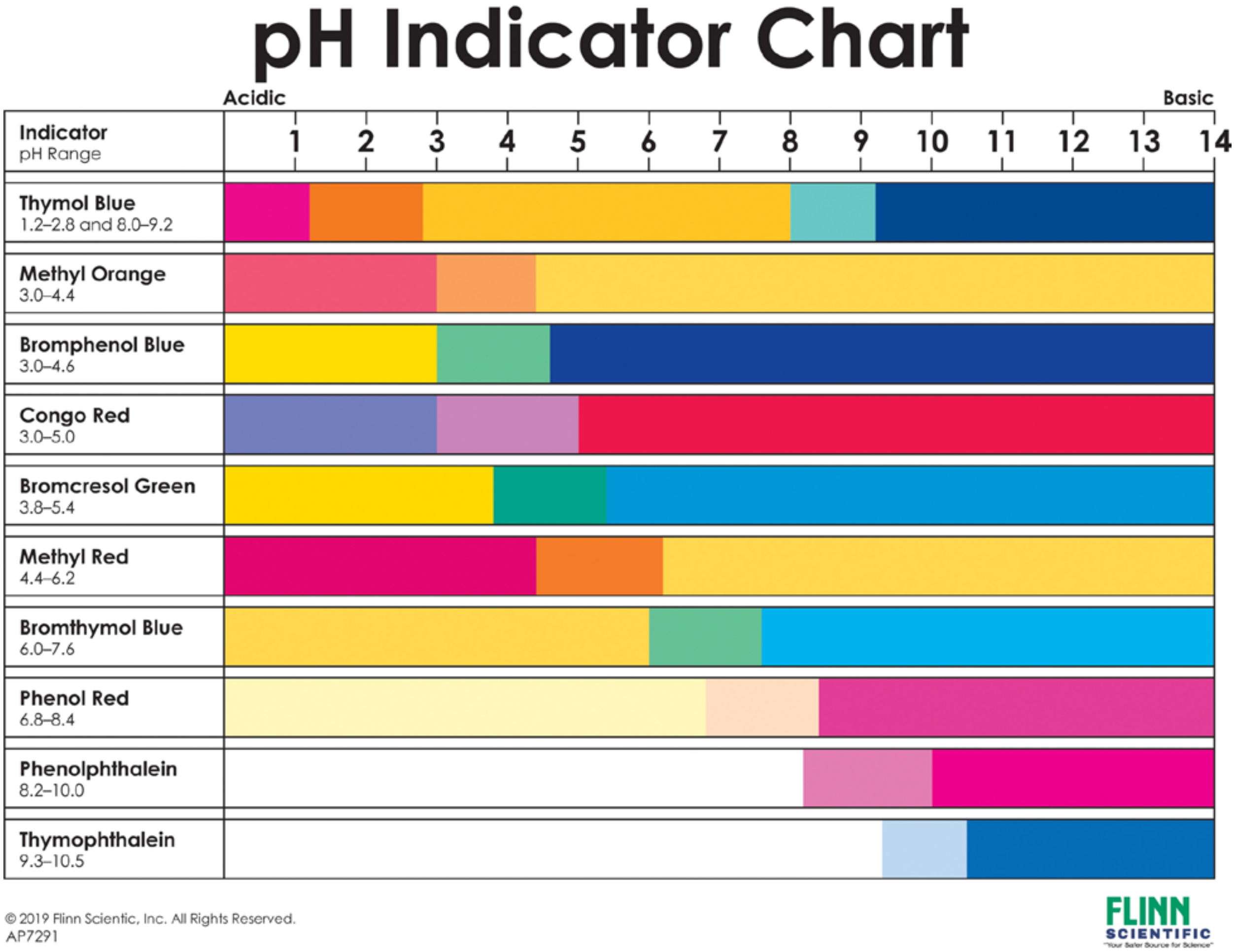


Figure C.2. pH indicator color chart ("pH Indicator Chart" 2019).

Results and Discussion

The results of each pH indicator at each time point are compiled by sample in Tables D1 through D11. pH indicator dyes applied as sprays to solid RCA sample do not produce consistent, recognizable color changes. Conversely, the concentration indicator dyes in water applied to RCA produce consistently vibrant color indications, that are not clearly correlated with pH risk associated with the given RCA sample. The use of Litmus paper to evaluate leachate pH at the designated time points does not produce consistent, nor distinguishable color changes that can be correlated with pH risk associated with the given RCA sample.

pH indicator dyes combined with leachate extracts at the designated time points are the most consistent and clear qualitative method to evaluate RCA leachate pH of the methods tested in this report. Leachate extractions made for pH indicator dyes at the 1 minute, 10 minute, 30 minute, and 120 minute time points can be used, but 24 hour time point often yields the clearest color indication (Figure C.3). Additionally, the 24-hour leachate pH has been correlated with portlandite content and peak pH of RCA (Chapter II).

Conclusions

Although a pH electrode is the preferred option for determining RCA leachate pH due to the accuracy and repeatability, pH indicator dyes present a straightforward, inexpensive method to characterize RCA leachate pH in the field. Phenolphthalein, thymolphthalein, and thymol blue dyes applied to leachate extracted from a batch reactor after 24 hours of contact time may be sufficient to characterize RCA and estimate associated leachate pH risk. The use of Litmus paper or spray applications of pH indicator dyes is not recommended.

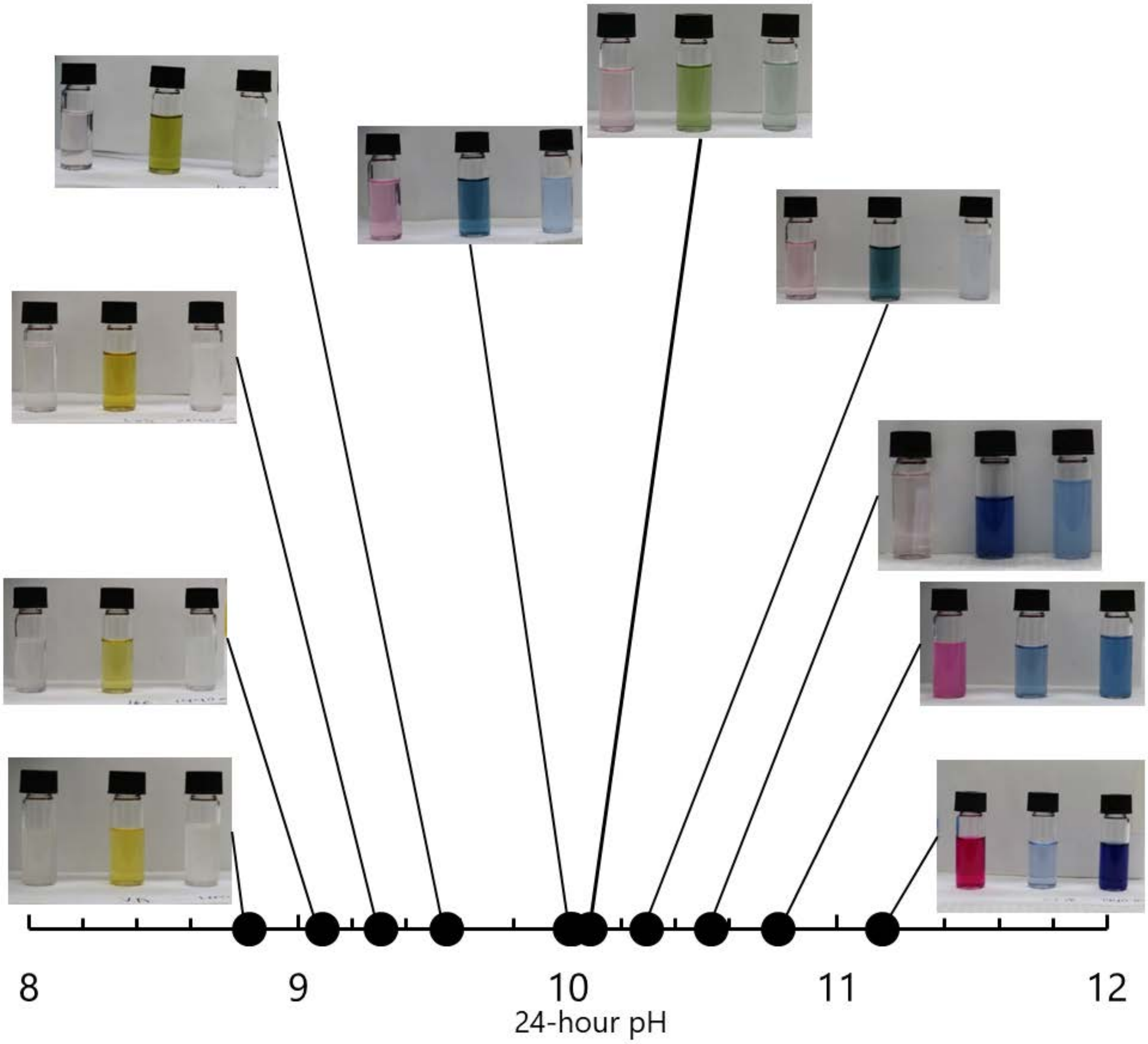


Figure C.3. pH indicators corresponding to 24-hour pH.

Table C.1. pH indicator results for sample CT18.

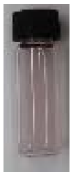
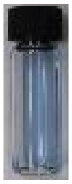
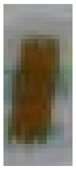
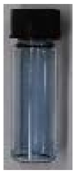
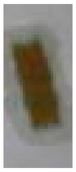
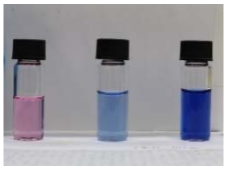
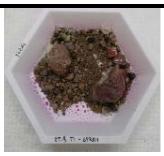
CT18	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All dyes
1 min	9.632					
10 min	10.245					
30 min	10.323					
120 min	10.9					
1440 min	11.17					
Spray						
Dye in water						

Table C.2. pH indicator results for sample PR18.

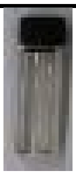
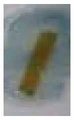
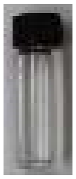
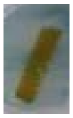
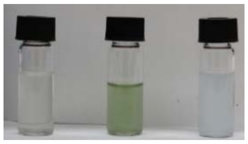
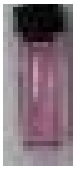
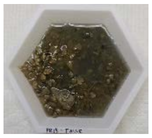
PR18	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	10.06					
10 min	10.137					
30 min	10.184					
120 min	10.186					
1440 min	10.086					
Spray						
Dye in water						

Table C.3. pH indicator results for sample ML18.

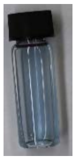
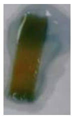
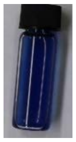
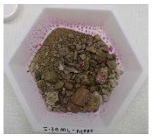
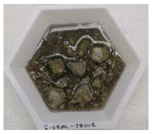
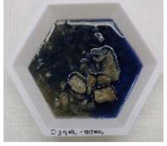
ML18	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	10.338					
10 min	10.455					
30 min	10.502					
120 min	10.668					
1440 min	10.784					
Spray						
Dye in water						

Table C.4. pH indicator results for sample WS18.

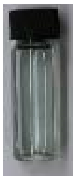
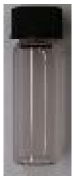
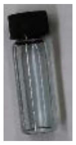
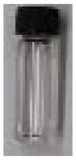
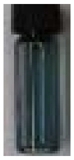
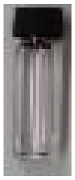
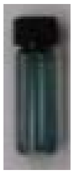
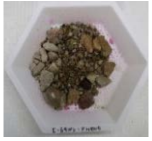
WS18	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.852					
10 min	10.03					
30 min	10.065					
120 min	10.059					
1440 min	10.008					
Spray						
Dye in water						

Table C.5. pH indicator results for sample CT17.

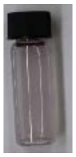
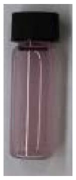
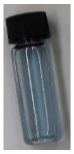
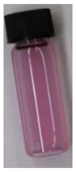
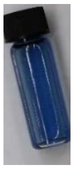
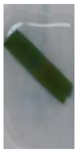
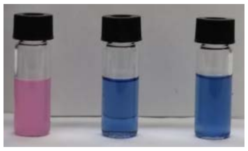
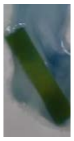
CT17	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	10.015					
10 min	10.084					
30 min	10.095					
120 min	10.554					
1440 min	10.021					
Spray						
Dye in water						

Table C.6. pH indicator results for sample OC17.

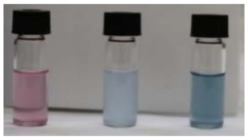
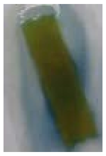
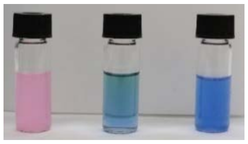
OC17	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	10.169					
10 min	10.297					
30 min	10.283					
120 min	10.742					
1440 min	10.534				--	
Spray						
Dye in water						

Table C.7. pH indicator results for sample WA17.

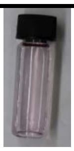
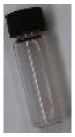
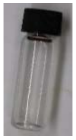
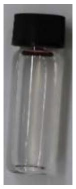
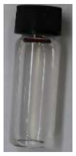
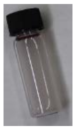
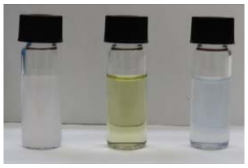
WA17	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.11					
10 min	9.663					
30 min	9.863					
120 min	9.982					
1440 min	10.293					
Spray						
Dye in water						

Table C.8. pH indicator results for sample 16C.

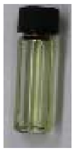
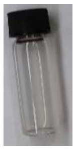
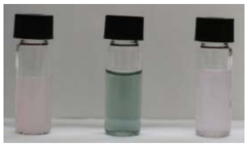
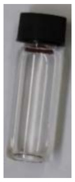
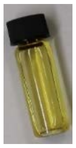
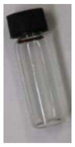
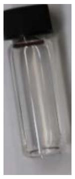
16C	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.594					--
10 min	9.851					
30 min	9.753					
120 min	9.675					--
1440 min	9.089					
Spray						
Dye in water						

Table C.9. pH indicator results for sample 16D.

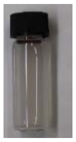
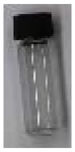
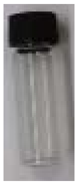
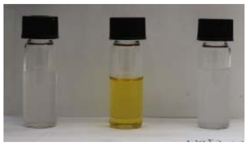
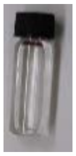
16D	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.66					
10 min	9.852					
30 min	9.809					
120 min	9.704					
1440 min	9.308					
Spray						
Dye in water						

Table C.10. pH indicator results for sample 16P.

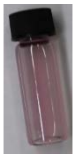
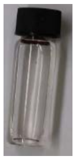
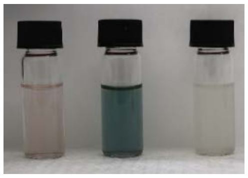
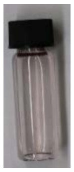
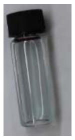
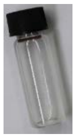
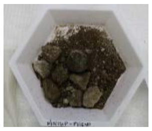
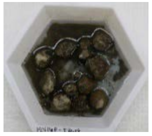
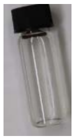
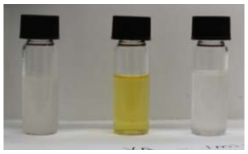
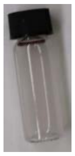
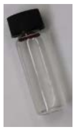
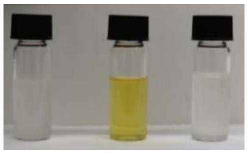
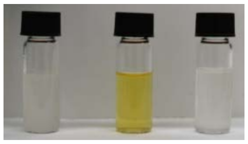
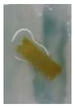
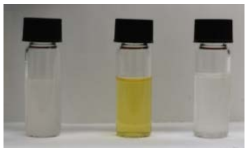
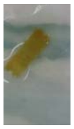
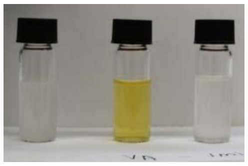
16P	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.876					
10 min	9.96					
30 min	9.972					
120 min	9.893					
1440 min	9.554					
Spray						
Dye in water						

Table C.11. pH indicator results for sample VA.

VA	Probe	Phenolphthalein	Thymol Blue	Thymolphthalein	Litmus Paper	All Dyes
1 min	9.672					
10 min	9.721					
30 min	9.741					
120 min	9.652					
1440 min	8.821					
Spray						
Dye in water