Assessing the Chemical and Physical Characteristics of Aged Recycled Concrete Aggregate in Road Construction

By

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EXECUTIVE SUMMARY

The use of recycled concrete aggregates (RCA) in pavement construction applications is well established and successful, particularly its use as a granular and/or stabilized base course. However, leaching of harmful substances, such as heavy metals, has been identified. The leaching mechanisms are strongly dependent on pore water pH conditions, and therefore the carbonation level (aging) of the concrete material. As a result, developing an understanding of the chemical and physical processes involved in the aging of RCA is crucial in assessing its environmental impacts.

This thesis examines the chemical and physical properties of aged RCA recovered from the MnROAD highway construction study site, in central Minnesota. In Chapter 1, a review of the existing body of academic and professional literature is provided. This chapter describes fundamental misconceptions of concrete and leachate chemistry in the existing literature. Furthermore, Chapter 1 is intended to provide the reader with sufficient knowledge of the concepts important to understand the physical and chemical processes involved in aged RCA use. Chapter 2 is a forensic examination of the physical and chemical characteristics of an aged RCA material, which was initially characterized by Chen at al. (2012, 2013) prior to an eight-year field deployment at a research facility in Minnesota. Chapter 2 provides a unique opportunity to determine the changes in RCA, used as subbase material, over a significant period of field deployment. Chapter 3 of this thesis is a study of the impact of contact time on RCA leachate pH and alkalinity in a laboratory setting. This chapter aims to address some oversights in conventional laboratory methodologies traditionally used to determine leachate chemistry, by more effectively simulating field conditions.

The literature review conducted in Chapter 1 identified that the existing body of work, while extensive, is generally lacking on several fronts. Particularly, previous laboratory-based studies conducted on the topic have used either contact times, or liquid to solid-ratios that are not representative of real-world RCA applications. Furthermore, the existing academic and professional literature characterizing leachate produced from contact with RCA uses the terms “high pH” and “alkaline/alkalinity” interchangeably. This subsequently leads to a great deal of confusion regarding the chemistry of RCA leachate, which has both a high pH and is high in alkalinity

The forensic examination of the aged MnROAD RCA, conducted in Chapter 2, showed an increase in the acid neutralization capacity (ANC) of the material over the eight-year field deployment. From the ANC curves, the finer particles continued to show a higher acid neutralization capacity than the coarser particles. Furthermore, the ANC curves indicated significant carbonation in the fine fractions of the aged MnROAD RCA. The increase in carbonation was supported by X-ray diffraction and thermogravimetric analyses.

The assessment of the impact on leachate chemistry of contact time with aged MnROAD RCA, conducted in Chapter 3, showed a slight increasing trend of effluent pH over time. Furthermore, a comparison of the effluent pH over a six-hour test duration showed significantly lower results, for both base course RCA and subbase soils, than material pH values from conventional batch test methods adapted in the study in Chapter 2. The results from this assessment supported the hypothesis that contact time and particle abrasion play a significant role in determining leachate pH in field conditions.

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LIST OF ACRONYMS

AASHTO	American Association of State Highway and Transportation Officials
ACPA	American Concrete Pavement Association
ANC	Acid neutralization capacity
ASTM	American Society for Testing and Materials
BNC	Base neutralization capacity
CCB	Continuing calibration blanks
CCV	Continuing calibration verifications
C&D	Construction and debris
C-S-H	Calcium silicate hydrate
EC	Electrical Conductivity
ICP-OES	Inductively coupled plasma optical emission spectrometry
MnDOT	Minnesota Department of Transportation
ODOT	Ohio Department of Transportation
ORP	Oxidation and Reduction Potential
PCC	Portland cement concrete
ppm	Parts per million
RCA	Recycled concrete aggregate
RCM	Recycled concrete material
rpm	Revolutions per minute
TGA	Thermogravimetric analysis
USCS	Unified Soil Classification System
WisDOT	Wisconsin Department of Transportation
XRD	X-ray diffraction

INTRODUCTION

The ever-increasing reconstruction of highway systems in the United States is causing a growth in the demand of virgin aggregate, and in the energy required to process and transport these materials (Lee et al., 2010). In 2016, 1.48 billion tons of crushed stones were produced for construction in the United States. Of the 1.54 billion tons of crushed stone consumed in the United States in 2016, it is estimated that around 76% was used as construction material, mostly for road construction and maintenance (Willet, 2016). Additionally, approximately 375 million tons of concrete waste was produced in 2014 from aging infrastructure (U.S. EPA, 2016). Disposal of these waste materials in landfills has been the traditional solution. However, various restrictions to their safe disposal and sustainability considerations have led to alternative ways of reusing demolition wastes through recycling.

Recycled concrete aggregate (RCA), also known as reclaimed concrete material (RCM), consists of high quality, well-graded aggregates bonded by hardened cementitious paste. The aggregates comprise approximately 60 to 75 percent of the total volume of concrete (Chesner et al., 1998). RCA is generated from the demolition of Portland Cement Concrete (PCC) in roads and other concrete structures. After demolition and excavation, the RCA is typically either hauled to a stockpiling facility (e.g., aggregate supplier), landfilled, or reused on-site. At the stockpiling facility or at the site, the RCA is crushed to the desired gradation and reinforcing steel is removed so that it can serve as high-quality base or subbase material (Chesner et al., 1998; Edil et al., 2012). RCA is processed exclusively through crushing operations, and is very angular in shape

(Chesner et al., 1998). The particle size distribution of an RCA can vary widely; with a lower particle density and greater angularity than would normally be found in more traditional virgin base aggregates. Residual mortar and cement paste are typically found on the surface of the RCA, as well as contaminants associated with construction and demolition debris (Kuo et al., 2002).

The use of RCA in many aggregate applications in pavement construction is well established and successful, particularly its use as a granular and stabilized base (Del Ponte, 2016). This is primarily due to its high durability; it is resistant to freeze/thaw cycling and a high pore water pH that can slow corrosion rates of embedded steel. The residual cementitious material in RCA provides bonding of the base material, providing good load transfer when placed on weaker subgrade. Additionally, the lower compacted unit weight of RCA aggregates compared to conventional aggregates results in higher yield (greater volume for the same weight).

The use of RCA as a substitute for natural aggregate can also reduce costs. The majority of costs associated with the use of natural aggregates are incurred from transportation of the material from the quarry to the job site (Robinson & Brown, 2002). The use of RCA allows old concrete pavement material to be recycled on-site, reducing the transportation costs incurred from hauling virgin material significantly. Furthermore, the re-use of the construction and debris (C&D) wastes eliminates the costs associated with mining or tipping fees. The main additional costs incurred are those associated with crushing, sorting, and handling the material on-site.

The use of RCA in highway construction has also led to significant environmental savings. Life-cycle analyses on the use of recycled highway construction material, including RCA, have shown significant savings in carbon dioxide emissions, energy consumption and water consumption. In 2012, WisDOT used approximately 1.95 million tons of recycled material (of which ~50% was RCA), and conserved approximately 250,000 kg of water, 750 TJ of energy and 46,000 Mg of CO_2 emissions (Del Ponte et al., 2017). These substantial environmental savings coupled with its advantageous mechanical properties make RCA a commonly used aggregate material in construction.

Despite these financial and environmental benefits, in many cases the acceptance of RCA in the market seems to be low, due to possible fluctuations in physiochemical properties (density, grading, cement paste content, leaching properties, etc.) (Engelsen et al., 2017). Additionally, characteristic leaching of harmful substances, such as heavy metals, have been identified in several studies (Engelsen et al., 2009, 2010; Galvín et al., 2014; Kosson et al., 2014). The leaching mechanisms are strongly dependent on pH and therefore the carbonation level (aging) of the concrete material. As a result, understanding the chemical and physical processes involved in the aging of RCA is crucial to assessing its environmental impacts.

OVERVIEW OF THESIS

This thesis aims to assess the environmental impacts of high pH leachate generated from recycled concrete aggregates (RCA) in highway construction. In Chapter 1, a review of the existing body of academic and professional literature is provided. This chapter identifies fundamental misconceptions of concrete and leachate chemistry in the existing literature. Furthermore, Chapter 1 is intended to provide the reader with sufficient knowledge of the fundamental concepts important to understand the physical and chemical processes involved in aged RCA use. Chapter 2 of this thesis is a forensic examination of the physical and chemical characteristics of an aged RCA material, which was initially characterized by Chen at al. (2012, 2013), prior to an eight-year field deployment at a research facility in Minnesota. Chapter 2 provides a unique opportunity to determine the changes in RCA used as subbase material over a significant period of field deployment. Chapter 3 of this thesis is a study of the impact of contact time on RCA leachate pH and alkalinity in a laboratory setting. This chapter aims to address some oversights in conventional laboratory methodologies traditionally used to determine leachate chemistry, by more effectively simulating field conditions.

1. BACKGROUND AND REVIEW OF EXISTING BODY OF ACADEMIC AND PROFESSIONAL LITERATURE

There is interest in determining the environmental impacts of using recycled concrete aggregate (RCA) in highway construction. This chapter aims to provide a critical review of the existing academic and professional literature that assesses solid-phase and leachate chemistry relating to RCA used in highway construction as base-course material.

The existing body of work, while extensive, is generally lacking on several fronts. Only two studies have extensively characterized the leachate chemistry from RCA utilized in roadbed applications. Additionally, lab based studies have generally used either contact times, or liquid to solid-ratios that are not representative of real-world RCA applications. Furthermore, no published studies examining neutralization of high pH/alkalinity RCA leachate by common sub-grade soils exist. This chapter contains an individual review and summary of several studies that have helped establish the basic conceptual understanding of RCA leachate chemistry.

In addition to a critical review of the existing literature, this chapter also provides a background of the chemical concepts involved in concrete aging (carbonation), and leachate pH and alkalinity. The existing academic and professional literature characterizing leachate produced from contact with RCA uses the terms “high pH” and “alkaline/alkalinity” interchangeably. Subsequently, this leads to a great deal of confusion regarding the chemistry of RCA leachate, which has both a high pH and is high in alkalinity. pH refers to the concentration of H^+ in solution–when pH is high the concentration is low. While alkalinity is a capacity term that refers to a solution’s ability to resist pH change. This has practical implications; for example, to decrease the pH of 1 liter of RCA leachate with a pH of 11 and an alkalinity of 1,000 milliequivalents to a pH of 8, it would require thousands of liters of pH 5 rainwater. Establishing such fundamental chemical concepts surrounding the application of RCA in highway construction is imperative for better understanding of the environmental impacts of using the material.

1.1 BACKGROUND

1.1.1 Concepts surrounding cement carbonation

Atmospheric carbon dioxide reacts with hydrated cement paste in the presence of moisture (Neville, 2011). This reaction can affect both the microstructure and durability of reinforced concrete. The pore solution in concrete initially has a high pH (usually >10) due to the dissolution of portlandite ($Ca(OH)_2$) in the cement paste. Carbonation of the hydrated Portland cement paste reduces the pH of the pore solution to values lower than 9 (as low as 8.3) (Papadakis et al., 1992). In addition to a drop in pore water pH, other notable changes in the properties of the concrete due to carbonation include changes in porosity, mechanical properties and appearance of cracks (Johannesson & Utgenannt, 2001). Furthermore, the ability of calcium bearing phases of cement paste to react with carbon dioxide can be advantageous since it inhibits leaching of alkali solids in RCA applications. It is therefore important to understand the way that CO_2 reacts with the main phases in cement paste, and the factors that influence this process. The two main phases in Portland cement paste outlined are portlandite (calcium hydroxide) and calcium-silicate hydrate (C-S-H).

1.1.1.1 Portlandite carbonation

Calcium hydroxide is the main phase in cement most commonly assumed to readily react with atmospheric carbon dioxide. Carbon dioxide may react with dissolved or solid calcium hydroxide, resulting in the precipitation of calcium carbonate in the pore spaces (García-González et al., 2006), as shown in Equation 1.

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O} \qquad \text{Equation 1}$$

According to García-González et al. (2006), carbonation of calcium hydroxide occurs in three main steps: (1) dissolution of calcium hydroxide; (2) absorption of $CO_{2(g)}$ and the formation of carbonate ions; (3) chemical reaction and precipitation.

Which calcium carbonate polymorph will form as a result of Equation 1 is dependent on which of two kinds of factors are dominant: kinetic or thermodynamic factors (Šavija & Luković, 2016). $CaCO_3$ will precipitate as aragonite or vaterite if kinetic factors predominate. Both these polymorphs will eventually convert to calcite, the more stable polymorph (Arandigoyen et al., 2006). Alternatively, calcite will precipitate if thermodynamic factors predominate.

1.1.1.2 Calcium-silicate-hydrate (C-S-H) carbonation

In a study by Groves et al. (1990), it is shown that although calcium hydroxide initially reacted more rapidly to form calcium carbonate, its rate of reaction declines over time, and is eventually overtaken by the rate of reaction of C-S-H. Hence, it is also important to understand the way CO_2 reacts with C-S-H. In the carbonation of C-S-H gel, calcium ions removed from the gel react with carbon dioxide, resulting in the formation of calcium carbonate and amorphous silica gel, as shown in Equation 2 below.

$$(\mathrm{CaO})_x(\mathrm{SiO_2})(\mathrm{H_2O}) + x\mathrm{CO_2} \rightarrow x\mathrm{CaCO_3} + \mathrm{SiO_2}(\mathrm{H_2O})t + (z-t)\mathrm{H_2O}$$

Equation 2

Carbonation of C-S-H generally results in the formation of calcite, aragonite and vaterite (Groves et al., 1991; Morandeau & White, 2015).

1.1.2 Concepts surrounding pH and alkalinity of aqueous solutions

1.1.2.1 pH

The technical definition of pH is the negative log of H^+ activity in an aqueous solution (Equation 3). The activity of an ion in solution can be related to the concentration of an ion in solution by Equation 4, where γ is the activity coefficient. Typically, γ = 1 for most freshwater solutions, therefore activity and concentration can be used interchangeably in most situations. However, in high ionic strength solutions (e.g., RCA leachate) γ decreases, hence activity and concentration are not necessarily equal. Typically, γ is calculated using either the Debye-Hückel or Davies equations. These equations and additional details on these calculations are available in many textbooks including Brezonik & Arnold (2011) or Benjamin (2014).

$$\mathrm{pH} = -\log a_{H^+} \qquad \text{Equation 3}$$

$$a_{H^+} = \gamma c_{H^+} \qquad \text{Equation 4}$$

Therefore, the pH of a solution is a measure of the concentration of protons in a solution. pH values commonly range for 1 – 14, with 7 considered “neutral pH”. pH values above 7 are often referred to as basic, while values below 7 are consider acidic.

1.1.2.2 Alkalinity

Alkalinity describes the acid neutralizing capacity (ANC) of a solution, which is the total amount of acid that can be consumed by the bases in a solution (Equation 5). In most aqueous solutions, strong bases are generally limited to OH^- (hydroxide) and strong acids are limited to H^+ (protons). In RCA leachate, the weak base concentration plays a critical role in determining the alkalinity of the solution. These weak bases commonly include CO_3^{2-} (carbonate) and HCO_3^- (bicarbonate). Hence, a solution with a pH of 11, but with a low carbonate and bicarbonate concentration, can have a lower alkalinity than a solution with a pH of 9.5 and a high concentration of carbonate/bicarbonate.

$$\mathrm{ANC} = \mathrm{Alkalinity} = \sum[\text{strong bases}] + \sum[\text{weak bases}] - \sum[\text{strong acids}]$$

Equation 5

1.1.2.3 Acidity

The converse of alkalinity is acidity or base neutralizing capacity (BNC). Similar to alkalinity, while a solution with a low pH may have a high acidity, this is not always the case and is generally a function of the concentration of weak acids in the solution (Equation 6). One example of this phenomenon is rainwater. While the pH of rainwater is often near 5, meaning that is acidic, rainwater's acidity is actually quite low.

$$\mathrm{BNC} = \mathrm{Acidity} = \sum[\text{strong acids}] + \sum[\text{weak acids}] - \sum[\text{strong bases}]$$

Equation 6

Weak acids in the system generally include H_2CO_3 and HCO_3^-, while H^+ is the only strong acid and OH^- is the only strong base.

These concepts are critical in understanding the potential environmental threat posed by high pH and high alkalinity leachate generated from RCA. For example, if 1 L of RCA leachate at a pH of 11 were mixed with 1 L of rainwater at pH 5, the pH of the resulting mixture would remain near 11. Depending on the exact chemical composition of the RCA leachate, several hundred liters of rainwater may need to be added to 1 L of leachate before the pH of the resulting mixture is below 9.

1.1.3 Chemistry of RCA Leachate

The generation of high pH leachate from RCA is generally driven by the dissolution of $Ca(OH)_2$ (portlandite) according to Reaction 1. This releases a calcium ion (Ca^{2+}), and two hydroxide ions (OH^-) then go on to consume a proton (Reaction 2), resulting in an elevated solution pH.

$\mathrm{Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-}$ Reaction 1

$\mathrm{2H^+ + 2OH^- \rightarrow 2H_2O}$ Reaction 2

At elevated pH values (e.g., >9), atmospheric CO_2 readily dissolves into water and may react with OH^- to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) as detailed in reactions 3-6.

$\mathrm{CO}_{2(g)} \leftrightarrow \mathrm{CO}_{2(aq)}$ Reaction 3

$\mathrm{CO}_{2(aq)} + \mathrm{H_2O} \leftrightarrow \mathrm{H_2CO_3}$ Reaction 4

$\mathrm{H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O}$ Reaction 5

$\mathrm{HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O}$ Reaction 6

$$\mathrm{CaOH}_{(s)} + \mathrm{CO}_3^{2-} \leftrightarrow \mathrm{CaCO}_{3(s)} + \mathrm{OH}^- \qquad \text{Reaction 7}$$

It is important to note, that although each of these reactions consumes an OH^-, the alkalinity of the solution does not decrease. Thus, when water reacts with portlandite, both the pH and the alkalinity will increase until either the portlandite is exhausted or it reacts with a dissolved constituent to form a less soluble mineral. Consequently, portlandite may react with dissolved CO_3^{2-} and/or HCO_3^- to form $CaCO_{3(s)}$ (Reaction 7). Calcium carbonate can also occur when dissolved Ca^{2+} reacts with dissolved CO_3^{2-}. In either case, the formation of $CaCO_{3(s)}$ can limit the long-term production of high pH leachate, as the dissolution of carbonate in the presence of atmospheric carbon dioxide produces a solution with a pH of approximately 8.2. In comparison, dissolution of portlandite in the presence of atmospheric carbon dioxide produces a solution with a pH>12 and extremely high alkalinity.

In addition to high pH, other potential environmental risks associated with alkaline effluent and heavy metal leaching from RCA have been reported by various state departments of transportation (Fitch, 2003; Sadecki at al., 1996; Steffes, 1999). Furthermore, heavy metals can also leach from concrete additives (e.g., fly ash and ordinary Portland cement) and natural stone (ACPA, 2009). Because cement phases (e.g., calcium silicate hydrate, portlandite, and ettringite) in RCA have the potential to generate alkaline leachate, the impact of pH as a master variable affecting heavy metal leaching from RCA is a continued focus of research (Engelsen et al., 2006; Mulugeta et al., 2011).

1.2 LITERATURE REVIEW

The existing body of academic and professional literature is critically reviewed in this chapter of the thesis. While it is extensive, the work is generally lacking on several fronts. Only two studies (Chen et al., 2013; Engelsen et al., 2009, 2010) have extensively characterized the chemistry of leachate produced from recycled concrete aggregate (RCA) utilized in highway applications. These studies incorporated long-term field leachate behavior in their studies. Leachate chemistry, including pH and inorganic constituent concentrations, were monitored in the field sites and compared with lab tests.

There have also been several laboratory studies of the chemistry of leachate produced from RCA. These studies range in complexity from simple batch tests (Mulligan, 2002; Ohio Department of Transportation, 2002) to “box tests” (Mulligan, 2002; Steffes, 1999), which are periodically saturated and then drained to field capacity, to continuously leached column tests (Chen et al., 2013). These lab-based studies have generally used either contact times, or liquid to solid-ratios that are not representative of real-world RCA applications. Generally, both lab and field studies also lack a thorough analysis of alkalinity of the leachate produced through contact with RCA. As a result, the existing literature characterizing leachate produced from contact with RCA uses the terms “high pH” and “alkaline/alkalinity” interchangeably. This leads to a great deal of confusion regarding the chemistry of RCA leachate, which has both high pH and high alkalinity.

In terms of environmental relevance, the lab-based tests that undergo periodic saturation and draining are the most relevant. However, when evaluating the results of these types of studies it is important to consider the amount of time that the RCA is allowed to remain saturated. In general, the shorter the amount of time, the more representative the experiment will be of the leachate produced from RCA utilized as a base course in road construction or while stockpiled. However, the results from experiments with longer saturation times (e.g. batch tests, continuously leached columns) will be more representative of environments where drainage is inadequate. Longer saturation times will result in the dissolution of protective $CaCO_3$ minerals that prevent water from interacting with the underlying cement phases.

Steffes, R. (1999). ***Laboratory Study of the Leachate from Crushed Portland Cement Concrete Base Material*****. Retrieved from http://publications.iowa.gov/id/eprint/19954**

The objective of this study was to simulate the drainage of distilled water through crushed RCA base-course material and record the resultant change of pH in the water over a one-year period. Three boxes were made of Plexiglas measuring 6 inches wide, by 6 inches high, by 48 inches long, with an inlet and an outlet allowing water to be added and drained. The boxes varied in content/distribution of fines. The first box had a 2-inch layer of fines (32 lbs) at the bottom, covered by a 4-inch layer (60lbs) of well-graded material. The second box had 10 lbs. of fines and 96 lbs of well-graded material mixed together. The third box was filled with 95 lbs of well-graded material. The well-graded material in all three boxes was classified as a #12-gradation aggregate, which is a granular sub base of 1.5 inches or smaller. The size of the fines was not described in the report; however, it is commonly considered less than 0.075 mm. Initially, distilled water was introduced into the boxes until the material was saturated. It was then allowed to remain saturated for 24 hours, after which the column was drained to field capacity. After seven days, 500mL of distilled water was poured into the upper end of the box and immediately allowed to drain out. Leachate drainage was typically completed in about two to five minutes, after which the pH of the leachate was measured. This testing cycle was repeated for one year.

The initial pH range of the leachate was around 12.5, which dropped to 11.5 after the first 10 weeks. The box containing the 2 inches of fines at the bottom consistently produced leachate with the lowest pH; however, it stabilized around pH 11. The pH of the leachate from the remaining two boxes remained above 11.5 even after 1 year of repeated exposure. The alkalinity of the leachate, or the solid-phase characteristics of the base material were not measured as part of this test.

From field observations related to this test, the report concluded that (1) the high pH levels of drainage would continue for many years following construction, (2) the high pH drainage water would leave precipitates at the edge of drain outlets, and (3) the high pH of the drainage water could kill or impede grass growth at the drain outlet.

Ohio Department of Transportation. (2002). *Recycled Portland Cement & Concrete/Soil Mixtures and pH*. Retrieved from https://www.dot.state.oh.us/Divisions/ConstructionMgt/Materials/In House Research/RPCC.pdf

This study was designed to investigate the ability of soil to reduce the pH of water exposed to RCA, by mixing with soil. Two different soils were investigated in this study, with each soil having initial material pH values of 9.4 and 4.75. The soils were run through a #8 sieve while the RCA was run through a 1-inch sieve. Pure soil, as well as soil/RCA mixtures ranging from 0% to 50% soil, at intervals of 10%, were investigated. Distilled water was added to each sample and shaken until the sample was saturated, after which the sample was left saturated for 21 days. Leachate samples were withdrawn after 48 hours, 120 hours, 7 days, 14 days and 21 days, and their pH values were measured upon collection.

The soil pH did not have an appreciable impact on the pH of the water in contact with the material. In all the cases studied, the pH of the leachate was lowest after 48 hours and increased steadily over the duration of the experiment. Initial pH values ranged from 9.2 to 12, while final pH values ranged from 9.5 to 12. Generally, the samples with the lowest final pH had the higher amounts of the pH 9.4 soil added.

This study revealed that the soil pH is not indicative of a soil's ability to decrease the pH of leachate from RCA. One of the likely factors that control a soil's ability to neutralize high pH leachate is the quantity and solubility of clay minerals it contains. Furthermore, this study also highlights the impact of contact time on leachate pH. A well-drained highway base layer would reduce the contact time between the RCA and pore-water, hindering dissolution.

Sadecki, R. W., Busacker, G. P., Moxness, K. L., Faruq, K. C., & Allen, L. G. (1996). *An Investigation of Water Quality in Runoff from Stockpiles of Salvaged Concrete and Bituminous Paving*. Retrieved from https://ntrl.ntis.gov/NTRL/dashboard/searchResults/titleDetail/PB97133177.xhtml

This study aimed to determine the presence and characteristics of leachate constituents occurring in water runoff from salvaged pavement stockpiles. The study constructed two experimental outdoor stockpiles of coarse concrete. One pile consisted of material passing a 19.0 mm sieve but being retained on the 4.75 mm sieve; and the second consisted of finer concrete material passing the 4.75 mm sieve. Each material was placed in 6.1-meter cone-shaped stockpiles, placed on a circular pad of coursegrained material. The pad was covered with an impermeable membrane and graded to direct the water flow to the edges of the piles. Leachate from the piles flowed through a sampling and flow monitoring system. The stockpiles were left in place for little longer than a year. The study assessed the pH, alkalinity and the inorganic contaminant concentrations in the leachate over the study period.

The median pH values of leachate from the coarse concrete was 9.8, with a minimum of 8.5 and a maximum of 10.9. Meanwhile, the pH of leachate from the finer concrete was 9.3, with a minimum pH of 7.4 and a maximum of 12.2. The study revealed that the long-term environmental concern results from suspended/total dissolved solids and leachate pH. The authors suggested that the acidity from the rainwater might be enough to neutralize the pH of the leachate; however, this hypothesis is incorrect, as it does not account for the high alkalinity of leachate generated from RCA stockpiles.

Mulligan, S. (2002). Recycled Concrete Materials Report. *Ohio Department of Transportation*. Retrieved from https://www.dot.state.oh.us/Divisions/ConstructionMgt/Materials/In House Research/RCM1.PDF

This study by the Ohio Department of Transportation (ODOT) investigated the pH of water in contact with RCA, and compared the results to the pH of water in contact with virgin aggregates under the same conditions. Past problems encountered by ODOT with using RCA as an aggregate base included high pH runoff and tufa formation (calcium deposits) clogging drains and filter fabrics. This study used a “bucket test” and a “box test” to investigate the pH of water in contact with aggregate. The “bucket test” consisted of soaking various aggregates in water, conducting several trials with different variations in size or gradation of material, mixing of materials (RCA and limestone aggregates) at different ratios, and periodically changing water in the bucket. The “box test” consisted of simulating an aggregate road base complete with drainage hoses and filter fabric, and percolating water through the system. In both sets of tests, only the pH of the leachate was measured; no studies on the alkalinity of the leachate were conducted.

Results from both the “bucket test” and “box test” indicated pH values from run-off water in contact with RCA of at least 10, exceeding the pH limit for run-off water of 9 according to EPA regulations. Nonetheless, results from the “bucket test” indicated that mixing limestone with RCA at a ratio of 60% (or more) limestone to 40% (or less) RCA would result in leachate water with a pH less than 9, below EPA regulations. However, no experimental details were provided in this report, only a summary of the conclusions.

The pH or water in equilibrium with limestone is ~8.2; however, the presence of unreacted portlandite would result in a pH exceeding 9. This clearly indicates that the addition of limestone both acts as a buffer of the pH in solution, and results in the passivation of unreacted portlandite via formation of a protective carbonate layer. It is possible that by optimizing this system one could increase the proportion of RCA in the mixture, while maintaining compliance with pH regulations.

Engelsen, C. J., Van Der Sloot, H. A., Wibetoe, G., Petkovic, G., Stoltenberg-Hansson, E., & Lund, W. (2009). Release of major elements from recycled concrete aggregates and geochemical modelling. *Cement and Concrete Research*, *39*(5), 446–459. https://doi.org/10.1016/j.cemconres.2009.02.001

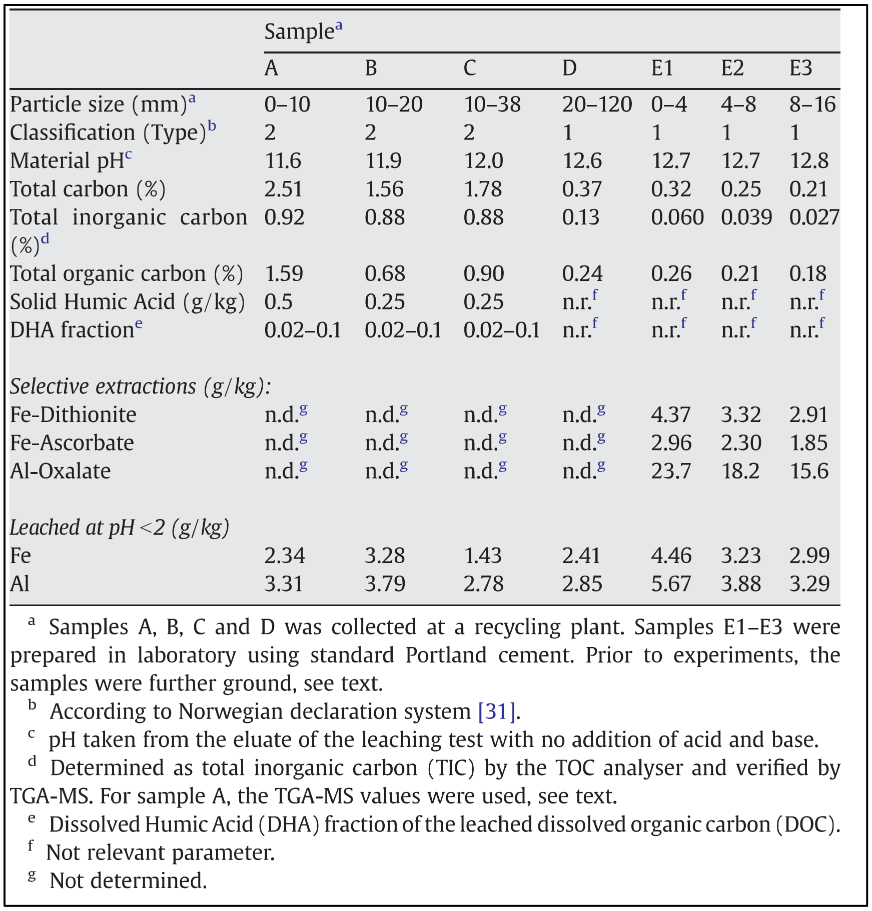
Engelsen, C. J., Van Der Sloot, H. A., Wibetoe, G., Justnes, H., Lund, W., & Stoltenberg-Hansson, E. (2010). Leaching characterisation and geochemical modelling of minor and trace elements released from recycled concrete aggregates. *Cement and Concrete Research*, *40*(12), 1639–1649. https://doi.org/10.1016/j.cemconres.2010.08.001

These studies examined the pH-dependent leaching characteristics for different types of recycled concrete aggregates, including real construction debris and freshly crushed concrete samples prepared in laboratory. The study investigated five different recycled concrete aggregates (RCA) batches, shown in Table ***1-1***. Sample batches A, B and C, each approximately 500 kg, were collected from the recycling facility BA Gjenvinning in Oslo. Sample batch D originated from a section of the highway E6 (25 km south of Oslo) that was constructed with concrete pavement in the early 1980s. Sample batch E was prepared in the laboratory using Portland cement, natural aggregate and admixture. The samples were all thoroughly characterized prior to conducting the experiments.

The main goal of this study was to determine the pH-dependent leaching patterns of metals, and not necessarily to assess the generation of high pH/alkalinity leachate. However, the material pH shown in Table ***1-1*** below was quite high for all RCA samples

(11.6 – 12.8), indicating that all samples contained appreciable amounts of portlandite. Alkalinity of the leachate was not measured as part of these studies.

Table 1-1 List of sample batches and sample properties. Table copied from Engelsen et al. (2009).



	Sample[a]						
	A	B	C	D	E1	E2	E3
Particle size (mm)[a]	0–10	10–20	10–38	20–120	0–4	4–8	8–16
Classification (Type)[b]	2	2	2	1	1	1	1
Material pH[c]	11.6	11.9	12.0	12.6	12.7	12.7	12.8
Total carbon (%)	2.51	1.56	1.78	0.37	0.32	0.25	0.21
Total inorganic carbon (%)[d]	0.92	0.88	0.88	0.13	0.060	0.039	0.027
Total organic carbon (%)	1.59	0.68	0.90	0.24	0.26	0.21	0.18
Solid Humic Acid (g/kg)	0.5	0.25	0.25	n.r.[f]	n.r.[f]	n.r.[f]	n.r.[f]
DHA fraction[e]	0.02–0.1	0.02–0.1	0.02–0.1	n.r.[f]	n.r.[f]	n.r.[f]	n.r.[f]
Selective extractions (g/kg):							
Fe-Dithionite	n.d.[g]	n.d.[g]	n.d.[g]	n.d.[g]	4.37	3.32	2.91
Fe-Ascorbate	n.d.[g]	n.d.[g]	n.d.[g]	n.d.[g]	2.96	2.30	1.85
Al-Oxalate	n.d.[g]	n.d.[g]	n.d.[g]	n.d.[g]	23.7	18.2	15.6
Leached at pH <2 (g/kg)							
Fe	2.34	3.28	1.43	2.41	4.46	3.23	2.99
Al	3.31	3.79	2.78	2.85	5.67	3.88	3.29

[a] Samples A, B, C and D was collected at a recycling plant. Samples E1–E3 were prepared in laboratory using standard Portland cement. Prior to experiments, the samples were further ground, see text.

[b] According to Norwegian declaration system [31].

[c] pH taken from the eluate of the leaching test with no addition of acid and base.

[d] Determined as total inorganic carbon (TIC) by the TOC analyser and verified by TGA-MS. For sample A, the TGA-MS values were used, see text.

[e] Dissolved Humic Acid (DHA) fraction of the leached dissolved organic carbon (DOC).

[f] Not relevant parameter.

[g] Not determined.

Engelsen, C. J., van der Sloot, H. A., & Petkovic, G. (2017). Long-term leaching from recycled concrete aggregates applied as sub-base material in road construction. *Science of the Total Environment*, *587–588*, 94–101. https://doi.org/10.1016/j.scitotenv.2017.02.052

Engelsen, C. J., Wibetoe, G., van der Sloot, H. A., Lund, W., & Petkovic, G. (2012). Long-term leaching from recycled concrete aggregates applied as sub-base material in road construction. *Science of the Total Environment*, *587–588*, 94–101. https://doi.org/10.1016/j.scitotenv.2017.02.052

In both these studies, leachate production from RCA used in road sub-base was examined during 10 years of field exposure. The release of inorganic constituents, the effect of small variation of pH and the impact of using de-icing salt during winter seasons were studied. The field site is located at the 4-lane highway (E6) 20 km south of Oslo in Norway. The lane used for field leaching studies was constructed with RCA, foam glass, asphalt and natural aggregates in the sub-base, sections of which are categorized as F1-F9. The test sections were covered with asphalt except for F7 and F8. Under the asphalt layers, the sub-base was constructed with coarse RCA (20–120mm) with a layer thickness of 900 mm. Gravel (0–42 mm) with a maximum layer thickness of 50mm was used as a levelling layer between the sub-base and the asphalt. Below the sub-base, a watertight high-density polyethylene (HDPE) membrane was placed. In order to prevent puncturing of the HDPE membrane, a layer of size reduced RCA (8–16mm) with 100 mm thickness was placed between the sub-base and the membrane. The RCA originated from an older part of the highway (E6) constructed in the beginning of 1980s and demolished in 2004 for reconstruction. Before recycling, the carbonation depth of the RCA was measured by the phenolphthalein method (NT BUILD 357, 1989), and it was found that the material was insignificantly carbonated. Portlandite was also identified in the material, showing that carbonation was at a low level and in agreement with the phenolphthalein indicator results.

In Figure ***1-1*** below, the on-line pH measurements of the collected leachate from the different test fields are shown (F3 is given as the average between F3W and F3E). The initial pH was found to be around 12.6 for the test fields with RCA, in agreement with the materials pH obtained in laboratory leaching tests. After one year of exposure, the pH in F7 had decreased to less than 9.5, whereas the pH in F3 remained at 11–12. The recorded infiltration volumes in the same period were 2900 L, 3750 L and 6580 L for F3W, F3E and F7, respectively. From Figure ***1-1***, it can be seen that after 2.5 years (April 2007) of exposure, pH values below 10 were obtained for F3. This major difference in the rate of decreasing pH, attributed to carbonation, was expected because of the asphalt layer covering unit F3, which reduces the infiltration volume as well as the direct air exposure.

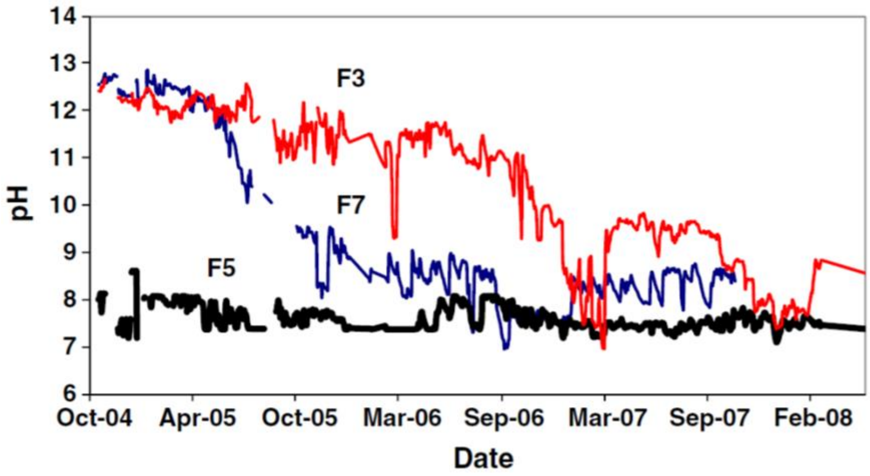


Figure 1-1 pH determined on-line for the collected infiltration water from the different test fields. F3 contains RCA covered with asphalt layer (average of F3W and F3E). F5 contains natural aggregates covered with asphalt layer (reference test field). F7 contains RCA not covered with asphalt layer. Data are given as daily average values and discontinuities in the curves occurred when the logging system was inoperative. Figure copied from Engelsen et al. (2012).

When phenolphthalein is sprayed onto a concrete surface, the color change from pink to colorless indicates a pH less than 10, hence indicating carbonation. In the samples collected from F7, the phenolphthalein test showed the whole surface on each particle to be carbonated. Cross-sections of the particles revealed that the thickness of the carbonated layer was 1–4 mm.

In the field-test section with natural aggregates (F5), the pH was 7–8 throughout the monitoring period. Material pH values obtained in the laboratory for nine different pulverized rock materials were reported to be in the range of pH 8–9. Additionally, the pH of the leachate from the field-test sections with crushed concrete covered with asphalt was found to decrease significantly slower than for the section with crushed concrete without an asphalt cover. After 2.5 years of exposure, the average pH of the asphalt-covered sections (F3W and F3E) was below 10, whereas the same pH was reached within one year for the un-covered section (F7). The study also examined metal leaching in the same leachate samples and revealed that concentrations of many metals actually increase as the pH of the leachate decreases.

At the same field site describe above, the pH of leachate samples collected after ~10 years of exposure was determined, as shown in Figure ***1-2***. A stable pH mostly around 7.5 and 8.0 was obtained for sections F5 and F7, respectively. Metal concentrations were also examined in these samples and little variation was observed over this time course.

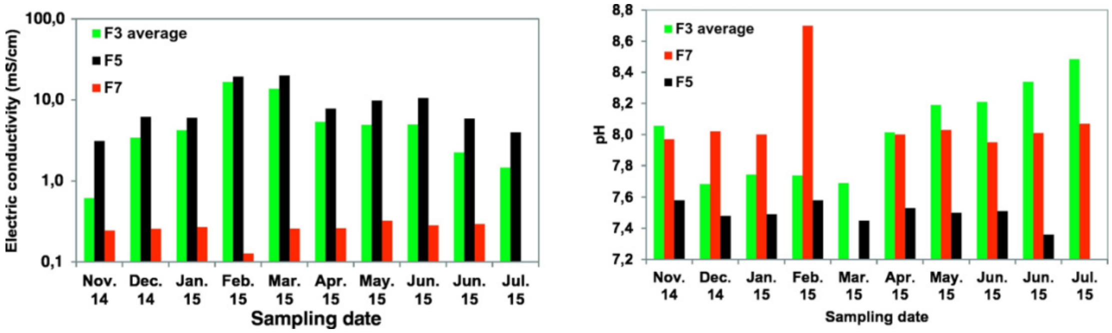


Figure 1-2 Electric Conductivity and pH measured in the collected samples. F3 represents the average values obtained for F3W and F3E. Figure copied from Engelsen et al. (2017)

Abbaspour, A., Tanyu, B. F., & Cetin, B. (2016). Impact of aging on leaching characteristics of recycled concrete aggregate. *Environmental Science and Pollution Research*, *23*(20), 20835–20852. https://doi.org/10.1007/s11356-016-7217-9

The focus of this study was to evaluate the effects of stockpiling (aging) on the leaching of elements from RCA that may contribute to tufa formation. The effects of stockpiling were studied by comparing freshly produced RCA with RCA aged as part of this study for 1 year, both in the laboratory and in the field. Leachate was generated using batch techniques with 18 h of exposure to the solids, according to ASTM D3987. All solid samples used in the batch tests were air-dried and sieved through U.S. No. 4 sieve (4.75 mm).

During the laboratory aging, it was observed that the carbonate content of RCA, measured as calcite equivalent, increased 20% (i.e., from ∼100 to 120 mg/g) within a year. The leachate extracted from RCA showed minor changes in pH decreasing from ~11 at the beginning of the aging to ~10 at the conclusion of the aging process. A comparison between laboratory and field samples revealed that over a one-year time frame the RCA aged much slower in the field than in the laboratory.

Chen, J., Tinjum, J., & Edil, T. (2013). Leaching of Alkaline Substances and Heavy Metals from Recycled Concrete Aggregate Used as Unbound Base Course. *Transportation Research Record*, *2349*, 81–90. https://doi.org/10.3141/2349-10

In this study, RCA material from a wide geographical area were investigated. Physical, chemical, and mineralogical properties were characterized and laboratory column leaching tests were conducted. Two field test sites were installed and instrumented, one at the Minnesota Road Research (MnROAD) facility in Minnesota and a second at a surface parking facility at the University of Wisconsin–Madison. The MnROAD site showed a neutral leachate pH (between 6.5 and 8.0) after 7 months of service life (1.2 pore volumes of flow (PVFs)); however, the pH from column leaching tests ranged between 11.0 and 12.5 and showed no decline over 100 PVFs.

Due to the large disparity between the field results at the MnROAD facility and the laboratory results, two samples of RCA were used in the Wisconsin field site in order to verify the Minnesota data and to investigate the long-term leaching of alkaline compounds and heavy metals. Of the two RCA samples used in the Wisconsin field site, one was from a recent demolition of concrete pavement (WR-F), while the other was from an RCA stockpile with an age of 5 to 10 years (WR-SP). WR-F RCA started with a high leachate pH (12.6) and remained constant for the next 5 PVFs; however, WR-SP RCA started at a lower pH (7.3) but showed a gradually increasing trend, up to pH = 11.9 for the remaining 2 PVFs.

Qin, Y., & Yang, H. (2015). Carbonation dominates the acid intake of recycled concrete aggregate subjected to intermittent leaching. *Construction and Building Materials*, *89*, 110–114. https://doi.org/10.1016/j.conbuildmat.2015.04.038

This study examined the processes that passivate RCA mineral surface, which in turn reduce the pH of leachate. It concluded that carbonation during unsaturated conditions dominates the acid intake. While the liquid added to the RCA (e.g., volume, pH) plays only a secondary role. The study suggested that column tests, which do not incorporate an unsaturated period with exposure to atmospheric CO_2, fail to represent the in-situ leaching of RCA. The authors suggested that it is necessary to redesign leaching tests for demolished cementitious waste subjected to intermittent leaching.

2. FORENSIC EXAMINATION OF THE CHEMICAL AND PHYSICAL CHARECTERISTICS OF AGED RECYCLED CONCRETE AGGREGATE

Co-authors include: Zoe Kanavas who helped collect and interpret the inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and physical characteristic data. Jared Rudolph worked on acid neutralization capacity (ANC), electrical conductivity (EC) and oxidation-reduction potential (ORP) data collection. Matthew Ginder-Vogel and Tuncer Edil contributed to editing the text as well as data interpretation.

2.1 BACKGROUND

Despite the benefits of using RCA in highway construction, in many cases the acceptance of RCA in the market seems to be low, due to possible fluctuations in physiochemical properties (density, grading, cement paste content, leaching properties, etc.) (Engelsen, van der Sloot, & Petkovic, 2017). Characteristic leaching patterns of harmful substances, such as heavy metals, have been identified extensively in many studies (Engelsen et al., 2009, 2010; Galvín, Agrela, Ayuso, Beltrán, & Barbudo, 2014; Kosson, Garrabrants, DeLapp, & van der Sloot, 2014). The leaching mechanisms are strongly dependent on pH and therefore the carbonation level (aging) of the concrete material. As a result, understanding the chemical and physical processes involved in the aging of RCA is crucial to assess its environmental impacts.

In the present study, RCA incorporated as base course material in a field test site was deconstructed after 8 years of field deployment, and characterized. The physical and chemical properties of this aged RCA was characterized and compared with the results from the original RCA characterization conducted by Chen at al. (2012, 2013). The level of carbonation and its impact on the RCA's acid neutralization capacity and trace element leaching are the primary focus of the research. Additionally, the spatial trends in acid neutralization capacity and carbonation are also studied and are discussed in this report.

2.1.1 Material Background

In a previous study by Chen at al. (2012 & 2013), the RCA material from MnDOT was obtained during construction of roadway cells at the MnROAD test facility in Maplewood, Minnesota for investigation of the field behavior. The MnROAD site was constructed on the MnROAD test facility mainline (westbound of I-94) between Saint

Cloud and Minneapolis, Minnesota, in September 2008. The material was obtained from a stockpile maintained by the Knife River Corporation at their pit located at 7979 State Highway 25 NE in Monticello, Minnesota.

Three experimental cells were installed and paved on the mainline: Cell 16 contained 100% Minnesota RCA, Cell 17 contained 50-50 Minnesota RCA-Class V mix, and Cell 19 contained 100% Class V natural aggregate. A 127-mm-thick, warm-mixed asphalt was placed above the base course, which consisted of one of these three materials, each 305 mm thick, underlain with a 305-mm-thick Class 3 aggregate and 178-mm-thick select granular material over the clay subgrade. Cell 16 was originally designed to investigate high-pH effluent from RCA, and Cell 17 was designed to test the neutralization of highly alkaline material by mixing with natural aggregate. Cell 19 was the control cell. Pan lysimeters (3 m x 3 m) were installed under each of the test materials (RCA, RCA-Class V, and Class V) to collect percolated leachate. Leachate was consistently in the range of 7.5 – 8.5 for all samples collected during the initial time-period after installation. Details of the site construction can be found in Chen et al. (2013). Additional leachate samples were collected monthly from April 2016 to July 2016 and analyzed. The pH values of these samples were consistently within the range of 7.5 to 8.5.

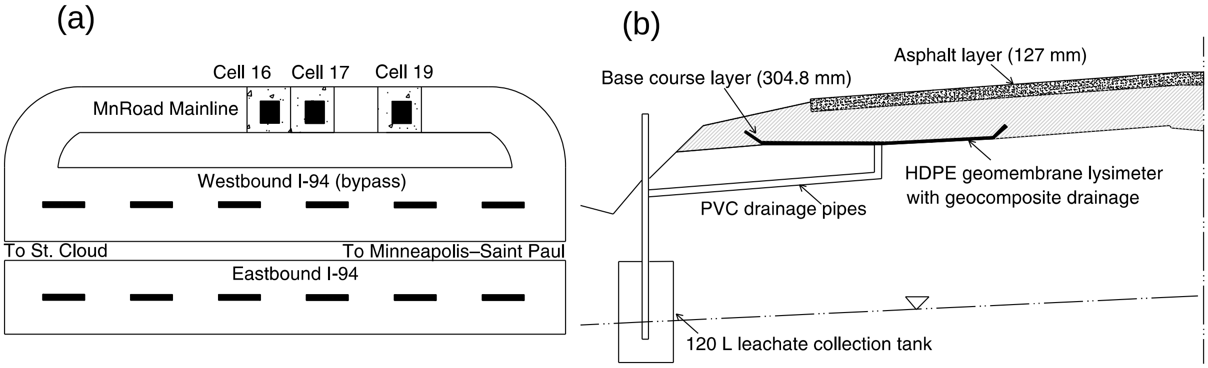


Figure 2-1 Site locations and lysimeter layout for (a) MnROAD and (b) lysimeter design (HDPE = high-density polyethylene, PVC = polyvinylchloride). Figures copied from Chen et al. (2013).

The test sections were deconstructed in the summer of 2016. After asphalt milling, six samples were collected from each of cell (16, 17 and 19). The sampling scheme is detailed in Figure ***2-2***. This sampling scheme ensured that samples were collected throughout the roadbed, in order to determine if location in roadbed leads to differences in RCA chemistry. Additionally, collection of subbase material from below the lysimeters allows comparison of the impacts of RCA leachate on subbase materials, as the lysimeter limits leachate infiltration from the RCA.

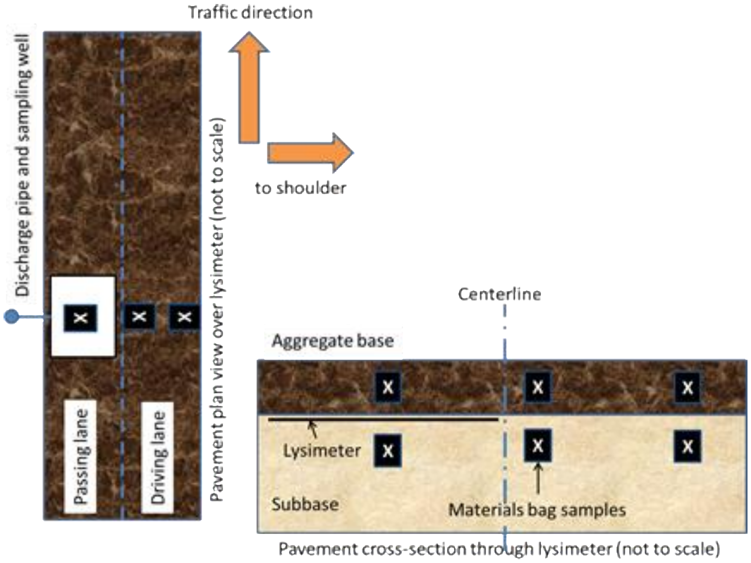


Figure 2-2 Representative location of grab samples collected during the decommissioning of cells 16, 17 and 19 at the MnROAD research facility in July of 2016.

Samples were then extensively characterized in order to determine the impact of 8 years of field deployment on the RCA and its leachate. The original RCA was the subject of extensive characterization prior to installation, as described in Chen et al. (2012, 2012). The current forensic analysis is focused on samples collected from Cell 16, which contained only RCA. The samples include 16P and 16D, which were collected from the passing and driving lanes, respectively, and sample 16C was just offset from the centerline, in order to avoid the geo-membrane lysimeters.

2.2 METHODOLOGY

2.2.1 Physical Properties

The physical and hydraulic properties of the aged MnROAD RCA materials were tested to standards of the American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO). The tests conducted include grain size analysis, residual water content, dry unit weight, absorption, specific gravity, compaction characteristics and Unified Soil Classification System (USCS) class.

Grain Size Analysis**:** The grain size distribution of the aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1 were determined according to ASTM D422. The bulk samples were oven dried at 105°C ±2°C for 24 hours prior to mechanical sieving. The samples were then sieved through sieve No. 4 and sieve No. 200 to isolate the gravel, sand and fine portions of the bulk sample.

Moisture Content**:** The moisture content for the aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1 were determined using the ASTM D2216 standard for soil and rock. A representative bulk sample was taken for each material and oven dried for 24 hours at 105°C ±2°C. The mass lost during drying was taken as the moisture in the bulk specimen.

Absorption and Specific Gravity**:** Absorption and bulk specific gravity were determined using AASHTO T85 – specific gravity and absorption of coarse aggregate. There were no deviations from the standard test procedure described.

Maximum Dry Density and Optimum Water Content**:** The Modified Proctor compaction tests performed on the aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1 followed

ASTM D1557.The maximum dry unit weights, along with their correlating moisture contents were determined using the compaction curves.

2.2.2 Chemical Properties

2.2.2.1 pH-Dependent Batch Tests

pH-dependent batch tests were conducted according to the methods outlined in Chen et al. (2012), using aged RCA stockpiled from the MnROAD site. RCA was sampled from the base course layer below the passing lane, driving lane and centerline from the site. One representative batch from each lane was collected, homogenized by hand mixing and oven-dried overnight. The batch was separated into two sets of samples: one was representative of the bulk sample, while the second set was size fractionated. The fractionated sample was sieved into three grain-sized fractions: fine particles (<0.075 mm), sand-sized particles (<4.75 mm, >0.075 mm), and gravel-sized particles (<75 mm, >4.75 mm). None of the samples were crushed, in order to accurately assess the impact of the aged surfaces on leachate chemistry. Fines, sands and bulk samples for batch tests consisted of 5g of RCA with 50mL of varying acid/base solutions. Gravel samples consisted of 50g of RCA in 500mL of varying acid/base solutions. The acid and base used in the batch tests were HNO_3 and NaOH respectively. All the samples were then agitated in an end-over-end tumbler at 30±2 revolutions per minute (rpm) for 24 hours, allowing the RCA and solution to react to completion.

Once the samples were prepared, each solution's pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were determined. The pH was determined using the Thermo Scientific Orion Combination pH Electrode, the electrical conductivity was determined using the Intellical CDC401 Graphite Conductivity probe, and the ORP was determined using the Intellical MTC101 ORP/RedOx probe. The acid neutralization capacity (ANC) curve of each material was determined from the pH-dependent batch tests by comparing the amount of acid/base added to each sample with the resulting pH of the solution. The EC and the ORP were similarly plotted against the amount of acid/base added to each sample. Following the batch tests, the samples were then stored at 4°C for further analysis.

The material pH is the pH of the solution resulting from a mixture of RCA and de-ionized water, i.e. the pH value without addition of acid/base. The same procedure for sample preparation used for the batch tests was adapted for the material pH samples. Material pH were determined for the all three samples of RCA, as well as for the two layers of subbase soils below the RCA samples. Bulk samples consisted of 50g of subbase soil in 500mL of de-ionized water.

2.2.2.2 Elemental Composition of Leachate

The concentration of leached elements considered in this study were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Vista-MPX CCD Simultaneous ICP-OES, Varian Inc., CA, US). The total elemental composition of each RCA specimen was determined by acid digestion according to the method outlined in ASTM D5198-09.

Prior to analysis, the initial solution samples (no acid or base added) from the batch tests were placed in a centrifuge for 10 minutes in order to isolate the solid phase. The leachate samples for the ICP test, collected from the centrifuged batch, were then diluted at 1:1 ratios, and preserved with 5% nitiric acid solution, in order to bring the elemental concentrations to within the ICP instrument's analytical range. Hence, the resulting values from the test were extrapolated to account for the dilution. Additionally, the ICP was calibrated by diluting certified concentrated standards, supplied by High Purity Standards (Charleston, North Carolina) and Fisher Scientific (Hanover Park, Illinois). The calibration standard solutions prepared were of Al, As, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Si and Zn at concentrations of 1, 5, 25 and 100ppm.

Quality control guidelines were followed, as outlined in USEPA procedure SW-846. Continuing calibration verifications (CCV) and continuing calibration blanks (CCB) were analyzed every 10 samples, while the sample duplicate was analyzed every 20 samples. Quality control requirements outlined in USEPA Method SW-846 were met for all calibrated wavelengths. The criteria required CCVs within 10% of expected values, CCBs below detection limits and concentrations of duplicate samples within 20% of the concentration in the original sample.

2.2.2.3 Solid-Phase Composition of RCA

To identify the crystalline material and bulk mineral composition of the three RCA batches, X-ray Diffraction (XRD) was used. The tests were conducted in accordance with ASTM Standard C1365-06. The fine fractioned samples were crushed using a mortar to a fine powder and packed into a small cylindrical tube. The analysis was done in the Rigaku D/Max Rapid II diffractometer through the S.W. Bailey X-ray Diffraction Laboratory. After the sample was placed in the diffractometer, the two-dimensional imaging plate (2D IP) was adjusted to keep the sample in frame at every angle. The diffractometer made rapid measurements of the diffraction pattern. The results were plotted as intensity (counts per second) versus 2-theta angle and compared to a database of mineral XRD patterns. Two X-ray Diffraction tests were conducted on each of the fine fractions of the samples, and the results were compared in order to reflect a representative composition of the entire sample.

Thermogravimetric analysis measures the change in mass of a sample vs. temperature. For example, bound water and structure water are the first compounds released at relatively low temperatures (~200°C), while calcium carbonate degrades to form CaO and CO_2 at a temperature of ~700°C following Reaction 8.

$$\mathrm{CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}} \qquad \text{Reaction 8}$$

By measuring the change in mass of the solid sample as CO_2 released, one can back calculate the amount of $CaCO_3$ in the sample. The degree of carbonation in each sample was determined using the model TGA/SDTA851^e through the Water Science and Engineering Laboratory at the University of Wisconsin–Madison. The tests were conducted in accordance with ASTM Standard E1131–08 (ASTM, 2014). An empty crucible was placed into the instrument, the furnace was closed, and the machine was tarred. A blank curve of the experiment method was run. The crucible was then removed and 50-100 mg of the fine fraction of the samples was packed into the crucible. The full crucible was replaced into the instrument and the experiment was run. The furnace was heated at a rate of 10°C/min from 25°C to 1000°C. Once the experiment was complete, the data was plotted as mass versus temperature, and the major drops in mass were analyzed.

2.3 RESULTS AND DISCUSSION

2.3.1 Physical Properties

A summary of the physical properties of the aged MnROAD RCA samples collected from the site is shown in Table ***2-1***. The grain-size distribution curves of all three bulk samples are shown in in Figure ***2-3***. The three samples had similar physical properties with specific gravities ranging from 2.13 to 2.50, moisture contents from 8.69% to 9.30%, optimum water contents from 12% to 13%, maximum dry densities from 21.0 kN/m^3 to 21.7 kN/m^3, and water contents at maximum density from 11.70% to 13.50%. All three samples were given a USCS classification of GW (well-graded gravel).

Table 2-1 Physical Properties of the original MnROAD RCA from Chen et al. (2012, 2013) and aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1.

Sample	Method	Original RCA	16 P-1	16 C-1	16 D-1
Specific Gravity	AASHTO T85	2.7	2.26	2.13	2.50
Moisture Content (%)	ASTM D2216	3.0	8.69	9.30	8.83
Absorption (%)	AASHTO T85	4.9	7.62	7.95	6.29
Optimum Water Content (%)	ASTM D1557	11.2	12	11.70	13.50
Max Dry Density (kN/m^3)	ASTM D1557	19.5	21.4	21	21.7
USCS Classification	ASTM D2487	GW	GW	GW	GW

Table 2-2 Particle size distribution by mass percent for the original MnROAD RCA from Chen et al. (2012, 2013) and aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1.

Particle Size Distribution	Method	Original RCA	16 P-1	16 C-1	16 D-1
75-4.75 mm (wt%)	ASTM D422	31.8	54.60	37.27	52.29
4.75-0.075 mm (wt%)		64.9	44.20	60.60	46.55
<0.075 mm (wt%)		3.3	1.20	1.12	1.16

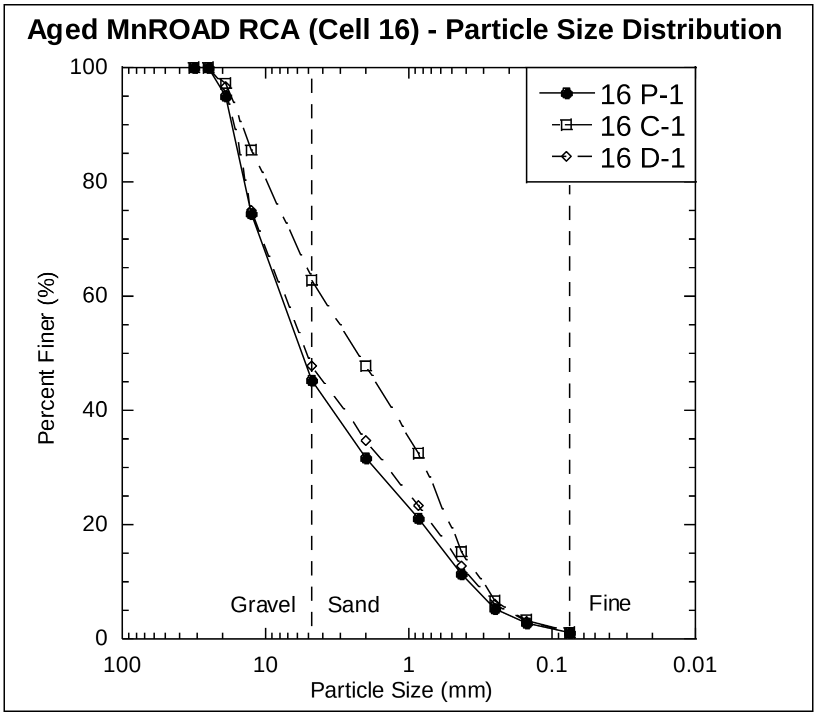


Figure 2-3 Aged MnROAD RCA particle size distribution curves for aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1.

2.3.2 Chemical Properties

2.3.2.1 Acid Neutralization Capacity – Acid/Base Addition and pH

The acid neutralization capacity (ANC) curves for each RCA sample are shown in Figure ***2-4***. The figure shows the curves for the bulk RCA samples, with their fractionated subsets (gravel, sand and fines). The ANC curves show the material response to addition of acid or base; hence, the resulting pH is plotted against the amount of acid/base added to each sample in mmol/g. The negative values in ANC plots represent base additions.

Similar ANC curves were observed for the bulk, sand and gravel fractions of all three RCA samples – a rapid drop in pH with a plateau observed between pH 4 and 7. However, the ANC curves observed for the fine fractions of all three samples (Figure ***2-5***) indicated two plateaus – the first over an elevated pH level of above 9, and the second between pH 5 and 7. The ANC trends for the fine-grained particles in comparison to the other size fractions showed that the fine particles are more resistant to acid attack. Generally, the larger the grain size, the steeper the ANC curve of the MnROAD RCA.

The material pH (no acid or base added) for each of the RCA fractions ranged between 10.7 and 11.4 (shown in Table ***2-3***). The material pH for the subbase soils were also recorded, and ranged between 10.15 and 10.91 (shown in Table ***2-4***).

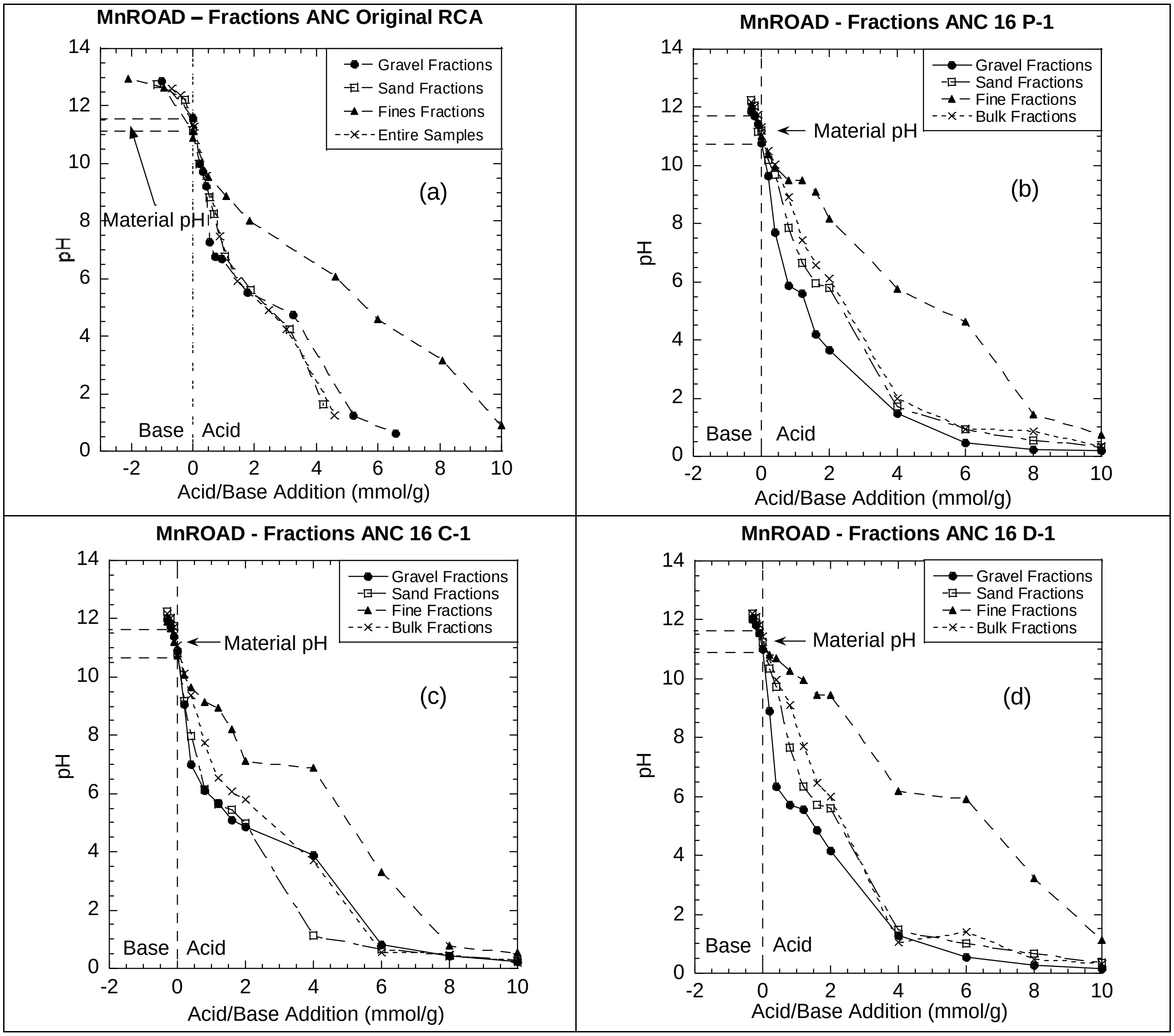


Figure 2-4 Acid neutralization capacity (ANC) curves for (a) original MnROAD RCA copied from Chen et al. (2012), and aged MnROAD RCA samples (b) 16 P-1, (c) 16 C-1 and (d) 16 D-1. Data includes bulk, fine, sand and gravel fractions.

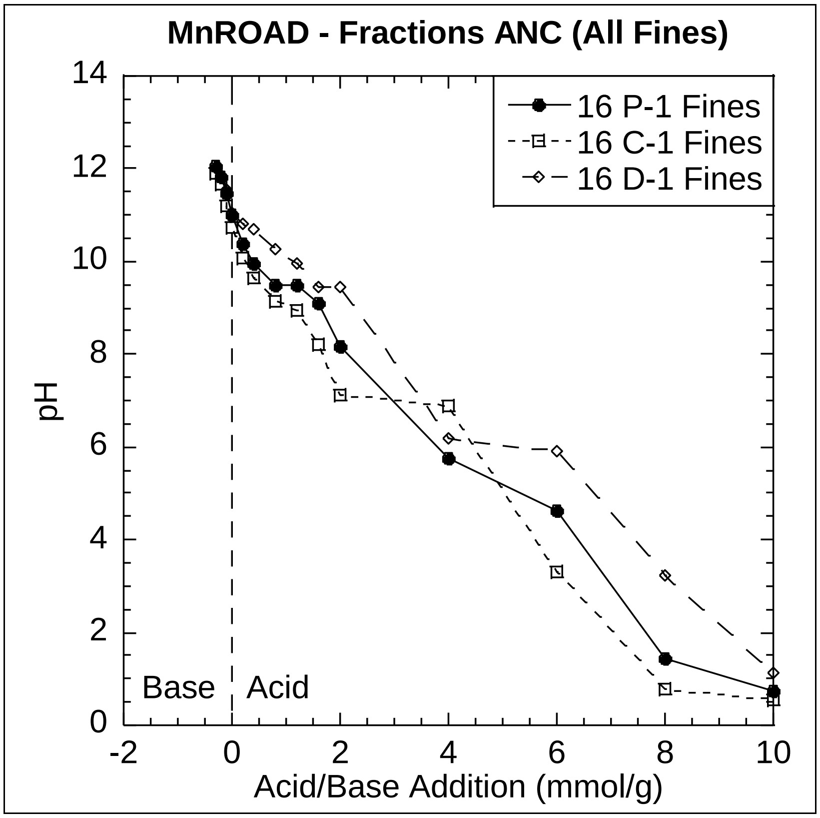


Figure 2-5 **Acid Neutralization Capacity (ANC) curves for aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1. Data includes only fine fractions**

Carbonation & Surface Chemistry

Garrabrants et al. (2004) and Chen at al. (2012) both concluded that the plateau in the ANC can be explained by dissolution of calcium carbonate (from carbonation) in the concrete. Carbonation in concrete is primarily caused by reactions between portlandite ($Ca(OH)_{2(s)}$) and calcium silicate hydrate (C-S-H), with carbon dioxide from the environment. The double plateau observed in the fine fractions can be explained by the two-stage protonation of the carbonate anions in the system.

The acid neutralization capacity curves for the fine fractions resembled a carbonate base titration curve, showing a two-stage protonation. An example titration curve of sodium carbonate with hydrochloric acid is shown in Figure ***2-6***. The pK_{a1} and

pK_{a2} of a carbonate base are 6.53 and 10.33 respectively. Despite the resembling two-stage protonation with a carbonic base, the fines fractions of the RCA showed differing equivalence points. The first plateau for the fine samples ranged between pH 9 and 9.5, while the second had a wider range between pH 5 and 7. These differences are likely attributed to the neutralization capacity of other alkali material available in the concrete.

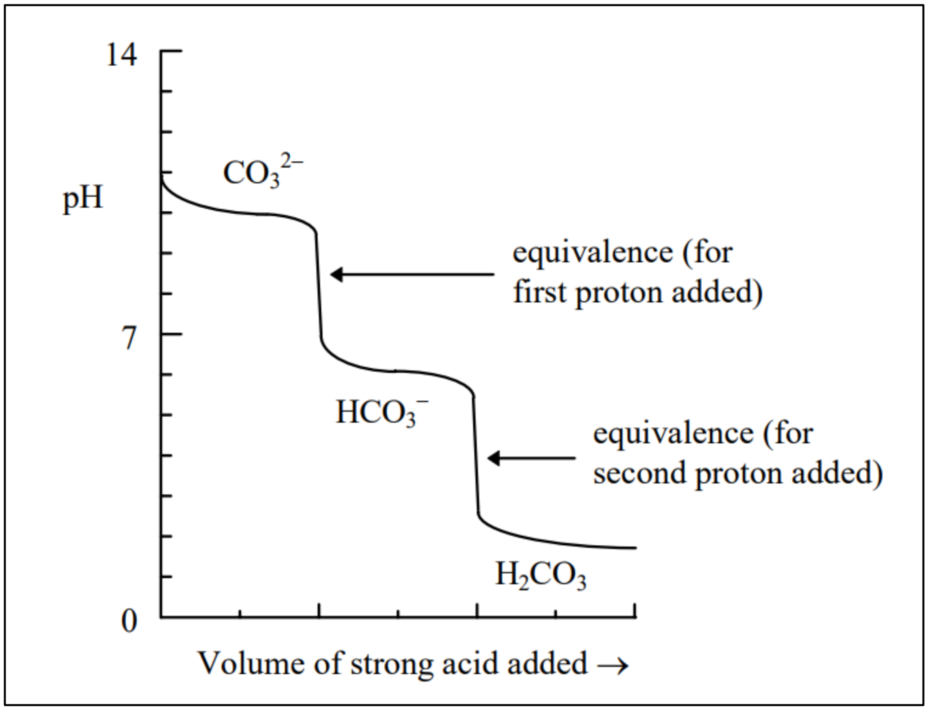


Figure 2-6 Titration of sodium carbonate with hydrochloric acid. Figure copied from Saunders (2003).

The presence of this trend in only the fine-grained fraction of the RCA shows that the level of carbonation in the fine-grained RCA is higher than that in the other size fractions. This higher level of carbonation per mass of sample can be attributed to the availability of reaction surfaces on the fine RCA, allowing for higher exposure of $Ca(OH)_2$ and C-S-H to form calcium carbonate. The acid neutralization behavior of the fine-grained material was also consistent with this interpretation, as the fine-grained material had a higher acid neutralization capacity due to the higher surface area available for the acid to react with surface carbonate and other alkali material in the RCA. Hence, it would require more acid to change the pH of the solution with the fine-sized particles compared to the gravel-sized particles.

Spatial Trends

There were similarities between the RCA under the passing and driving lanes (16 P-1 and 16 D-1 respectively). Both samples had a distinct ANC plateau for the bulk, sand and gravel size fractions around a pH of 6. While the plateau observed in 16 C-1 was more gradual, and over a wider pH range (between pH 7 and 4). Additionally, apart from the sand-sized fraction, the 16 C-1 samples generally had shallower ANC curves compared to the 16 P-1 and 16 D-1 samples. These trends illustrate a slightly higher acid neutralization capacity of the RCA under the centerline. The fine-fractions, which generally control the bulk material's acid neutralization capacity, showed a second plateau around a pH of 6 for both 16 P-1 and 16 D-1, while the second plateau for 16 C-1 occurred at a pH of 7. However, the titration end-points for all three fines samples were between 2 and 3 mmol/g. It should be noted that the second plateau for 16 P-1 was not very clear from the data shown in Figure ***2-4***, however, data collection at a higher resolution could better illustrate the plateau.

Highway pavements are generally constructed to drain water away from the center of the road, with the pavement sloped away from the centerline. Consequently, the material under the centerline would drain faster, draining into the adjacent passing and driving lanes. This would allow for longer dry periods under the center of the road compared to under the passing and driving lanes, accommodating carbonation around the surface of the RCA grains. The longer dry periods compared to the adjacent two lanes would also allow for less dissolution of alkali material over time. The slightly higher acid neutralization capacity trends observed in the 16 C-1 samples (specifically in the bulk and gravel fractions) suggests that contact time with leachate and surface carbonation are two possible factors that determine the pH of the leachate observed in the field. However, this spatial trend is not clear from the results.

Base and Subbase Material pH

The material pH for all the size fractions of the aged MnROAD RCA are shown in Table ***2-3***. The sand-sized particles (44%-62% by mass) had higher material pH (10.80 to 11.24) than the fine particles (10.72 to 11.05) and the gravel particles (10.76 to 11.00), and likely control the pH of the bulk (unfractionated) pH (11.08 to 11.45). The initial hypothesis was that the fine fractions would have a lower material pH due to the higher possibility of carbonation, accommodated by the higher surface area. Subsequently, the courser fractions were expected to have a higher material pH due to lower levels of carbonation with decreasing surface area. A combination of carbonation and available surface area for material dissolution is one probable reason for the observed pH difference among the fractions. The higher surface area of the fine and sand particles, in comparison to the gravel particles, allows for a larger extent of carbonation to occur. Carbonation utilizes the alkali phases from the cement, hence, the material pH drops. However, even if the gravel particles had more calcium hydroxide, the limited surface available for dissolution of the alkali material could limit how high the material pH can rise. The sand fraction controls the material pH of the bulk RCA, likely due to a combination of these two factors. Additionally, a large proportion of the bulk mass constitutes of the sand-size fraction, allowing the sand to control the bulk material properties.

Alternatively, the trends in material pH observed for the different size fractions may be attributed to the mechanisms involved in the standard sample preparation techniques used for batch tests in this study. All the samples were prepared and placed in an end-over-end tumbler for 24 hours as per the standard. This process leaves the RCA particles susceptible to abrasion during the tumbling process, allowing for the exposure of fresh surfaces. The trends in material pH among the four fractions are only slightly different. This could be attributed to the abrasion during sample preparation discounting the impact of surface chemistry on carbonation.

In order to understand the leaching mechanisms in the roadway, the material pH of the local subbase soils (clayey sand) were also recorded (Table ***2-4***). The results generally showed that the material pH reduced with depth from the RCA base layer. However, the measured material pH of the subbase soils was higher than hypothesized. These higher material pH values could be attributed to precipitation of hydroxide phases on the particle surface. To understand the soil chemistry better, the physical and chemical properties of the subbase soils need to be characterized further. Additionally, the mechanisms involved in the sample preparation expressed previously could also explain these unexpected results.

Table 2-3 Material pH for aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1. Data includes bulk, gravel, sand and fine fractions

RCA Fractions Material pH			
Fraction	**16 P**	**16 C**	**16 D**
Bulk	11.31	11.08	11.45
Sand	11.21	10.8	11.24
Fine	10.99	10.72	11.05
Gravel	10.76	10.91	11.00

Table 2-4 Bulk material pH for aged MnROAD RCA samples and subbase soils under 16 P, 16 C and 16 D

Bulk Material pH			
Unit	**16 P**	**16 C**	**16 D**
1 - RCA	11.31	11.08	11.45
2 - Subbase Soil	10.41	10.47	10.91
3 - Subbase Soil	10.15	10.53	10.61

2.3.2.2 Oxidation-Reduction Potential & Electrical Conductivity

The oxidation-reduction potential (ORP) data of the effluent from each RCA sample are shown in Figure ***2-9*** and Figure ***2-8*** in the Appendix. The material ORP ranged between -8.5 mV to 173.5 mV. The data showed a trend of increasing ORP with the addition of acid. This is due to the number of ionic species dissolved in the leachate as more acid reacts with the RCA.

The electrical conductivity data of the effluent from each RCA sample are shown in Figure ***2-9*** and Figure ***2-10*** in the Appendix. The material electrical conductivity ranged from 0.373 mS/cm to 3.370 mS/cm. Similar to the ORP trends observed the electrical conductivity of the leachate increases with the addition of acid to the system. This is due to the increase in the number of ionic species dissolved from the RCA as pH decreases.

2.3.2.3 Elemental Composition of Leachate

The results from the ICP-OES quantification of leachate element concentrations are shown in Figure ***2-11*** through Figure ***2-16*** in the Appendix. In general, all three samples showed high leachate concentrations of Ca (maximum of 237.7 ppm), Si (maximum of 31.0 ppm), Na (maximum of 72.1 ppm) and K (maximum of 26.1ppm). Additionally, the results showed maximum leachate concentration levels for Cr between 0.034 ppm and 0.160 ppm, for Zn between 0.178 ppm and 0.202 ppm, and no detectable concentration levels for Cu. The leachate from the fine-grained samples generally had the largest elemental concentration, followed by the sand and the gravel fractions. Due to the low weight composition of the fine fractions (~1% by mass), the leachate behavior of the bulk samples is likely primarily controlled by the behavior of the sand fractions (44%-62% by mass).

2.3.2.4 Solid-Phase Composition of RCA

The results from the X-ray diffraction (XRD) tests for all three samples are shown in Table ***2-5*** below. Unfortunately, XRD data is not available for the original RCA prior to its installation at the MnROAD research facility. Depending on the hydration stage in pure calcium-silicate paste, $Ca(OH)_2$ crystals have variable morphology with persistently good cleavage (Taylor, 1997). Additionally, there is evidence indicating that $Ca(OH)_2$ in cement paste may exist in the amorphous or cryptocrystalline forms (intimately mixed with C-S-H) (Taylor, 1997). Hence, Taylor (1997) explains that quantitative XRD methods tend to underestimate (or in some cases not detect) the $Ca(OH)_2$ due to the existence of these forms. Based on the XRD results it can be inferred that the crystalline form of $Ca(OH)_2$

(portlandite) was not present above 5% by mass in this RCA, most likely due to leaching and carbonation.

From the XRD results of the aged MnROAD RCA, all three samples contained approximately 24.2% to 35.7% quartz, 33.1% to 48.1% anorthite and 25.6% to 31.1% calcite/dolomite. The amount of calcite in each sample is consistent with the amount of $CaCO_3$ determined from the TGA measurements (discussed in section 2.3.3 below, see page 51).

Table 2-5 Major crystalline minerals in the fines fraction of the aged MnROAD RCA sample. Quantified using X-ray diffraction

Sample	% Quartz	% Anorthite	% Calcite	% Dolomite
16 P-1	26.9	47.5	13.6	12.0
16 C-1	35.7	33.1	13.8	17.3
16 D-1	24.2	48.1	13.5	14.3

2.3.3 Comparison of aged RCA with original RCA

2.3.3.1 Acid neutralization capacity and Carbonation

The acid neutralization capacity curves for the bulk and fractionated RCA samples were initially assessed by Chen et al. (2012 & 2013), and are shown in Figure ***2-4***. The most significant difference in acid neutralization behavior between the original and aged RCA is the development of the double plateau in the fines fractions. The fines fraction of the original RCA does not indicate the presence of any equivalence points, suggesting that the level of carbonation was insignificant. The presence of the double plateau in all the fines-sized samples indicates that the aged RCA has developed significant carbonation.

Another significant difference in the acid neutralization capacities between the original and aged RCA is the difference in the gravel and sand fractions. The original RCA show similar responses to acid attack for the gravel and sand fractions, with the ANC curves showing similar trends. The ANC curves for these fractions in the aged RCA are spread out more and show significantly different responses. The sand fractions show a higher resistance to acid attack in 16 P-1 and 16 D-1, between 0 mmol/g and 4 mmol/g addition of acid. This change in trends indicates the surface chemistry changes over the lifetime of the RCA.

A comparison of the material pH between the original and aged RCA, shown in Table ***2-6*** below, identifies a slight drop in material pH in the aged RCA. The maximum values in the range of material pH for the original RCA were all above 11.8, while the maximum material pH recorded in the aged RCA was 11.45, in the bulk fraction of sample

16 D-1. According to Chen et al. (2012), a lower material pH indicates a higher carbonation level on the material surface, inhibiting the alkali content in the cement paste from dissolving.

Table 2-6 Material pH for the original MnROAD RCA from Chen et al. (2012, 2013), and aged MnROAD RCA samples 16 P-1, 16 C-1 and 16 D-1. Data includes bulk, gravel, sand and fine fractions for aged RCA.

RCA Fractions Material pH				
Fraction	**Original RCA *(Chen et al, 2012 & 2013)***	**16 P**	**16 C**	**16 D**
Bulk	11.3 – 12.1	11.31	11.08	11.45
Sand	11.1 – 11.9	11.21	10.8	11.24
Fine	10.9 – 11.8	10.99	10.72	11.05
Gravel	11.5 – 12.1	10.76	10.91	11.00

The higher level of carbonation indicated in the material pH results is supported by the results from the thermogravimetric analysis. The degree of carbonation in each sample is shown in Table ***2-7*** below. The results showed the carbon content between 2.2% and 2.4% for all three aged RCA samples. These values are significantly higher than the carbon content recorded in the original MnROAD RCA (1.6%). This higher carbon content illustrates that carbonation of the samples has occurred during the 8 years the material was in place at the MnROAD research facility. This is also similar to the degree of carbonation in the aged RCA that was studied by Engelsen at al. (2009). The difference in the spatial variation of carbon content is deemed insignificant and no inferences can be made from it. A more accurate method of data collection would be required to assess those trends.

Table 2-7 Carbon Content as a percent of sample mass, for the original MnROAD RCA from Chen et al. (2012, 2013), and aged MnROAD samples 16 P-1, 16 C-1 and 16 D-1.

Sample ID	Percent Inorganic Carbon (%)	Percent $CaCO_3$
Aged MnROAD Sample 16 P-1[1]	2.4	20.3
Aged MnROAD Sample 16 C-1[1]	2.3	19.4
Aged MnROAD Sample 16 D-1[1]	2.2	18.6
Original MnROAD RCA[2]	1.6	13.3

[1] Data was collected by thermogravimetric analysis (TGA) (Mettler, Toledo)

[2] Data was collected using a sulfur and carbon analyzer (LECO, Inc.)

2.3.3.2 Metal Leaching

Leachate analysis on Cu, Zn and Cr were conducted in an initial study of the original MnROAD RCA by Chen at al. (2012 & 2013), the results of which are shown in Figure ***2-17*** in the Appendix. The initial study analyzed the leaching patterns vs increasing pH conditions of these elements, from the three size fractions. The current analysis of the aged MnROAD RCA material assessed the leachate concentrations of the same three elements at the material pH of approximately 11.3. Table ***2-8*** below presents a comparison between the results from the two studies.

Table 2-8 Comparison of element leaching from the original MnROAD RCA from Chen et al. (2012, 2013), and aged MnROAD RCA at pH = 11.3. Table shows leaching data for gravel, sand and fine size fractions.

pH = 11.3	Original MnROAD RCA (mg/kg = ppm)			Aged MnROAD RCA (mg/l = ppm)		
Sample	**Cu**	**Zn**	**Cr**	**Cu**	**Zn**	**Cr**
Gravel	0.18	0.005	0.8	0	0.202	0.046
Sand	0.18	0.005	0.21	0	0.178	0.034
Fine	1.00	0.010	0.4	0	0.252	0.160

The leachate concentrations of Cr and Cu in the aged RCA are lower than the concentrations observed in the original sample for all three fractions. The drop in these values may be attributed to the dissolution of Cu and Cr through the lifetime of the RCA on site. However, the leachate concentrations of Zn are higher in the aged RCA analysis compared to the original RCA samples. This increase in leachate concentration shows a change in leaching patterns with varying pH that was initially studied by Chen et al. (2012). Higher Zn concentrations in the RCA could be attributed to a change in the predominant mineral phase of Zn in the RCA, to a less soluble phase. Additionally, studies have shown that the concentrations of Zn and other heavy metals can increase over time due to other external sources, such as tire and brake abrasion, combustion exhaust and the application of road salt in the winter period (Gunawardana et al., 2012; Shaw et al., 2012). Furthermore, a study by Radziemska et al. (2015) on the Warsaw Expressway in Poland showed that the highest values of heavy metal concentrations, including Zn, occurred closest to the roadway. These various factors could explain the leaching patterns of Cu, Cr and Zn in the aged MnROAD RCA.

2.4 CONCLUSIONS

The forensic examination of the MnROAD recycled concrete aggregate (RCA) showed an increase in the acid neutralization capacity of the material over the eight-year field deployment. From the acid neutralization capacity curves, the finer particles continued to show a higher acid neutralization capacity than the coarser particles. Furthermore, the acid neutralization capacity curves indicated significant carbonation in the fines-fractions of the aged MnROAD RCA. The aging of the MnROAD RCA was quantified further through material pH, X-ray diffraction and thermogravimetric analyses. These tests indicated a higher carbon content in the aged RCA than in the original RCA characterized by Chen et al. (2012 & 2013). The X-ray diffraction analysis on the fine fractions highlighted the absence of significant amounts of crystalline portlandite in the aged RCA. Furthermore, the leaching of inorganic elements was also assessed as part of this forensic examination. The ICP-OES results indicated a decrease in Cu and Cr concentrations in the aged RCA, but showed an increase in Zn concentrations.

As background to this study, leachate observations were made from both field and lab tests during the eight years that the MnROAD facility was operational. Column leaching tests conducted in the lab showed significantly different results from the leachate pH observed in the field tests (Chen et al., 2012). Furthermore, the material pH of both the base-course RCA and the subbase soils determined in this forensic study were also significantly higher than the leachate pH determined from the pan lysimeters at the MnROAD facility, which ranged between 6.5 and 8.0 after 7 months (Chen et al., 2012). These discrepancies in pH suggest that the material pH of RCA and subgrade soils are not representative of the leachate pH that can be expected from real world conditions.

There are two likely explanations for this. In the case of the RCA, the utilization of an end-over-end tumbler to determine material pH may result in particle abrasion and removal of the protective calcium carbonate layer that would otherwise limit the material pH. In the case of the subbase soils, the high water to solid ratio and extended contact time likely allow more extensive dissolution of calcium carbonate minerals, and the concomitant large increase in pH.

A preliminary characterization of the initial RCA installed at the MnROAD site revealed that the material pH was quite sensitive to contact time, shown in Figure ***2-24***, which is likely a critical factor in controlling the leachate pH and alkalinity. After one hour of contact with RCA in a column, the pH of the solution was only 7.8. However, exposure over longer subsequent time periods rapidly increased the leachate pH. In order to effectively simulate field conditions, it is important to study the behavior of leachate from the recycled concrete aggregate (RCA) while controlling the contact time, solid to liquid ratio and particle surface abrasion.

2.5 APPENDIX A

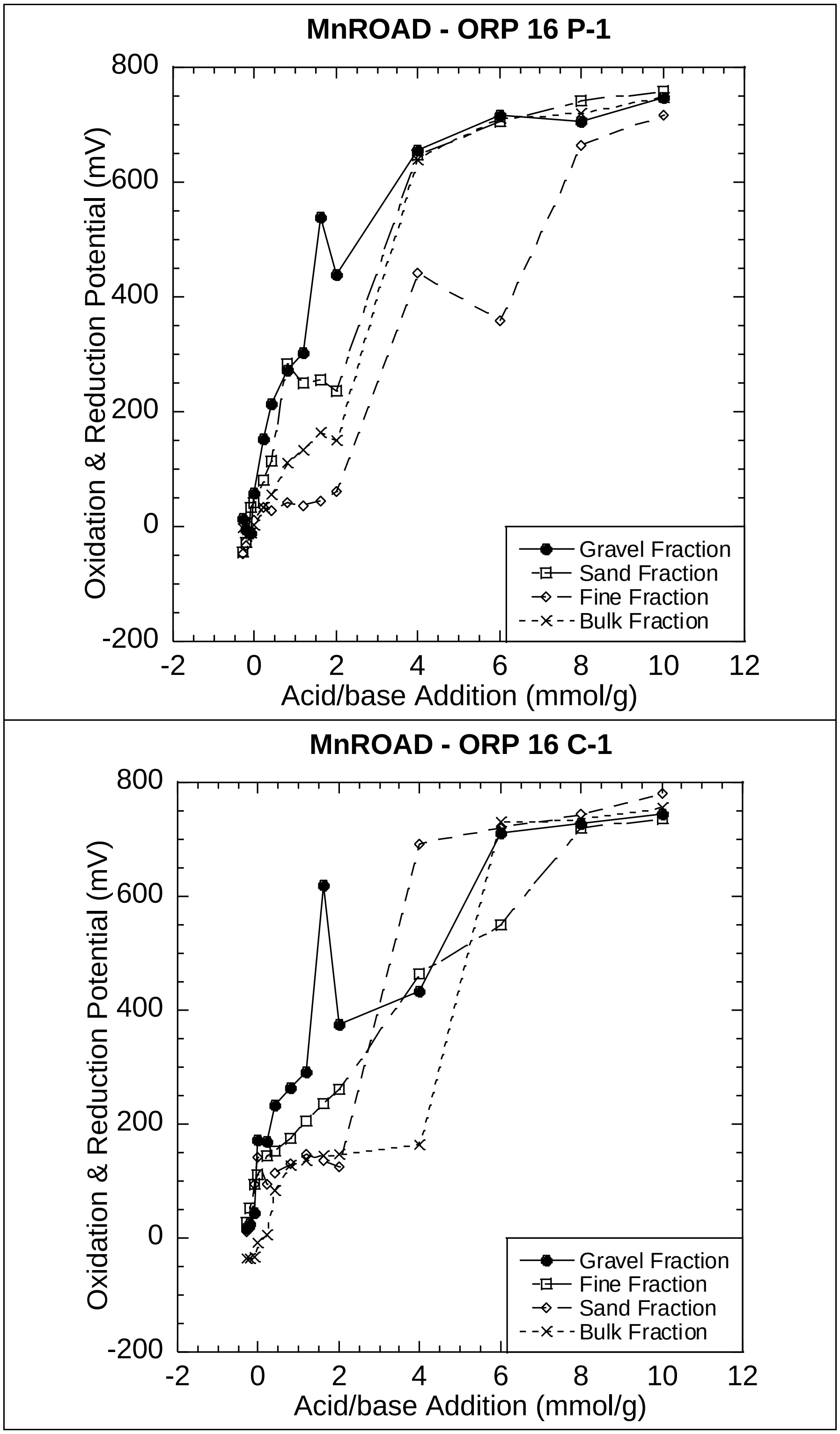


Figure 2-7 Oxidation & Reduction Potential graphs for aged MnROAD RCA samples 16 P-1 and 16 C-1

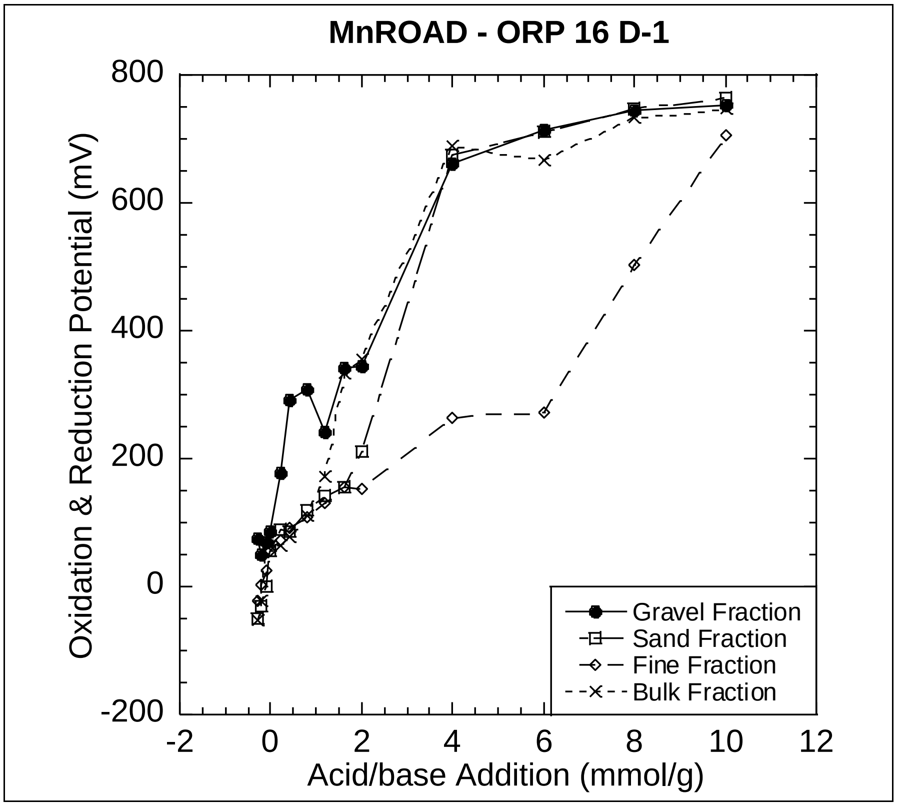


Figure 2-8 Oxidation & Reduction Potential graphs for aged MnROAD RCA samples 16 D-1

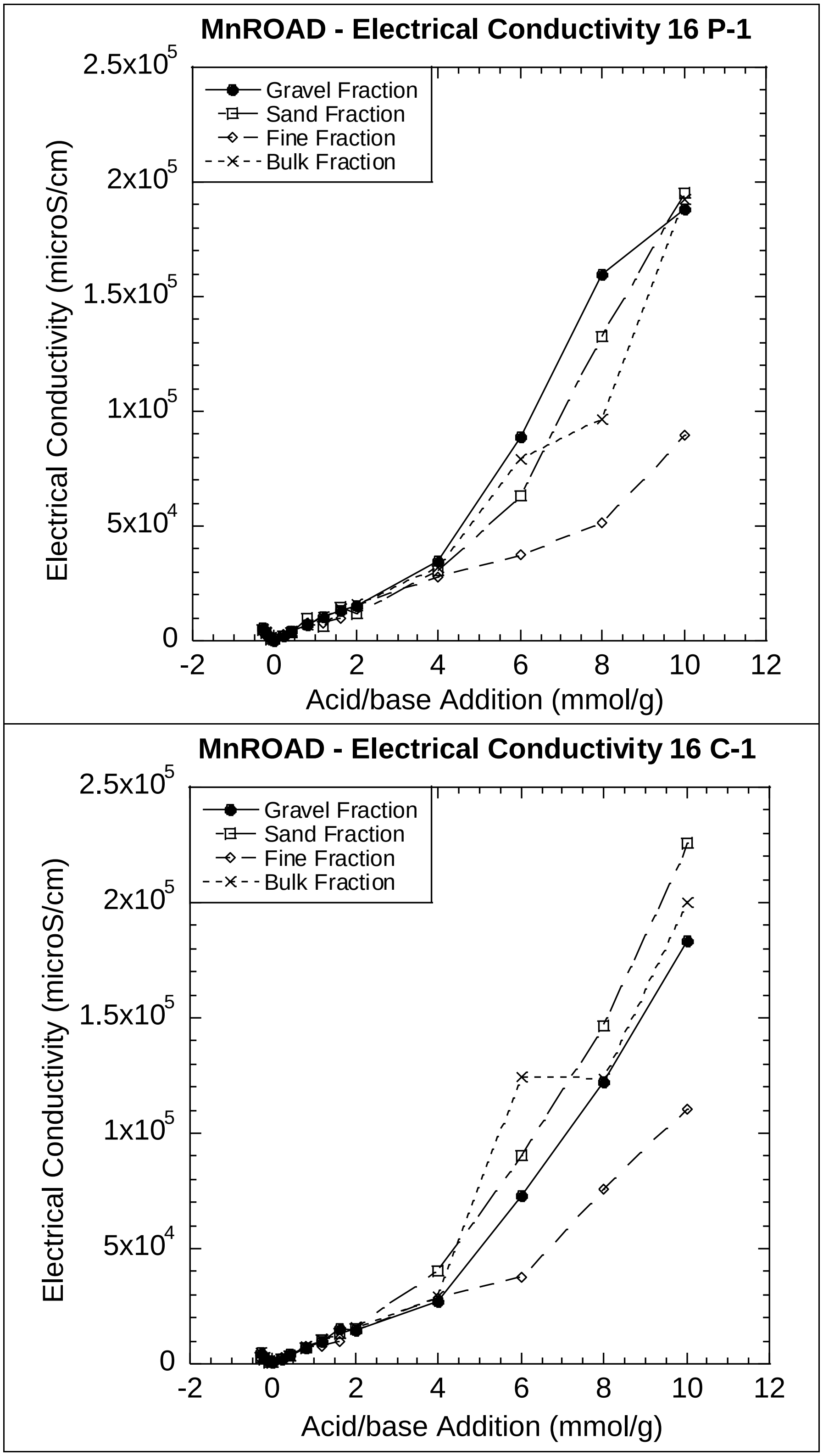


Figure 2-9 Electrical Conductivity graphs for aged MnROAD RCA samples 16 P-1 and 16 C-1

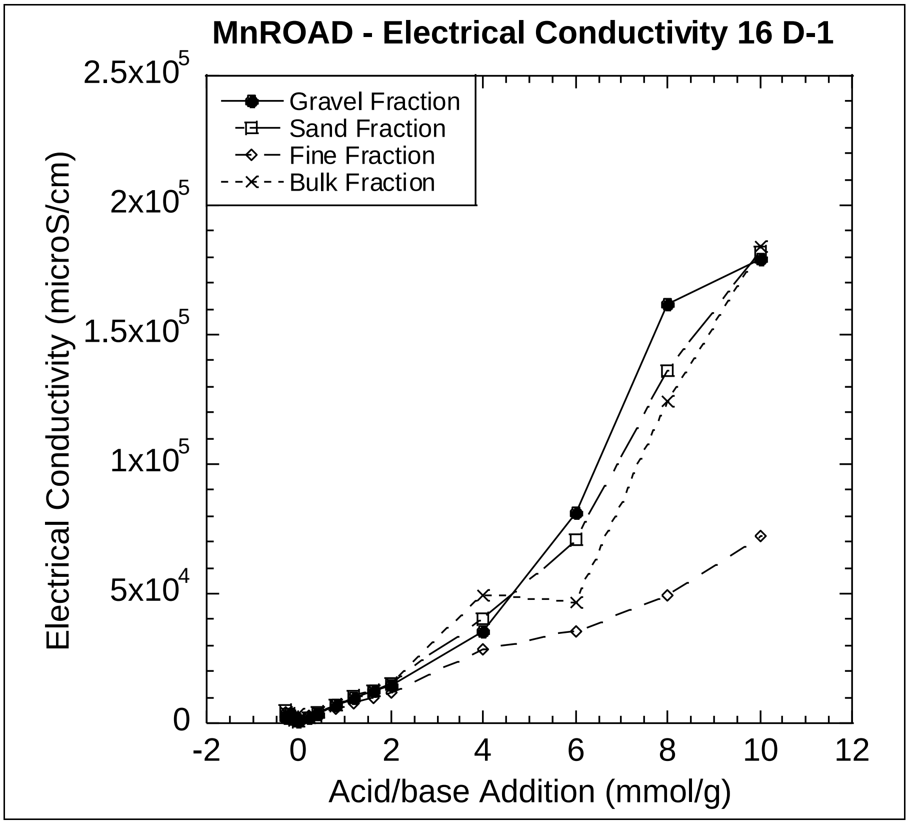


Figure 2-10 Electrical Conductivity graphs for aged MnROAD RCA samples 16 D-1

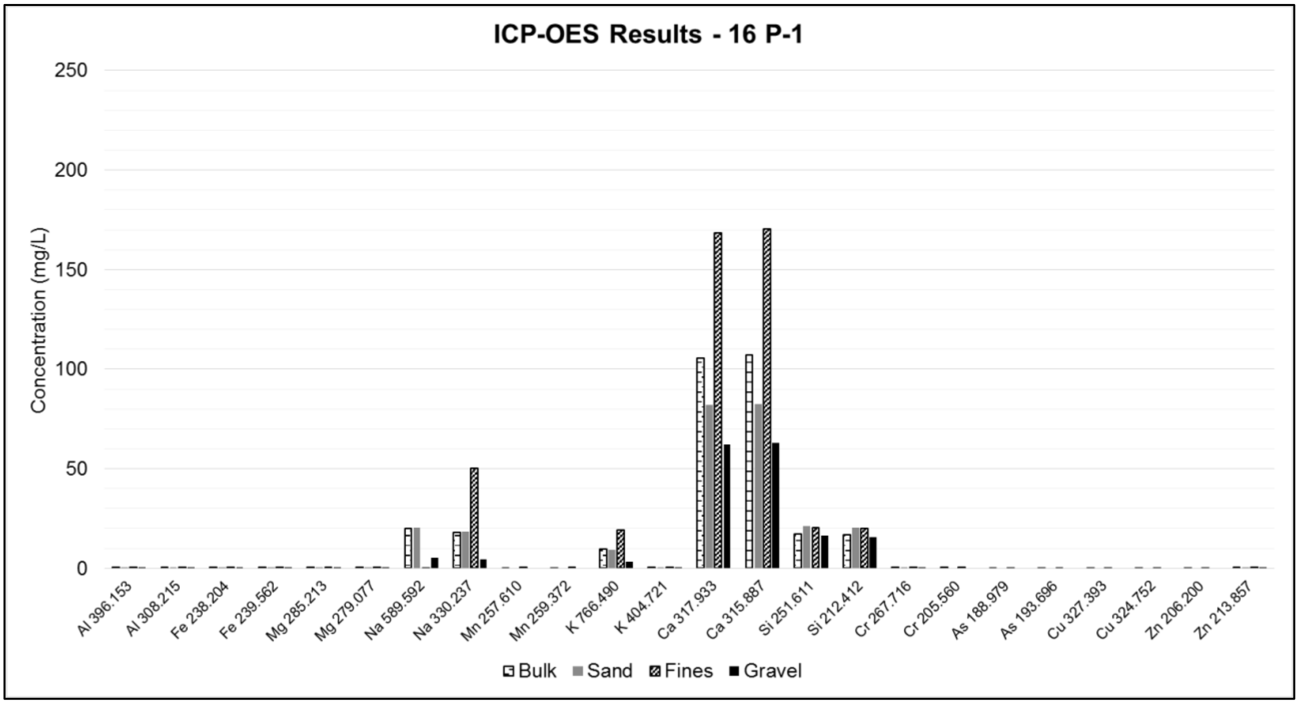


Figure 2-11 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 P-1. All elements tested

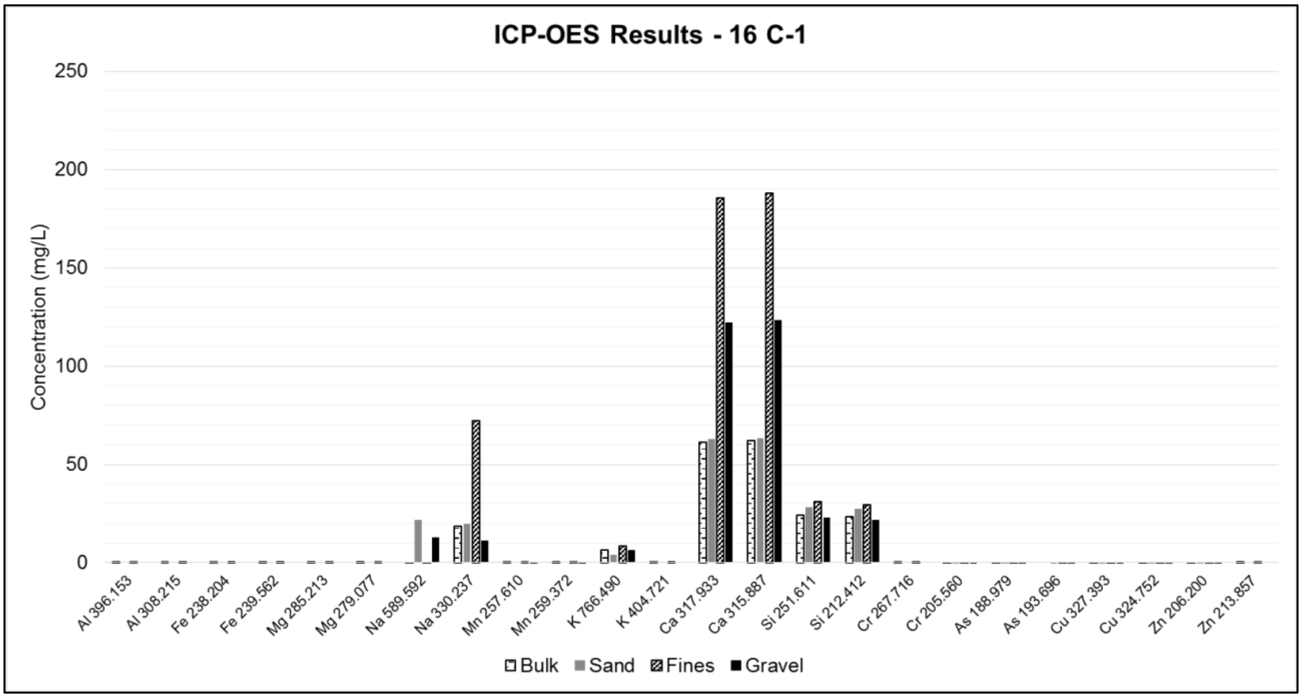


Figure 2-12 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 C-1. All elements tested

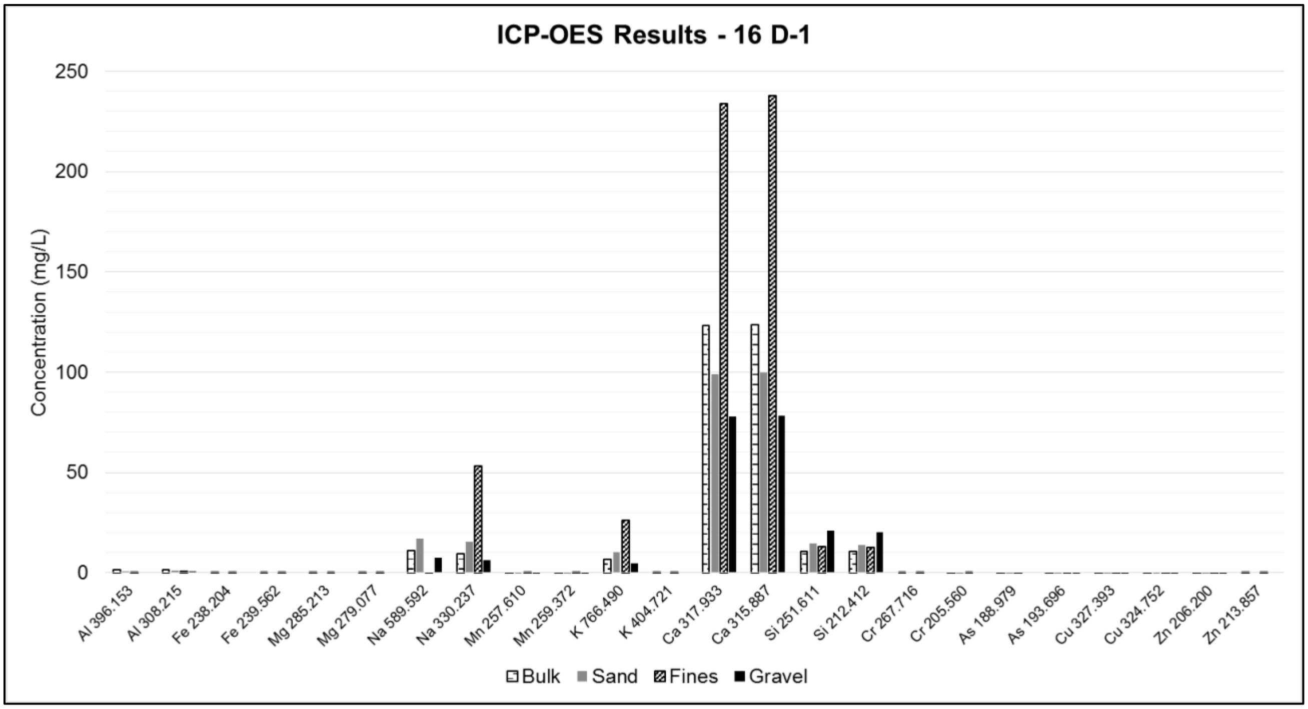


Figure 2-13 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 D-1. All elements tested

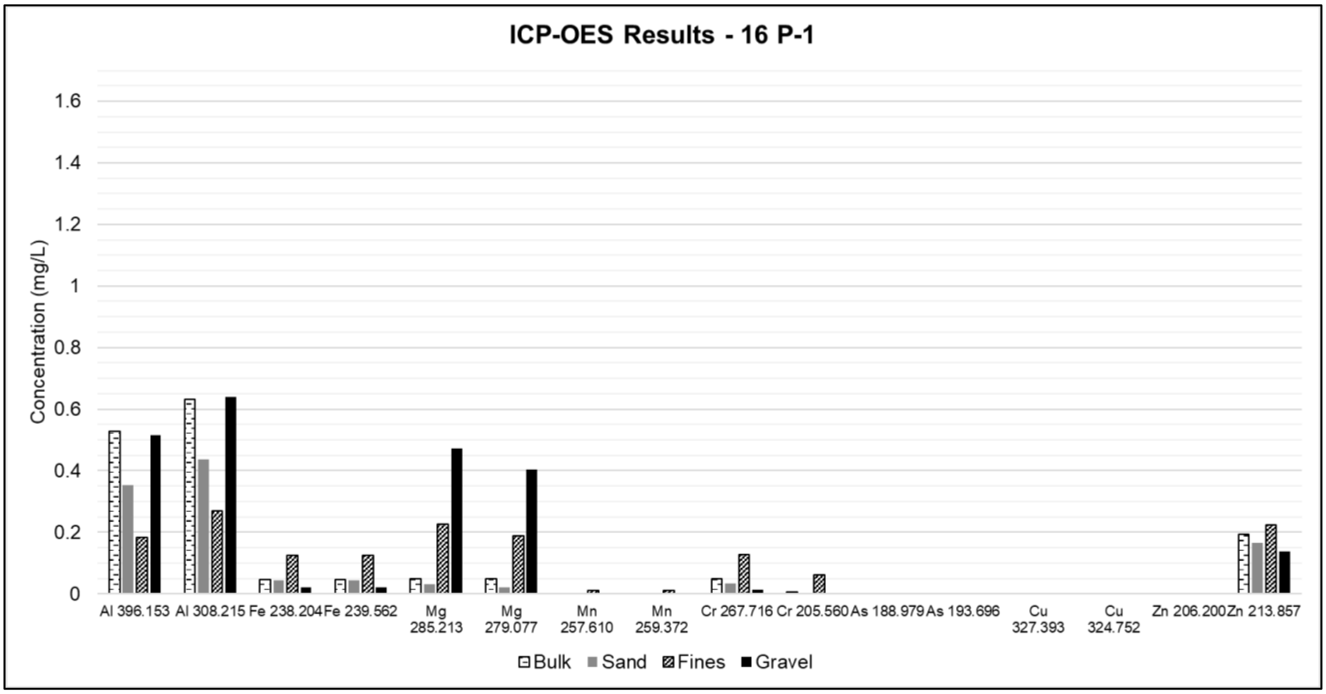


Figure 2-14 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 P-1. Elements Al, Fe, Mg, Mn, Cr, As, Cu, Zn

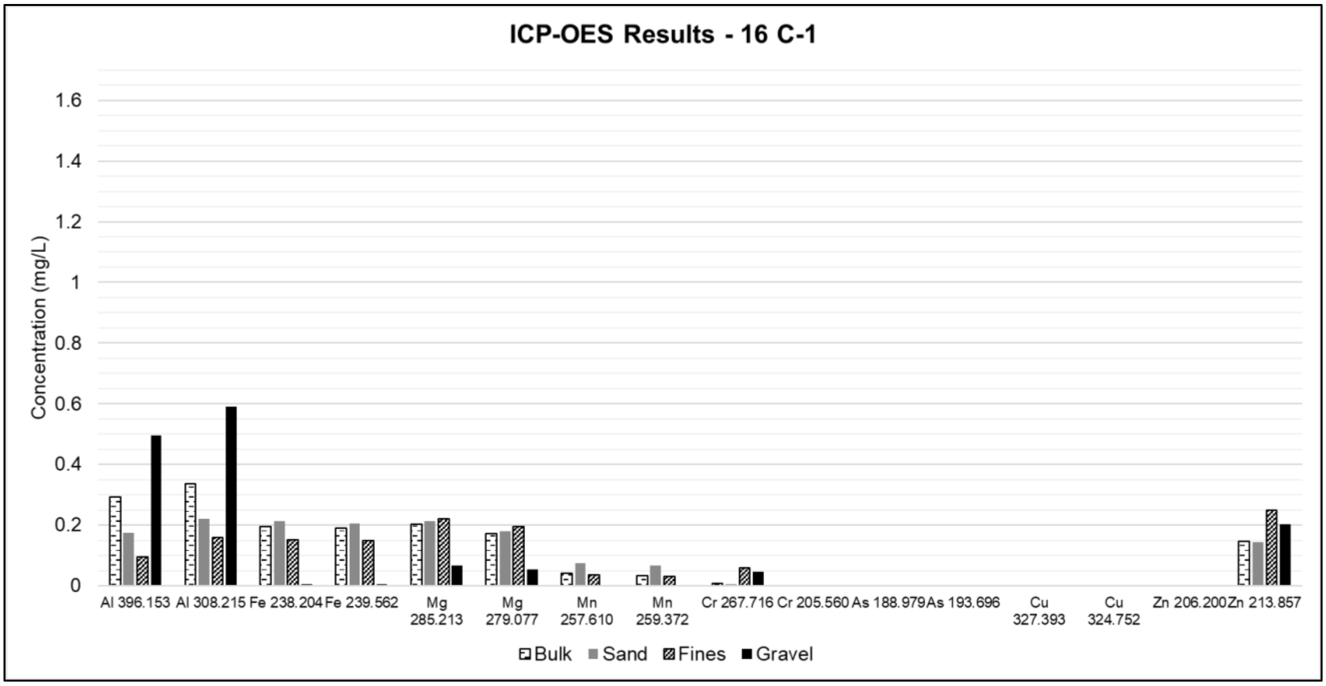


Figure 2-15 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 C-1. Elements Al, Fe, Mg, Mn, Cr, As, Cu, Zn

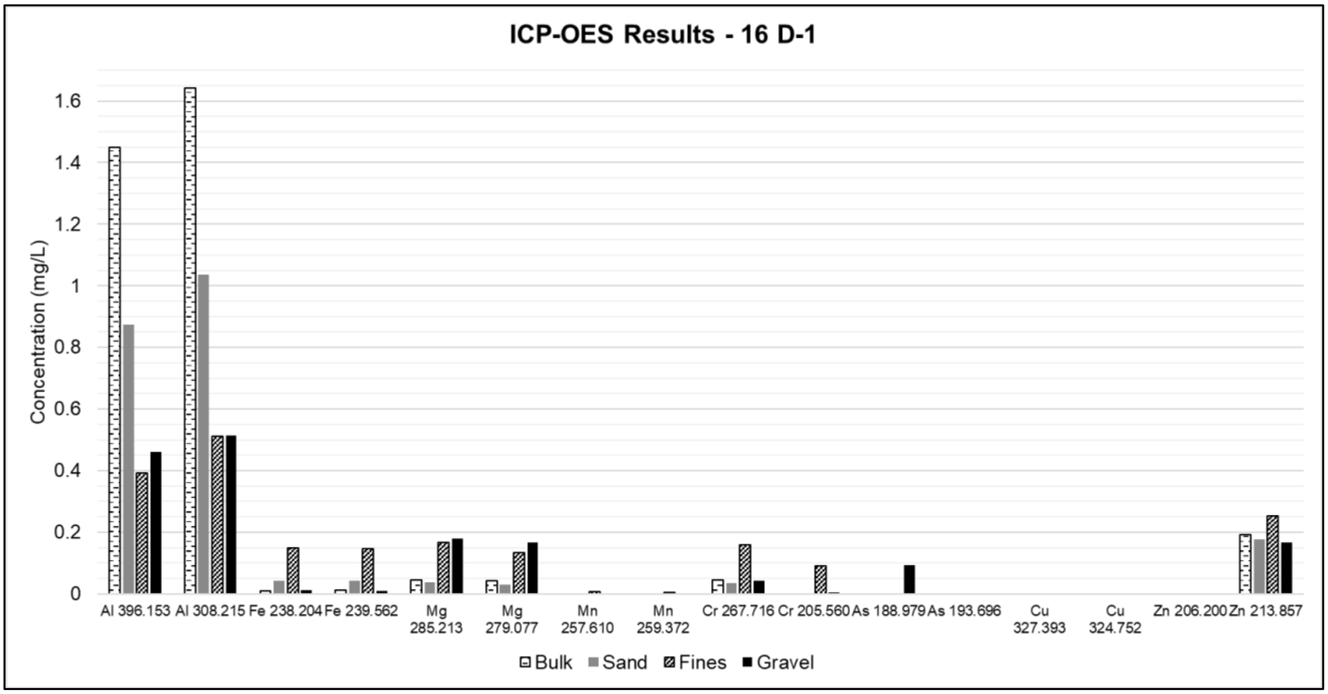


Figure 2-16 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) results for aged MnROAD RCA sample 16 D-1. Elements Al, Fe, Mg, Mn, Cr, As, Cu, Zn

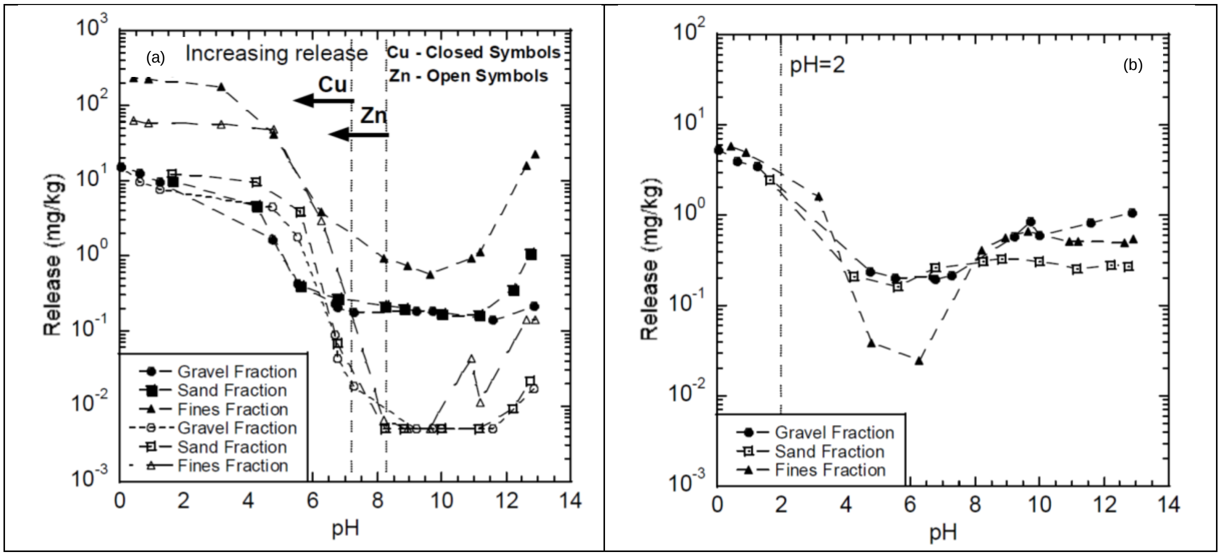


Figure 2-17 Trace element release from original RCA leachate with increasing pH. Results for Cu, Zn and Cr (Chen et al. 2013)

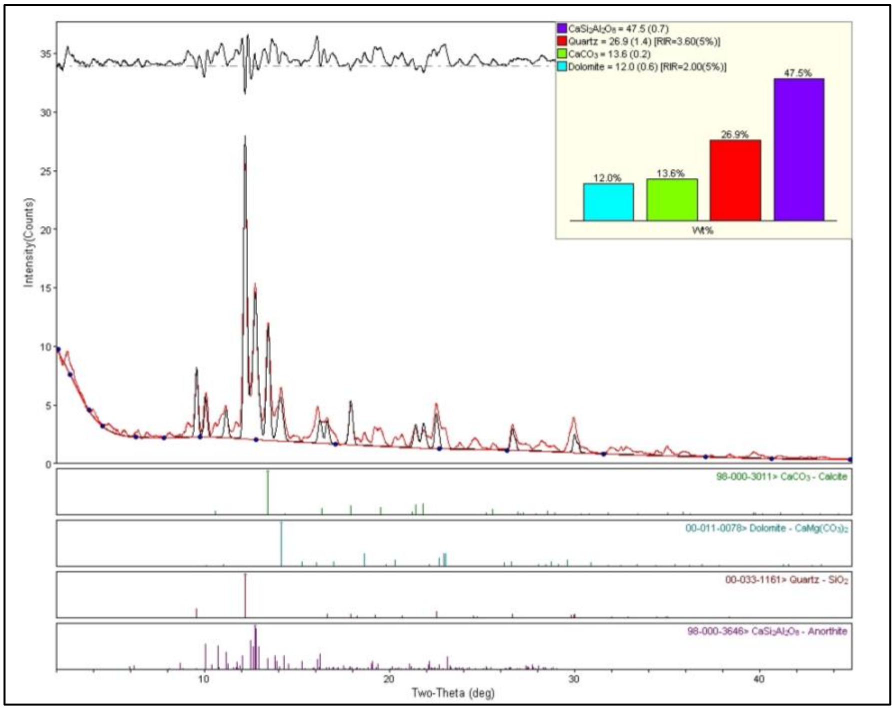


Figure 2-18 X-Ray Diffraction Spectroscopy results for aged MnROAD RCA sample 16 P-1

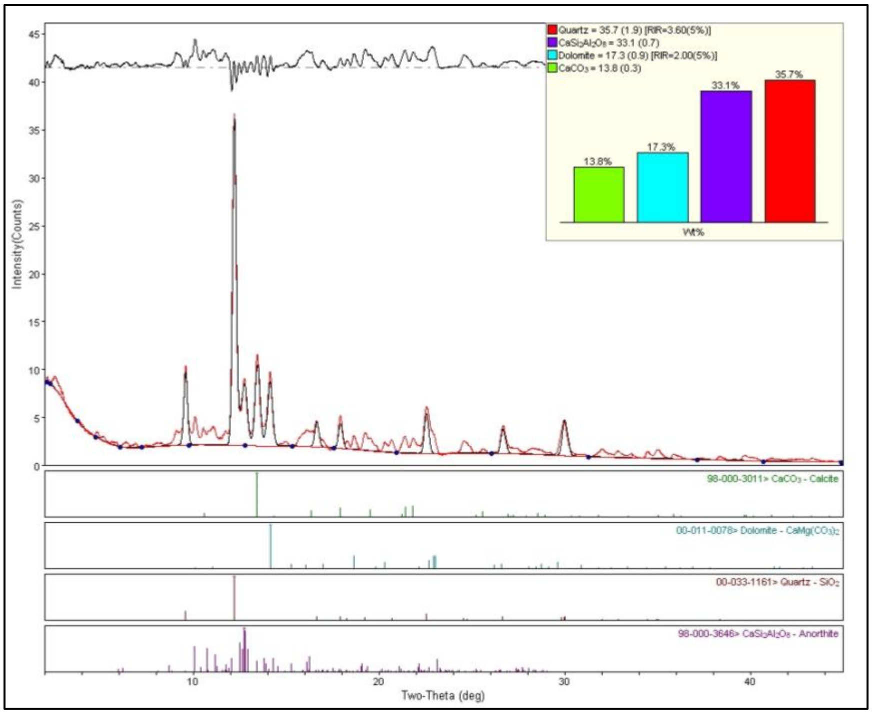


Figure 2-19 X-Ray Diffraction Spectroscopy results for aged MnROAD RCA sample 16 C-1

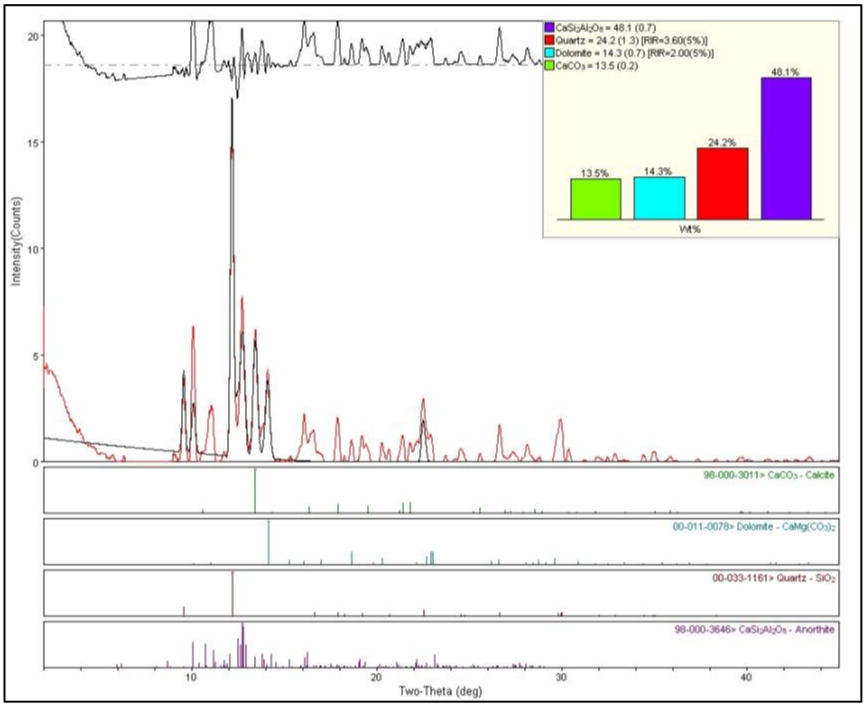


Figure 2-20 X-Ray Diffraction Spectroscopy results for aged MnROAD RCA sample 16 D-1

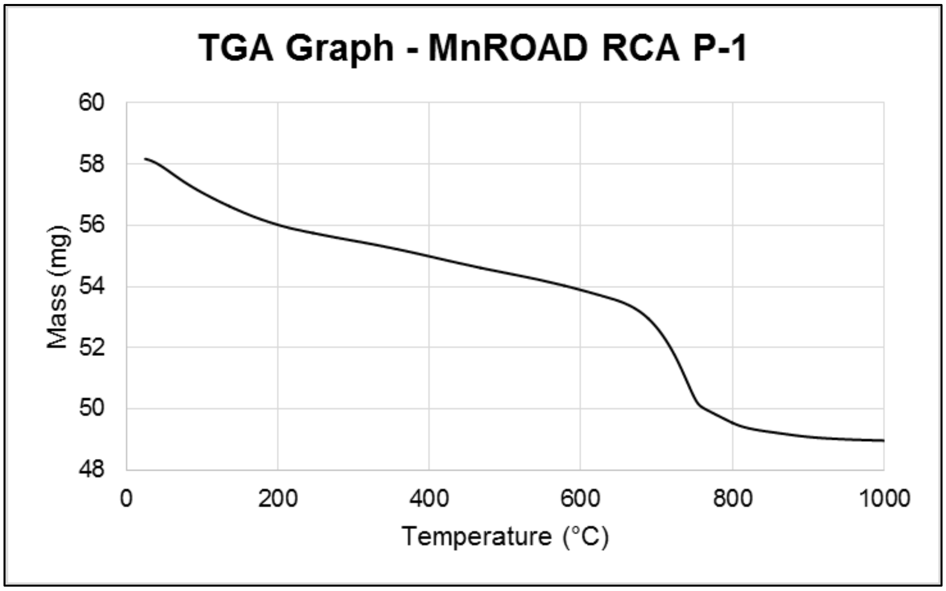


Figure 2-21 Thermogravametric Analysis graph for aged MnROAD RCA sample 16 P-1

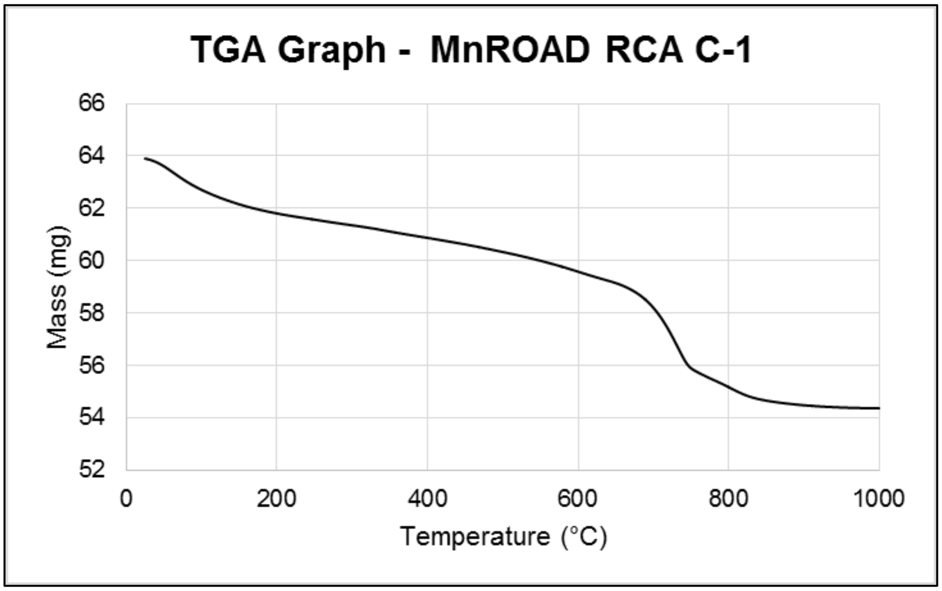


Figure 2-22 Thermogravametric Analysis graph for aged MnROAD RCA sample 16 C-1

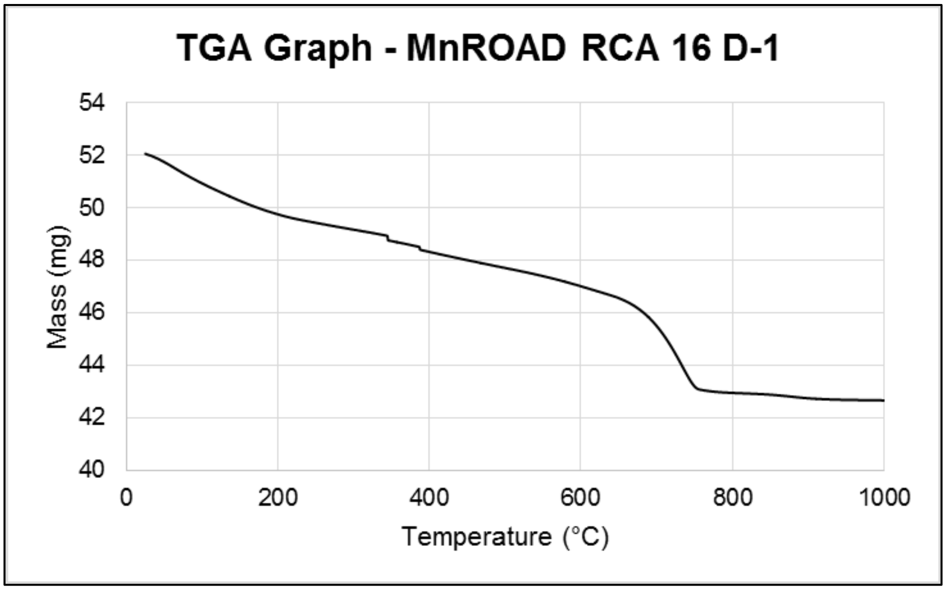


Figure 2-23 Thermogravametric Analysis (TGA) graph for aged MnROAD RCA sample 16 D-1

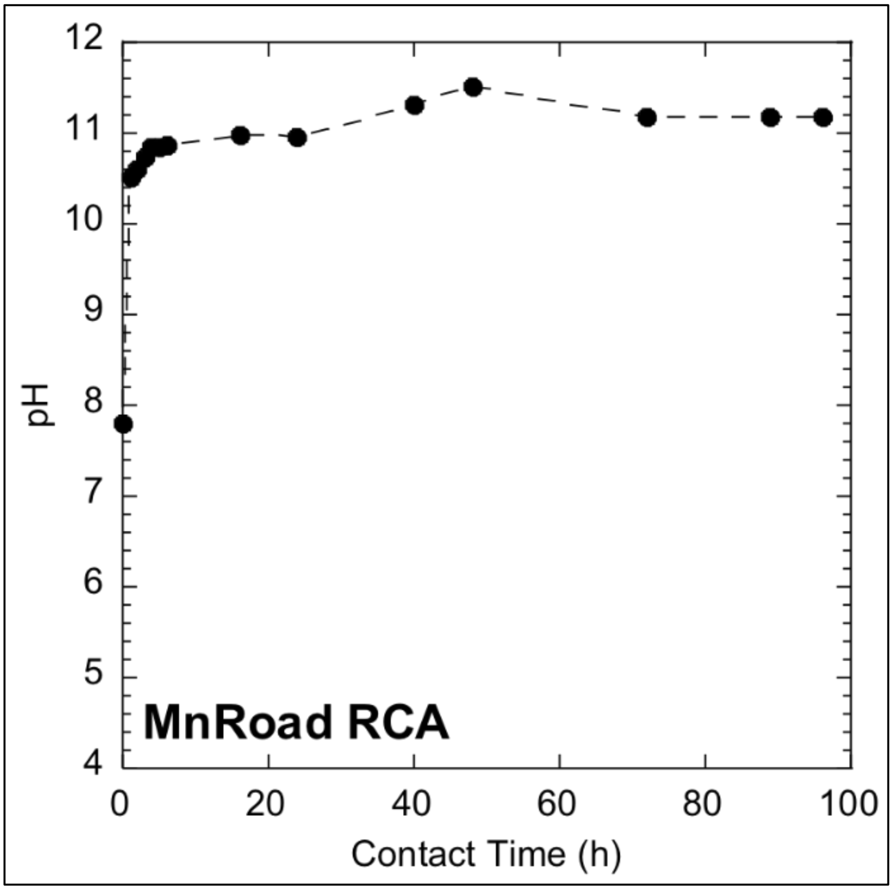


Figure 2-24 Change in pH of water in contact with original MnROAD RCA

Figure 2-25 Fine, sand, gravel and bulk fractions of 16 P-1

Figure 2-26 Gravel samples prepared for batch tests

Figure 2-27 Fine and sand samples prepared for batch tests

Figure 2-28 End-over-end tumbler used to agitate batch samples before testing

Figure 2-29 Inductively coupled plasma optical emission spectrometer (ICP-OES, Vista-MPX CCD Simultaneous ICP-OES, Varian Inc., CA, US)

Figure 2-30 Rigaku D/Max Rapid II diffractometer used for X-ray diffraction analysis

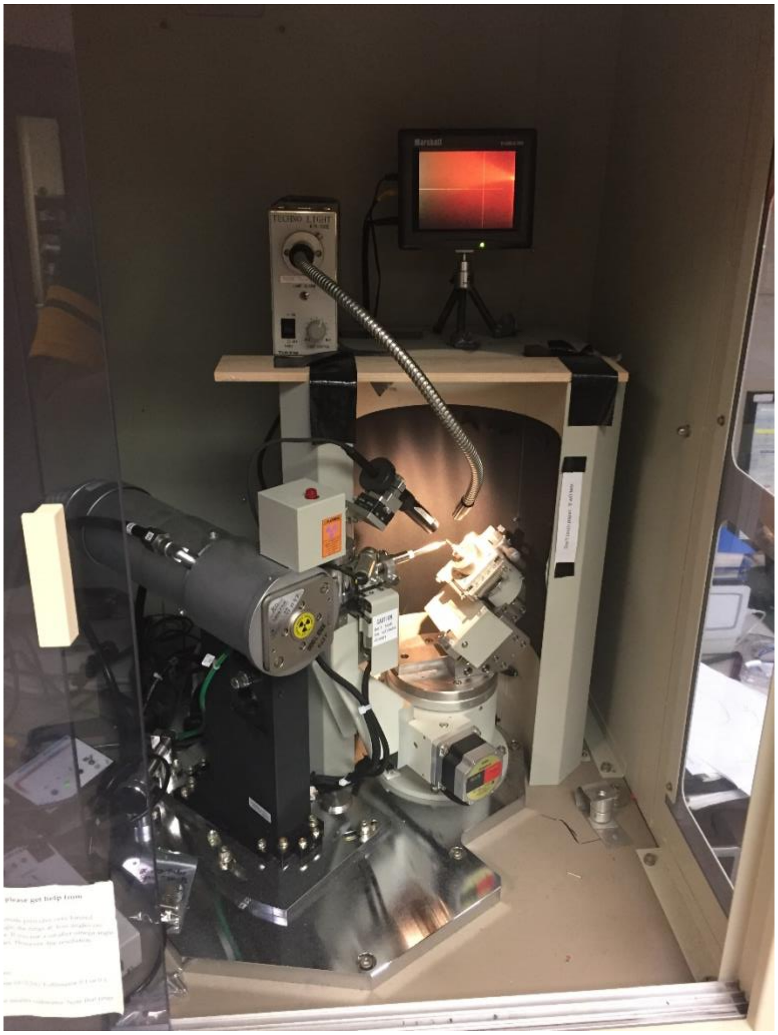


Figure 2-31 Interior of Rigaku D/Max Rapid II diffractometer used for X-ray diffraction analysis

3. IMPACT OF CONTACT TIME ON LEACHATE CHEMISTRY FROM RECYCLED CONCRETE AGGREGATES

Co-authors include: Zoe Kanavas who helped collect and interpret the inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and physical characteristic data. Jared Rudolph worked on acid neutralization capacity (ANC), electrical conductivity (EC) and oxidation-reduction potential (ORP) data collection. Matthew Ginder-Vogel and Tuncer Edil contributed to editing the text as well as data interpretation.

3.1 BACKGROUND

Many studies have characterized recycled concrete aggregate (RCA) material using conventional laboratory batch tests (Chen et al., 2012; Lewis et al., 2015). However, there still exists discrepancies between these laboratory batch tests and field leachate data. The results from the study in Chapter 2 showed such discrepancies between material pH from laboratory batch tests and pH from field leachate collected at the MnROAD research facility. Field leachate data collected at the MnROAD facility consistently showed near neutral pH, between 6.5 and 8.0, after 7 months (Chen et al., 2012). However, material pH from laboratory batch tests of the original RCA ranged between 11.0 and 12.1 (Chen et al., 2012), while the material pH of the aged MnROAD RCA characterized in Chapter 2 of this thesis ranged between 10.7 and 11.5. The study in Chapter 2 of this thesis also assessed the material pH of the clayey local subbase soils used at the MnROAD site. The material pH determined in the study ranged between 10.15 and 10.9, higher than was expected for clayey soils. These disparate results illustrate the need for a better understanding of the mechanisms involved in the conventional batch tests, as well as the need for alternative methodologies that better emulate field conditions.

The discrepancies in pH suggest that the material pH of RCA and subgrade soils determined from laboratory batch tests are not representative of the leachate pH that can be expected from real world conditions. There are two likely explanations for this. In the case of the RCA, the utilization of an end-over-end tumbler to determine material pH may result in particle abrasion and removal of the protective calcium carbonate layer that would otherwise limit the material pH. In the case of the subbase soils, the high water to solid ratio and extended contact time likely allow more extensive dissolution of calcium carbonate minerals, and the concomitant large increase in pH.

Contact time, which is overlooked in most conventional laboratory batch tests, is likely a critical factor controlling the leachate pH and alkalinity. A preliminary characterization of the original RCA installed at the MnROAD site revealed that the material pH was quite sensitive to contact time, shown in Figure ***3-1***. After one hour of contact with RCA in a column, the pH of the solution was only 7.8. However, exposure over longer subsequent time periods rapidly increased the material pH.

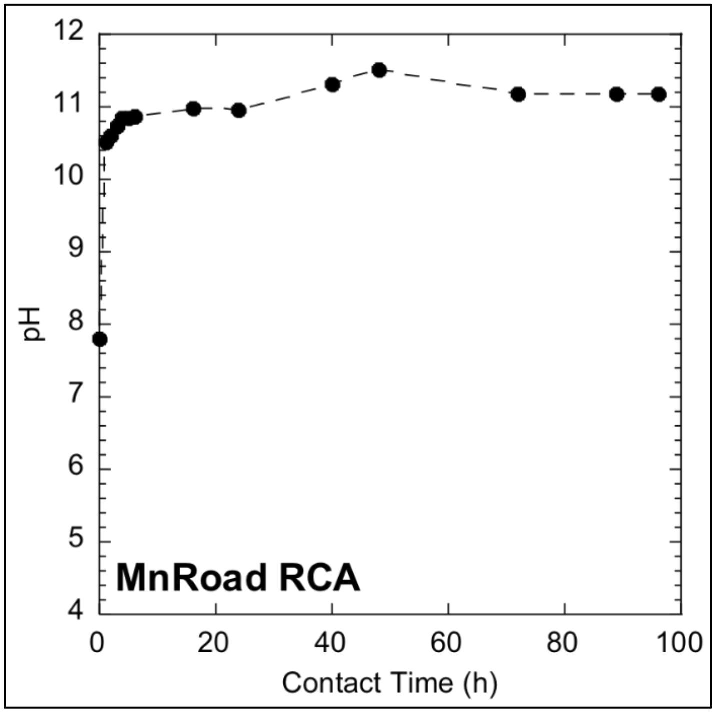


Figure 3-1 Change in pH of water in contact with original MnROAD RCA

In the present study, the impact of contact time in laboratory batch tests on the leachate chemistry from the aged MnROAD RCA and subbase soils was examined. Additionally, the methodology in this study aimed to minimize the impact of particle abrasion, thus preserving the carbonate layer around RCA particles. The results from the modified laboratory batch tests were compared with the results from the conventional laboratory batch tests conducted in the study in Chapter 2.

3.2 METHODOLOGY

The dependence of pH and alkalinity on contact times with recycled concrete aggregates (RCA) and subbase soils was tested in the laboratory using batch test methods. RCA was sampled from the base course layer below the passing lane, driving lane and centerline from the MnROAD research facility. Additionally, subbase soils below the passing lane, driving lane and centerline were also sampled at two different depths (sampling locations are outlined in more detail in Chapter 2). One representative batch from each lane was collected, homogenized by hand mixing and oven-dried overnight. Batch test samples were prepared with a solid to liquid ratio of 1:10 (50 g to 500 mL) with deionized water. To ensure homogeneity while minimizing abrasion between particles, the batch samples were continuously shaken on a stir plate (shown in Figure ***3-8***) for six hours, during which solution samples were taken periodically to measure pH and alkalinity. For the first ten minutes, solution samples were taken every minute. After the first ten minutes, samples were taken every five minutes until the first hour had passed. Following the first hour, samples were taken at half-hour intervals until the second hour passed. Samples were then collected every hour until the six-hour mark. This sampling methodology was adapted in order to obtain a higher resolution of data during the crucial initial periods of contact between the soil material and solution. Subsequently, for each of the samples collected in the six-hour test duration, the solution pH and alkalinity were tested.

The pH was determined using the Thermo Scientific Orion Combination pH Electrode. In order to determine the alkalinity of the samples, 5mL of each sample was first diluted with 25mL of deionized water. The 30 mL samples were tested in a Mettler

Toledo Compact Titrator. Each sample was titrated to a pH of 4.5 with 0.1 N H_2SO_4. The final two volumes of acid added and the resulting sample pH were recorded; these were then used to calculate the volume of acid required to bring each sample to a pH of 4.5. The total volume of each sample and the volume of acid to bring each sample to a pH of 4.5 were then used to find the alkalinity in terms of mg $CaCO_3$/L. Alkalinity was only determined for the samples obtained from contact with RCA, and not for the samples obtained from the subbase soils.

3.3 RESULTS AND DISCUSSION

3.3.1 Base-Course RCA Effluent pH and Alkalinity

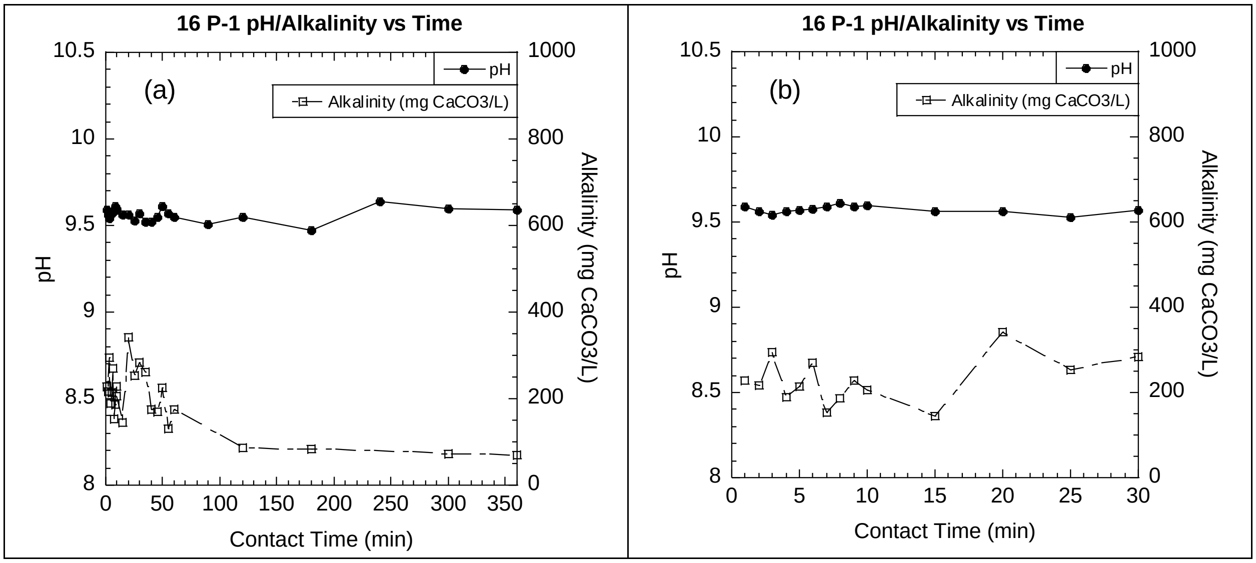


Figure 3-2 Changes in pH/Alkalinity with contact time for MnROAD aged RCA 16 P-1. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test

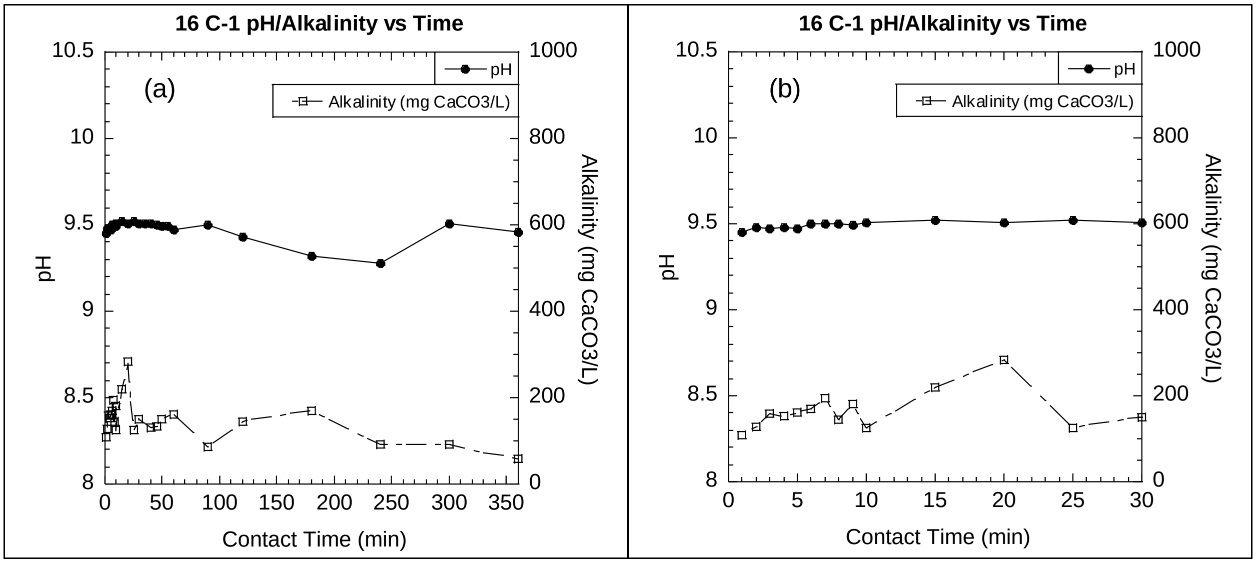


Figure 3-3 Changes in pH/Alkalinity with contact time for MnROAD aged RCA 16 C-1. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test

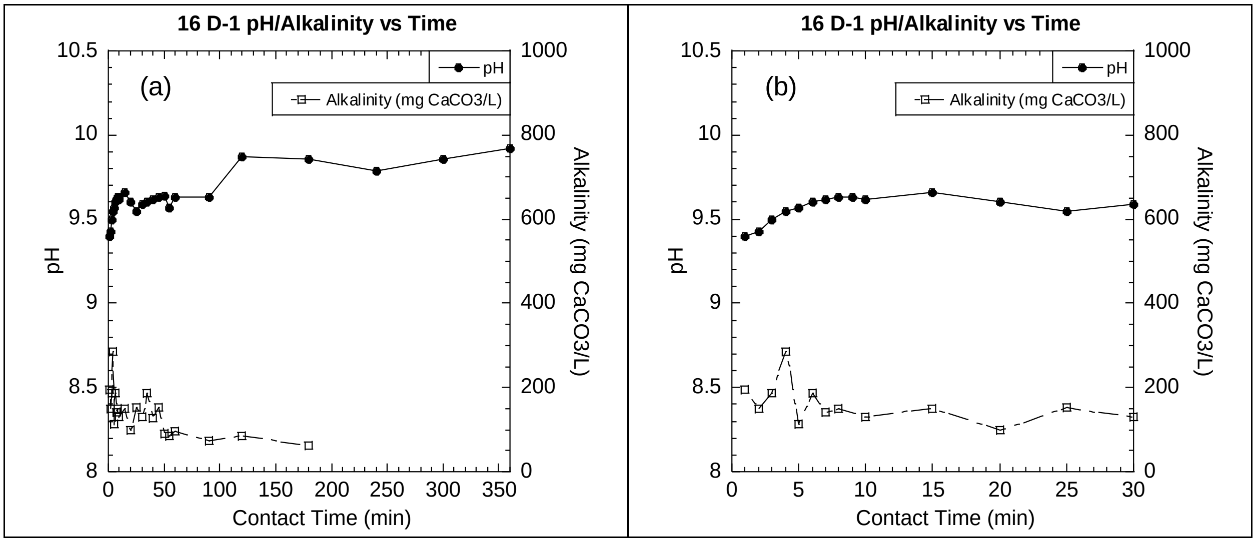


Figure 3-4 Changes in pH/Alkalinity with contact time for MnROAD aged RCA 16 D-1. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test

The response of pH and alkalinity to contact time with the aged MnROAD RCA are shown in Figure ***3-2***, Figure ***3-3*** and Figure ***3-4***. Samples 16 P-1 and 16 C-1 showed consistent pH throughout the whole test period, ranging between 9.3 and 9.7. Sample 16 D-1, however, showed an increasing trend in pH over time, with a wider range of pH between 9.4 and 9.9. All three samples showed alkalinity values ranging within 50 and 350 mg $CaCO_3$/L, with alkalinity generally decreasing over time.

Base-course in highway pavements are designed to drain easily, reducing pore water pressure build-up. As a result, the chemical characteristics of leachate within the first few minutes of contact with RCA are crucial to assess. The response of pH and alkalinity to contact time with the aged MnROAD RCA over the initial half hour of the test are shown in Figure ***3-2***(b), Figure ***3-3***(b) & Figure ***3-4***(b). All three RCA samples showed consistent pH through the initial half hour of the test, ranging between 9.4 and 9.7. Additionally, all three samples showed alkalinity values fluctuating between 100 and 350 mg $CaCO_3$/L.

3.3.2 Subbase Soil Effluent pH

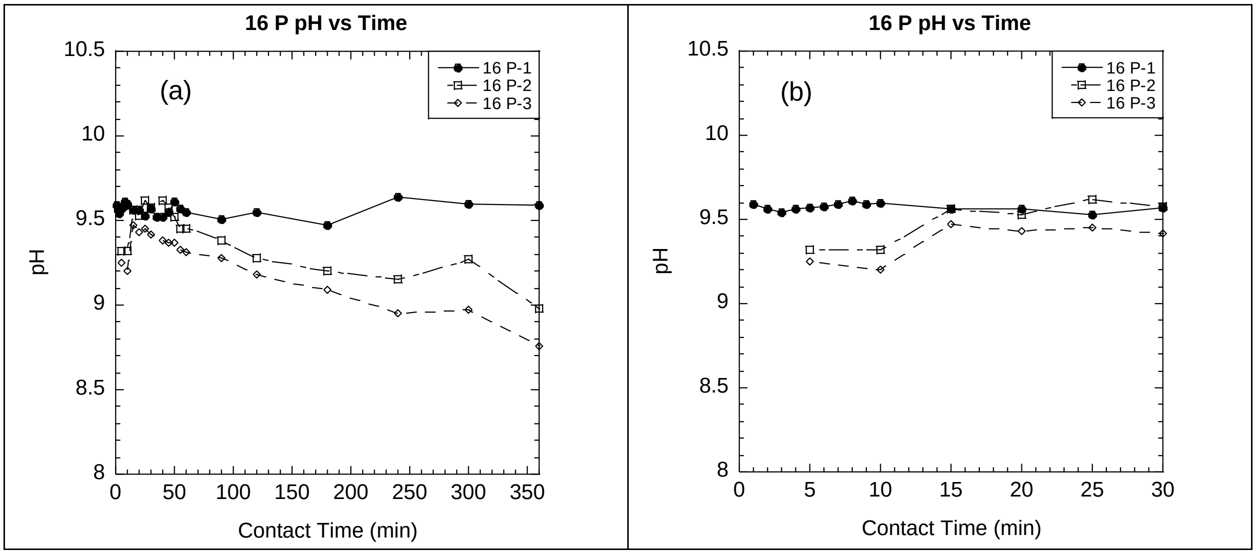


Figure 3-5 Changes in pH with contact time for MnROAD aged RCA 16 P-1 and subbase soils 16 P-2 and 16 P-3. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test.

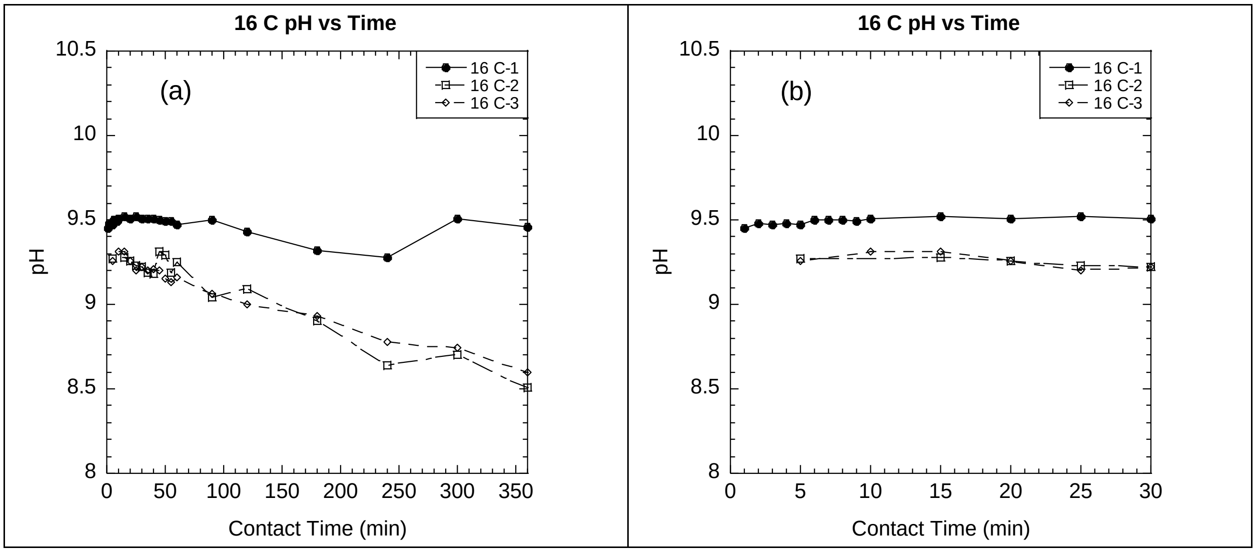


Figure 3-6 Changes in pH with contact time for MnROAD aged RCA 16 C-1 and subbase soils 16 C-2 and 16 C-3. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test.

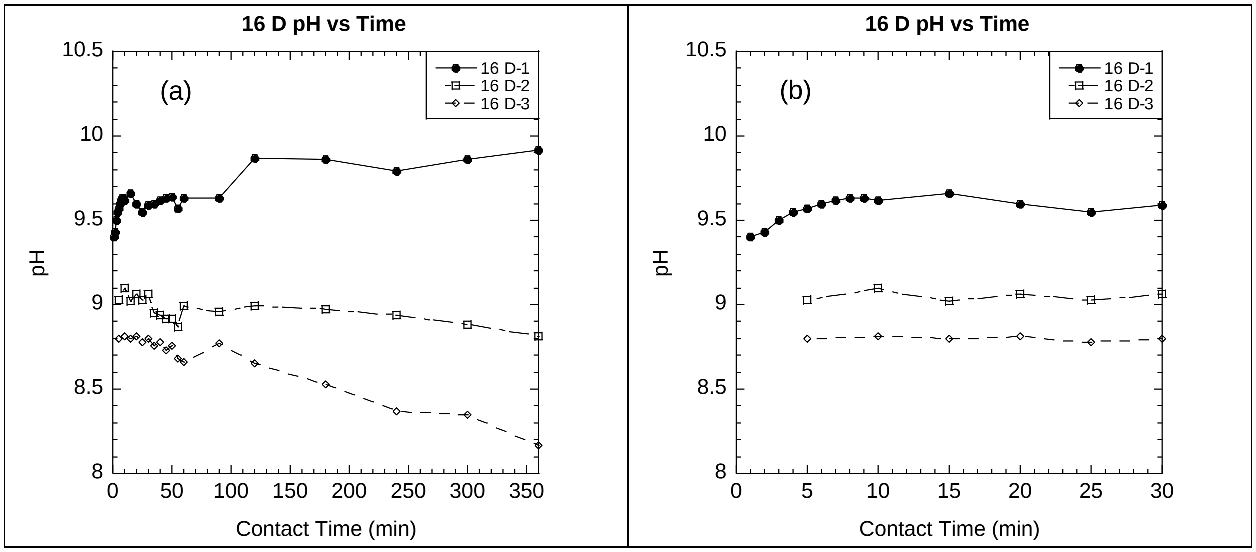


Figure 3-7 Changes in pH with contact time for MnROAD aged RCA 16 D-1 and subbase soils 16 D-2 and 16 D-3. Results shown over (a) six-hour duration of test and (b) first 30 minutes of test.

The response to contact time with the aged MnROAD RCA and the subbase soils are shown in Figure ***3-5***, Figure ***3-6*** and Figure ***3-7***. All the subbase soil samples showed decreasing trends in pH over time. Generally, the deeper subbase samples, 16 P-2 and 16 D-2, showed lower pH over time. The subbase soils from sample 16 P showed the highest pH values, ranging between 8.8 and 9.6. The subbase soils from sample 16 C showed pH values between 8.5 and 9.3. Finally, the subbase soils from sample 16 D showed the lowest pH values, ranging between 8.2 and 9.2. Through the first half hour of the test (shown in Figure ***3-5***(b), Figure ***3-6***(b) and Figure ***3-7***(b)), all six subbase samples showed very consistent pH, subsequently decreasing over the rest of the test.

The results indicated a slight decrease in effluent pH from the subbase soils. This decreasing trend could be due to the dissolution of surface hydroxyl and carbonate phases first, followed by the dissolution and subsequent precipitation of Al^{3+} from the clay surface, leading to more acidic conditions. Another possible explanation for the decreasing pH could be the dissolution of $CO_{2(g)}$ in the system, leading to more acidic conditions. An assessment of the solid phase composition of the subbase soils could help better understand this behavior.

The results also showed a decrease in effluent pH with depth. The presence of lower pH away from the RCA layer could suggest some retention of hydroxide species in the soil layers closer to the RCA. An assessment and development of hydroxyl species transport and precipitation models could provide better justification for this trend with depth. It was initially expected that the subbase soils in 16 P would have a lower pH response, due to the presence of the pan lysimeter above unit 16 P-2 during field deployment. However, samples for 16 P-2 and 16 P-3 could have also been collected away from the pan lysimeter, explaining the similarities in the pH response with those from the subbase soils in 16 C and 16 D. No other significant spatial trends were determined from the results.

3.3.3 Comparison of Effluent pH Between Methodologies

The material pH determined for the aged MnROAD RCA and subbase soil samples in Chapter 2 are shown in Table ***3-1*** below. The results from the current study showed significantly lower effluent pH than the material pH determined in Chapter 2.

Table 3-1 Bulk material pH for aged MnROAD RCA samples and subbase soils under 16 P, 16 C and 16 D. Values determined through conventional batch test methods used in Chapter 2

Bulk Material pH			
Unit	**16 P**	**16 C**	**16 D**
1 - RCA	11.31	11.08	11.45
2 - Subbase Soil	10.41	10.47	10.91
3 - Subbase Soil	10.15	10.53	10.61

The RCA effluent pH in the six-hour duration of the test were generally consistent. The effluent from contact with the aged MnROAD RCA resulted in pH values ranging between 9.3 and 9.9. These pH values were significantly lower than the material pH determined using conventional batch test methods outline in Chapter 2, which ranged between 10.8 and 11.45. This significant difference in pH is likely attributed to the limited particle abrasion in the current test, which was established by using a stir plate instead of an end-over-end tumbler, as is standard in conventional batch tests. The resulting pH is more consistent with carbonate dissolution, which generally produces a solution pH of approximately 8.2 in the presence of atmospheric carbon dioxide. The slightly higher pH than 8.2 is likely due to the dissolution of other alkali cement phases in the RCA. These results support the hypothesis that contact time and particle abrasion play a significant role in determining leachate pH in field conditions.

The effluent from contact with subbase soils resulted in pH values ranging between 8.2 and 9.6, which were lower than the effluent pH in contact with the aged RCA. These pH values were also significantly lower than the material pH determined using conventional batch test methods outline in Chapter 2, which ranged between 10.15 and 10.91. The effluent pH from contact with the subbase soils showed decreasing pH over the six-hour duration of the test, however, the material pH from the conventional batch test methods in Chapter 2 showed a higher material pH after the standard 24 hours of reaction. The impact of contact time on effluent pH from subbase soils needs to be studied over a longer duration in order to address this discrepancy. Additionally, an assessment of dissolution/precipitation and transportation mechanisms of species in the subbase soils could also help understand the effluent pH response with contact time.

3.4 CONCLUSIONS

This assessment of the impact on leachate chemistry of contact time with aged MnROAD recycled concrete aggregate (RCA) showed a slight increasing trend of effluent pH over time. The study also showed decreasing trends of effluent pH from contact with subbase soils over the six-hour duration of the test. Furthermore, a comparison of the effluent pH over a six-hour test duration showed significantly lower results, for both base course RCA and subbase soils, than material pH values from conventional batch test methods adapted in the study in Chapter 2. Additional characterization of the subbase soils could address some trends and discrepancies observed in this study. A geochemical model assessing the dissolution/precipitation and transportation mechanisms relating to the subbase soil could provide further insight into these trends. In conclusion, the results from this study support the hypothesis that contact time and particle abrasion play a significant role in determining leachate pH in field conditions.

3.5 APPENDIX B

Figure 3-8 Stir plate used to mix batch samples

CONCLUSIONS AND RECOMMENDATIONS

This thesis assesses the physical and chemical characteristics of aged recycled concrete aggregates (RCA) in highway construction. The first chapter identifies the established fundamental chemical and physical concepts regarding RCA use, as well as the shortcomings in the primary literature. The second chapter is a forensic examination of the physical and chemical characteristics of an aged RCA material used at the MnROAD research facility over an eight-year period. The third chapter of this thesis is a study of the impact of contact time on RCA and subbase soil leachate chemistry in a laboratory setting. The chapter addresses some of the common oversights in conventional laboratory methodologies used to determine leachate pH, by more effectively simulating field conditions.

The literature review conducted in Chapter 1 identified that the existing body of work, while extensive, is generally lacking on several fronts. Only two studies have extensively characterized the leachate chemistry from RCA utilized in roadbed applications. Additionally, previous laboratory-based studies conducted on the topic have generally used either contact times, or liquid to solid-ratios that are not representative of real-world RCA applications. Furthermore, no published studies examining neutralization of high pH/alkalinity RCA leachate by common sub-grade soils exist. Finally, the existing academic and professional literature characterizing leachate produced from contact with RCA uses the terms “high pH” and “alkaline/alkalinity” interchangeably. This subsequently leads to a great deal of confusion regarding the chemistry of RCA leachate, which has both a high pH and is high in alkalinity.

The forensic examination of the aged MnROAD RCA, conducted in Chapter 2, showed an increase in the acid neutralization capacity (ANC) of the material over the eight-year field deployment. From the ANC curves, the finer particles continued to show a higher acid neutralization capacity than the coarser particles. Furthermore, the ANC curves indicated significant carbonation in the fine fractions of the aged MnROAD RCA. The aging of the MnROAD RCA was quantified further through material pH, X-ray diffraction and thermogravimetric analyses. These tests indicated a higher carbon content in the aged RCA than in the original RCA characterized by Chen et al. (2012, 2013). The X-ray diffraction analysis on the fine fractions highlighted the absence of significant amounts of crystalline portlandite in the aged RCA. Furthermore, the leaching of inorganic elements was also assessed as part of this forensic examination. The ICP-OES results indicated a decrease in Cu and Cr concentrations in the aged RCA, but showed an increase in Zn concentrations.

As background to this forensic examination, leachate observations were made from both field and lab tests during the eight years that the MnROAD facility was operational. Column leaching tests conducted in the lab showed significantly different results from the leachate pH observed in the field tests (Chen et al., 2012). Furthermore, the material pH of both the base-course RCA and the subbase soils determined in this forensic study were also significantly higher than the leachate pH determined from the pan lysimeters at the MnROAD facility, which ranged between 6.5 and 8.0 after 7 months (Chen et al., 2012). These discrepancies in pH suggest that the material pH of RCA and subgrade soils are not representative of the leachate pH that can be expected from real world conditions.

The assessment of the impact on leachate chemistry of contact time with aged MnROAD RCA, conducted in Chapter 3, showed a slight increasing trend of effluent pH over time. The study also showed decreasing trends of effluent pH from contact with clayey subbase soils over the six-hour duration of the test. Furthermore, a comparison of the effluent pH over a six-hour test duration showed significantly lower results, for both base course RCA and subbase soils, than material pH values from conventional batch test methods adapted in the study in Chapter 2. The results from this assessment supported the hypothesis that contact time and particle abrasion play a significant role in determining leachate pH in field conditions.

FUTURE RESEARCH OPPORTUNITIES

This thesis found substantial knowledge gaps in the behavior of subbase soils in pavements using recycled concrete aggregates (RCA), which need to be evaluated in order to have a holistic understanding of the impact of RCA as a highway construction material. A study on the solid-phase chemistry of the MnROAD subbase soil could establish the cause of high material pH, which were determined in Chapter 2 of this thesis. Furthermore, a study modelling dissolution/precipitation and transportation mechanisms of RCA species could further justify the behavior of the underlying subbase soils found in this thesis. Another major knowledge gap identified by this thesis is the lack of studies assessing the ability of subbase soils to neutralize high pH/alkalinity leachate from RCA. A study modelling dissolution/precipitation and transportation mechanisms of RCA species would also help establish the effectiveness of various types of subbase soils in doing so. The ability to identify these soils, and a general understanding of their chemical behavior, will allow for a more widespread use of RCA as a pavement construction material.

Finally, Chapter 3 of this thesis identified that contact times play a significant role in RCA leachate chemistry. These results have practical implications on how pavements using RCA should be designed to minimize contact times with pore water in the field. Subsequently, identifying specific design criteria for pavement design using RCA, such as compaction (max dry density ranges), hydraulic conductivity, gradation, etc, could help better translate the findings of such studies to effective industry application. These design criteria are imperative for the safe and effective use of RCA, and could help satisfy both environmental regulations as well as mechanical performance standards.

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