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Review

Recycled concrete aggregate in base course applications: Review of field and laboratory investigations of leachate pH

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ABSTRACT

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

1. Introduction

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

The supply of C&D waste, particularly concrete, and simultaneous aggregate demand for construction purposes presents the opportunity to recycle C&D waste materials as a substitute for virgin aggregate. Recycling asphalt, crushed stone, and Portland cement concrete for recycled remains limited across much of the United States (Silva et al., 2017). Some identified barriers to recycling C&D aggregate for use in road construction applications include: few or limiting standards and specifications; insufficient financial incentive; long hauling distance to recycling plants; variable supply and demand; client perception and preconceptions; variable quality; and environmental concerns (Silva et al., 2017). Despite these identified barriers, recycling of C&D waste materials is on the rise; the reported amount of asphalt, crushed stone, and Portland cement concrete recycled in the United States increased by nearly 4% between 2015 and 2016 (Willett, 2017).

Recycled substitutes for virgin aggregate in pavement construction applications are becoming more prevalent, particularly as granular and stabilized base course. Most commonly, recycled concrete aggregate (RCA) and recycled asphalt pavement aggregate are used as unbound base course in pavement construction (Fig. 1) (Bozyurt et al., 2012). The primary functions of pavement base course are to provide

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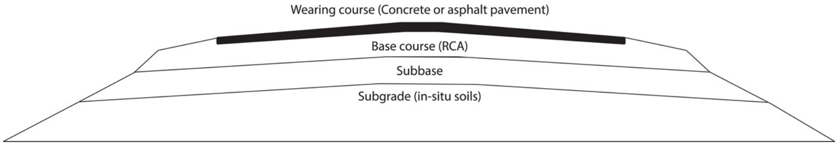

Fig. 1. Pavement profile schematic.

structural support, stiffness, and drainage (FHWA, 2017). A well-designed base course system is constructed with a well-graded, durable material and is freely draining (FHWA, 2017). Many studies have evaluated the use of RCA as pavement base course, and in general, RCA is recognized as a mechanically sufficient base course substitute for virgin aggregate. For example, RCA has a higher resilient modulus (Vieira and Pereira, 2015; Bozyurt et al., 2012; Bennert et al., 2000; Bestgen et al., 2016a; Edil et al., 2012; Kuo et al., 2002), higher shear strength (Vieira and Pereira, 2015; Saeed et al., 2006), lower plastic strain (Bozyurt et al., 2012; Edil et al., 2012), lower permanent deformation (Bennert et al., 2000; Saeed et al., 2006), and higher California Bearing Ratio (Vieira and Pereira, 2015; Bestgen et al., 2016a; Saeed et al., 2006) than virgin aggregate. In addition to exceeding the mechanical performance of virgin aggregate, RCA base course are more resistant than virgin aggregate to stiffness loss from freeze/thaw cycles (Edil et al., 2017).

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

Although RCA base course exhibits desirable mechanical properties and life-cycle benefits, environmentally responsible applications of RCA must consider the high pH leachate and trace element leaching risks reported in the literature. RCA leachate generation from stockpiles and pavement systems is unavoidable, and therefore it is of great interest to understand the fate and transport of the leachate. Existing laboratory investigations consistently measure high leachate pH, pH 10 to 14; conversely, long-term highway field studies demonstrate that, after an initial phase of high pH, leachate approaches neutral pH within one to two years of construction (Engelsen et al., 2006, 2012; Engelsen et al., 2017; Chen et al., 2012, 2013). Discrepancies in leachate pH from laboratory and field studies suggest that the laboratory methodology does not accurately represent field conditions. Many of the existing laboratory investigations of RCA leachate chemistry are designed to investigate the pH-dependent release of major and trace elements; future investigations of RCA leachate pH should be motivated by the physicochemical conditions of base course systems in designing the laboratory methods.

The existing literature examining laboratory and field investigations of RCA leachate is often contradictory and measures varying risks associated with RCA leachate pH and alkalinity. As there are presently no literature reviews of RCA leachate chemistry, there is a need to evaluate the methodological limitations and contradictions in RCA leachate pH and alkalinity among the many existing studies. The purpose of this paper is to provide a state-of-the-art review of the existing laboratory and field investigations of RCA leachate chemistry. In this manuscript, the fundamental chemistry related to pH and alkalinity of RCA leachate establishes the basis of understanding for the critical evaluation of the existing literature. Then, this review presents the methodology, results, and limitations of existing RCA leachate investigations, including long-term field monitoring, batch reactor tests, and column leaching tests methodology. Critical evaluation of existing investigations indicates that conventional laboratory methodology is not representative of field conditions. The authors recommend that future laboratory investigations consider intermittent wetting and drying cycles, eliminate particle abrasion, employ relevant contact times, and consider additional environmental processes that reduce leachate pH.

2. Chemical characteristics of RCA

Portland cement concrete becomes RCA when it is crushed after its usable life as a monolith. Portland cement concrete is a mixture of coarse and fine aggregate in Portland cement paste; Portland cement paste consists of calcium carbonate ($CaCO_3$), ettringite (Afm), monosulfate (Aft), calcium hydroxide, also known as portlandite ($Ca(OH)_2$), calcium-silicate hydrate (C-S-H) ($1.7CaO{\cdot}SiO_2{\cdot}xH_2O$), and trace amounts of unreacted cement (e.g., $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$) (Brunauer and Copeland, 1964; Matschei et al., 2007; Hidalgo et al., 2007; Papadakis et al., 1989; Bache et al., 1966; Groves et al., 1990; Engelsen et al., 2009; Groves et al., 1991; Hyun Nam et al., 2016; Richardson and Groves, 1993). The amount of unreacted cement in fresh RCA depends on the water-to-cement ratio in the original concrete formulation. Older concrete pavements may have higher water-to-cement ratios (e.g., $w/c > 0.45$) (Carino and Meeks, 2001; Mouret et al., 1997). The cement paste in these concretes can reach a degree of hydration above 90% (i.e., < 10% of cement is left unreacted in the hardened paste) (Carino and Meeks, 2001; Mouret et al., 1997). However, starting in the 1990s, highway pavement began to adopt high performance concrete, which is generally made with low water-to-cement ratios (e.g., $w/c = 0.35$) and additional pozzolans (e.g., silica fume) (FHWA, 2006; Burnham et al., 2006). High performance concretes can have degrees of hydration less than 70% and contain substantially less portlandite in the paste compared with regular concrete (e.g., < 6% by weight and 12% by weight, respectively) (Carino and Meeks, 2001; Poon et al., 2001; Wong and Buenfeld, 2009). The unreacted cement is relatively stable and does not carbonate unless hydrated, during which it forms portlandite. As such, if RCA is from high performance concrete pavement, the formation of portlandite by unreacted cement, rather than dissolution of portlandite from the hardened cement paste, may be the primary source of the high pH in the leachate.

The solid phase chemistry of the cement paste changes after emplacement through several processes; however, the extent of carbonation is critical to determining the pH of leachate from RCA. Initially, completely hydrated cement paste contains up to 15% to 25% calcium hydroxide present in macrocrystalline, microcrystalline, slightly crystalized, and/or amorphous forms (Brunauer and Copeland, 1964; Hidalgo et al., 2007; Bache et al., 1966). During carbonation, cement hydrate phases in hardened cement pastes, such as calcium hydroxide and calcium-silicate-hydrate, are converted to calcium carbonate in vaterite and calcite forms (Papadakis et al., 1989; Groves et al., 1991; Silva et al., 2015; Arandigoyen et al., 2006; Van Gerven et al., 2006; Šavija and Luković, 2016; Garrabrants et al., 2004; Gervais et al., 2004; Papadakis et al., 1992). Calcium carbonate nucleates on the surface of portlandite crystals, forming masses around small amounts of unreacted calcium hydroxide (Groves et al., 1990, 1991; Galan et al., 2015). Carbonation requires diffusion of carbon dioxide into water in contact with calcium hydroxide, where the reaction takes place in the aqueous phase. Carbonation rate and depth depends on carbon dioxide diffusion,

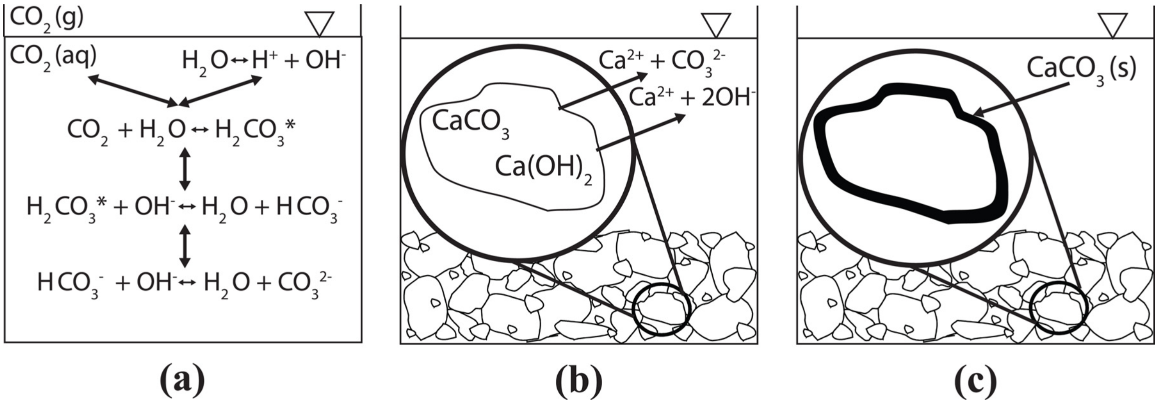

Fig. 2. RCA leachate chemistry (a) carbonate system of natural waters; (b) dissolution of calcium hydroxide and calcium carbonate from RCA surface; (c) carbonation of RCA surface as represented by the black layer.

relative humidity, and intermittent wetting and drying cycles (Van Gerven et al., 2006; García-González et al., 2006). Optimal conditions for conversion of calcium hydroxide to calcium carbonate occur at 20 degrees Celsius and 40–80% relative humidity (Galan et al., 2015; Abbaspour et al., 2016).

Carbonation begins at the exposed surface of the concrete monolith and progresses inward. At the end of its usable life as a monolith, concrete is crushed to create RCA and the uncarbonated inner matrix is exposed (Groves et al., 1990; Van Gerven et al., 2006). In base course applications, RCA surfaces are exposed to atmospheric carbon dioxide and the carbonate present in rainwater (Fig. 2a). Saturation of the fresh surfaces facilitates chemical interactions between the water and base course material. The characteristic high pH and alkalinity (acid neutralization capacity) of RCA leachate is controlled by differences in solid phase composition of RCA. Primarily, dissolved carbonate and hydroxide species released from portlandite and calcium carbonate dissolution (Fig. 2b); additionally, unreacted cement phases may be exposed in the crushing and compaction of RCA in construction applications, and hydration of these phases will produce additional portlandite for dissolution. Although AFm/Aft carbonation and dissolution may contribute leachate pH, portlandite dissolution and/or formation from unreacted cement phases provides the release of hydroxide ions required to achieve the high pH observed in RCA leachate chemistry.

With intermittent saturation and exposure to atmospheric carbon dioxide, the process of carbonation continues for RCA, progressing inward from the aggregate surface and creating zonation: a carbonated outer zone, a partially-carbonated transition zone, and an uncarbonated inner matrix (Groves et al., 1990; Van Gerven et al., 2006). Carbonation and the formation of the protective carbonate surface layer, the carbonated outer zone, limits the mass transport and dissolution of calcium hydroxide into the leachate, therefore the relative amounts of unreacted cement, calcium hydroxide, and calcium carbonate influence the alkalinity and initial pH of RCA leachate (Fig. 2c) (Van Gerven et al., 2006; Garrabrants et al., 2004; Gervais et al., 2004; Galan et al., 2015). Carbonation of the RCA material should be a critical consideration in RCA leachate investigations and in RCA construction applications, as the aggregate surface chemistry, not the bulk mineral composition, governs the leaching behavior (Bestgen et al., 2016a; Engelsen et al., 2009; Abbaspour et al., 2016; Ginder-Vogel et al., 2005; Loncnar et al., 2016; Mulugeta et al., 2011; Sanchez et al., 2002).

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

3. Existing body of work

The following literature review presents the existing RCA leachate investigations, including long-term field monitoring, batch reactor tests, and column leaching tests methodologies. RCA leachate pH measurements determined by the existing field and laboratory investigations are summarized in Table 1 along with the investigation methodology and RCA sample source. Table 1 also infers the primary factor controlling pH in each investigation based on the critical evaluation herein.

3.1. Laboratory investigations of leachate pH

3.1.1. Methodology used in batch reactor investigations of leachate pH

Batch reactor leaching experiments are the most common method for investigating RCA leachate chemistry because the methodology is inexpensive, straightforward, and yields reasonably reproducible results in waste or soil leaching experiments (Kalbe et al., 2007). The existing studies of RCA leachate chemistry follow one of the following standard methods: *SR002.1 – Alkalinity, Solubility, and Release as a function of pH* (Kosson et al., 2002); *European Committee for Standardization Technical Standard CEN/TS* 14429 *pH dependence leaching test* (CEN, 2005); *European Committee For Standardization CEN 12457-1 Characterisation of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 1* (CEN, 2002); *Liquid-solid partitioning as a function of liquid-to-solid ratio in solid materials using a parallel batch reactor procedure - Method 1316* (EPA, 2012); *ASTM D3987 Standard Practice for Shake Extraction of Solid Waste* (ASTM, 2012); *ASTM D5233 Standard Test Method for Single Batch Extraction Method for Wastes* and *ASTM D4793 Standard Test Method for Sequential Batch Extraction of Waste with Water* (ASTM, 2017a, b); and *USGS Field Leach Test for Assessing Water Reactivity and Leaching Potential of Mine Wastes, Soils, and Other Geologic and Environmental Materials Techniques and Methods 5-D3* (Hageman, 2007).

Each of the commonly used standards employs a fundamentally similar procedure: construction of a batch reactor at a prescribed liquid-to-solid ratio, vigorous agitation of the batch reactor, and extraction of a leachate sample for analysis. Specifically, the SR002.1 method recommends batch reactors with a liquid-to-solid ratio of 10 are agitated in an end-over-end tumbler at 28 rpm (± 2 rpm) (Kosson et al., 2002). The European standards for leaching tests also recommends batch reactors with a liquid-to-solid ratio of 10 (CEN, 2005) or with a liquid-to-solid ratio of 2 are agitated in an end-over-end tumbler (CEN, 2002). Similarly, the United States Environmental Protection Agency (EPA)

Table 1
Summary of existing field and laboratory determinations of RCA leachate pH.

Authors	Field pH	Batch pH	Column pH	Method	Sample Source	Primary factor controlling pH
Abbaspour et al. (2016)		10.4-11.3		ASTM D3987	Freshly-crushed	No carbonation (Fresh RCA)
		9.9-10.3		ASTM D3987	Carbonated in laboratory	Particle abrasion (Carbonation removed)
		11.2-11.4		USGS 5-D3	Stockpile	Particle abrasion (Carbonation removed)
		10.1-10.6		USGS 5-D3	Carbonated in laboratory	Particle abrasion (Carbonation removed)
Bestgen et al. (2016a)		10.5-12.0		ASTM D5233	Freshly-crushed	No carbonation (Fresh RCA)
Bestgen et al. (2016b)		10.5-12.5		ASTM D4793	Freshly-crushed	No carbonation (Fresh RCA)
Butera et al. (2014)		11-13		CEN/TS 12457	Stockpile	Particle abrasion (Carbonation removed)
Chen et al. (2012), Chen et al. (2013)		11.3-12.1		SR002.1	RCA base course	Particle abrasion (Carbonation removed)
	6.5-8.0			7 mos post-construction (paved)	RCA base course	Open system reactor (CO_2)
			10.8-12.5	ASTM D4874	RCA base course	No carbonation (Continuous saturation); Closed system reactor (No CO_2)
Coudray et al. (2017)		11.0-12.5		CEN/TS 12457	Stockpile	Particle abrasion (Carbonation removed)
Engelsen et al. (2006)	9.5			1 yr post-construction (unpaved)	RCA base course	Carbonation (Wet/dry cycles)
	11.5			1 yr post-construction (paved)	RCA base course	Carbonation slowed by pavement
Engelsen et al. (2009), Engelsen et al. (2010)		11.6-12.7		CEN/TS 14429	RCA base course	Particle abrasion (Carbonation removed)
Engelsen et al. (2012)	< 10			2.5 yrs post-construction (paved)	RCA base course	Carbonation (Wet/dry cycles)
Engelsen et al. (2017)	7.3 - 8.7			10 yrs post-construction (paved)	RCA base course	Carbonation (Wet/dry cycles)
Gupta et al. (2017)		10.5-12.3		EPA Method 1316	Stockpile	Particle abrasion (Carbonation removed)
Mulligan (2002)			> 10	Box Test	NA	Carbonation (Wet/dry cycles); Closed system reactor (No CO_2)
Madras Natarajan et al. (2019)		11.2-11.4		SR002.1	RCA base course	Particle abrasion (Carbonation removed)
			7.2-7.4	8 yrs post-construction (paved)	RCA base course	Open system reactor (CO_2)
Mulugeta et al. (2011)		11.5-11.9		CEN/TS 14429	Stockpile	Particle abrasion (Carbonation removed)
		12.4-12.5		CEN/TS 14429	Freshly-crushed	No carbonation (Fresh RCA)
		10.3-11.8		CEN/TS 14429	Carbonated in laboratory	Particle abrasion (Carbonation removed)
Sadecki et al. (1996)	9.3-9.8			1 yr monitoring	Stockpile	Carbonation (Wet/dry cycles)
Sanchez et al. (2002)		11.0-11.8		SR002.2 (similar to SR002.1)	Carbonated in laboratory	Particle abrasion (Carbonation removed)
Steffes (1999)			11.5-12.5	Box Test	Stockpile	Carbonation (Wet/dry cycles); Closed system reactor (No CO_2)

Method 1316 recommends five parallel batch leaching extractions at varying liquid-to-solid ratios (0.5, 1, 2, 5, and 10) that are agitated in an end-over-end tumbler at 28 rpm (± 2 rpm) (EPA, 2012). ASTM standard methods recommend batch reactors with a liquid-to-solid ratio of 10–20 are agitated in an end-over-end tumbler at 29 rpm (± 2 rpm) for 18 hours–72 h (ASTM, 2012, 2017a; ASTM, 2017b). The United States Geological Survey (USGS) 5-D3 method is designed to determine leaching potential in the field, and therefore recommends batch reactors constructed with a liquid-to-solid of 20 are shaken vigorously by hand for 5 min of every hour for the duration of the experiment (Hageman, 2007). Comparison studies designed to isolate the relative importance of experimental parameters conclude that liquid-to-solid ratio has little to no effect on measured RCA leachate pH (Bestgen et al., 2016a; Gupta et al., 2017); however, particle size variation, particularly an excess of fines fraction, may or may not affect leachate pH measurements in batch reactors (Bestgen et al., 2016a; Coudray et al., 2017).

3.1.2. Results of batch reactor leaching investigations of leachate pH

Batch reactor leaching investigations of RCA leachate pH generally yield high pH measurements (Table 1). Existing batch reactor leaching studies, which differ in RCA source and degree of carbonation, measure RCA leachate pH ranging from pH 9.9 to 13.0 (Bestgen et al., 2016a; Chen et al., 2012; Butera et al., 2014; Madras Natarajan et al., 2019; Bestgen et al., 2016b; Chen et al., 2013; Engelsen et al., 2009; Abbaspour et al., 2016; Mulugeta et al., 2011; Sanchez et al., 2002; Engelsen et al., 2010; Gupta et al., 2017; Coudray et al., 2017), compared to pH 9 for leachate from limestone virgin aggregate (Gupta et al., 2017).

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

3.1.3. Limitations of batch reactor leaching investigations of leachate pH

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

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

3.2. Column leaching tests

3.2.1. Methodology used in column leaching investigations of leachate pH

Column leaching tests offer a laboratory technique to measure RCA leachate pH that simulates percolation conditions relevant to RCA base course leaching. Column leaching tests are considered more environmentally relevant than batch reactors because column leaching experiments use representative liquid-to-solid ratios and preserve the carbonate surface coating by mitigating particle abrasion, (López Meza et al., 2012). With lower liquid-to-solid ratios, column leaching tests equilibrate faster than batch reactors and, due to the short mass transfer distances, are often assumed to reach equilibrium conditions instantaneously (Grathwohl, 2014).

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

3.2.2. Results of column leaching investigations of leachate pH

Existing column leaching investigations of RCA leachate pH also yield high pH measurements, pH 10 to 12.5 (Table 1) (Chen et al., 2012, 2013; Qin and Yang, 2015; Mulligan, 2002; Steffes, 1999). Much of the initial work to investigate RCA leachate was conducted by state departments of transportation concerned about the impeded vegetation growth, soil erosion, and crystalline deposits of tufa on the drain outlet wire mesh observed in field applications of RCA base course (Steffes, 1999). Both the Iowa Department of Transportation (IDOT) and Ohio Department of Transportation (ODOT) conducted a variation of column leaching test methodology called box tests. Box tests simulate a percolation environment using intermittently saturated, down-flow lysimeter columns. ODOT box tests measured RCA leachate pH to be at least 10 (Mulligan, 2002; ODOT, 2002). IDOT employed intermittent wetting and drying cycles with box tests to measure RCA leachate pH over the course of a year, and found carbonation decreases the leachate pH from an initial pH 12.5 to pH 11.5 over the course of the year-long experiment (Steffes, 1999).

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

3.2.3. Limitations of column leaching investigations of leachate pH

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

Column leaching experiments are designed to simulate percolation conditions relevant to RCA base course leaching. The pH measured as the leachate leaves the column apparatus is analogous to the pH of leachate as it leaves the base course layer and drains to the subbase/subgrade pavement system (Fig. 3a) or to edgedrains (Fig. 3b). After the leachate drains and is no longer in contact with RCA, there is no longer a source of strong base for the leachate. Instead, the leachate will interact with carbon dioxide and soil acidity from soil minerals, and the pH will decrease (Gupta et al., 2017). Therefore, the leachate pH measured in column leaching experiments represents the maximum pH of the leachate in the environment.

3.3. Field-scale studies of leachate pH

3.3.1. Methodology used in field monitoring of leachate pH

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

3.3.2. Results of field monitoring investigations of leachate pH

Long-term field studies demonstrate that, after an initial phase of high pH, RCA leachate approaches neutral pH within one to two years of base course construction or stockpiling (Table 1). Stockpiling RCA before construction is a common practice and offers a potential method to carbonate RCA before emplacement in base course construction. The Minnesota Department of Transportation (MnDOT) investigated and characterized leachate from RCA stockpiles by monitoring two outdoor RCA stockpiles for 13 months: one of coarse, gravel-sized RCA and the other of finer material (Sadecki et al., 1996). MnDOT found the coarse RCA to have pH between 8.5 and 10.9, median 9.8, while the leachate from the finer RCA was between 7.4 and 12.2, median 9.3 (Sadecki

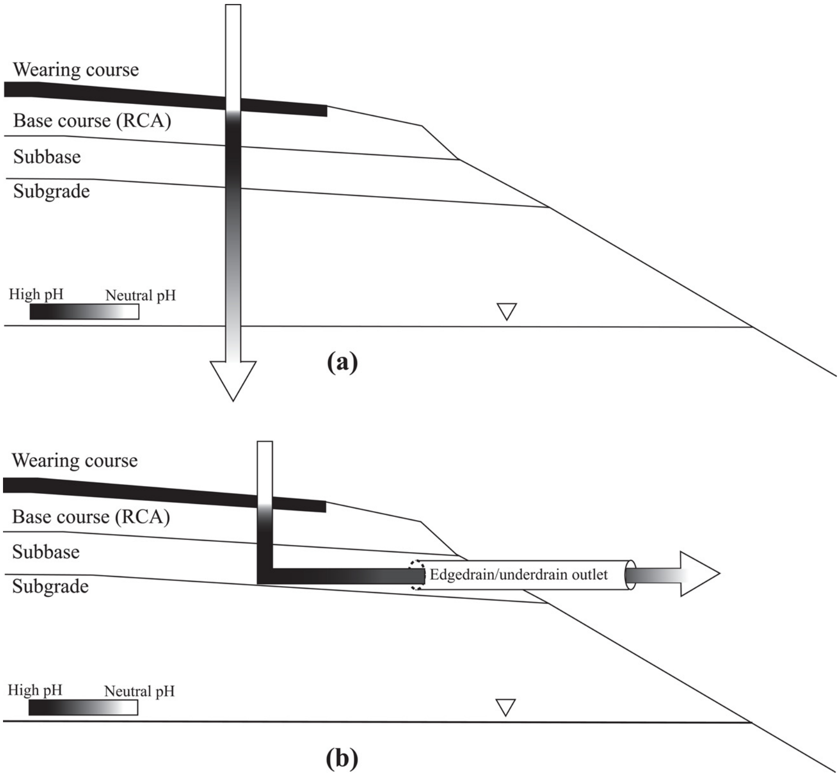

Fig. 3. Additional processes that reduce leachate pH for different base course drainage designs (a) subbase drainage; (b) edgedrain/underdrain outlet.

et al., 1996). Over the course of the experiment, the pH gradually decreased as the result of field carbonation (Sadecki et al., 1996).

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

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

3.3.3. Limitations of field monitoring investigations of leachate pH

Field experiments encompass many, if not all, of the variable parameters that are difficult to recreate in the laboratory. When measured with a data logger, leachate pH in the field is measured as leachate exits the RCA base course or stockpile (Engelsen et al., 2006, 2012; Engelsen et al., 2017; Sadecki et al., 1996). Leachate pH measured in field monitoring experiments with a data logger represents the maximum pH of the leachate in the environment because when the leachate drains from the RCA base course layer to the subbase/subgrade pavement system (Fig. 3a) or through the edgedrain to the drainage ditch (Fig. 3b), it loses the source of strong base and is introduced to sources of acidity from carbon dioxide infiltration and soil minerals (Gupta et al., 2017). Conversely, when leachate is collected via a pan lysimeter and a collection tank, and is sampled later, the leachate has been exposed to carbon dioxide without a source of hydroxide from the RCA layer for weeks or months, resulting in a lower pH (Chen et al., 2012, 2013). Time-dependent leachate pH behavior after the leachate drains from the RCA base course layer has not been examined and is an opportunity for future research.

4. Conclusion and recommendations

The reviewed literature demonstrates the variability in results obtained from field and laboratory investigations of RCA leachate chemistry, even when comparing the same RCA material. Engelsen et al. (2006, 2009, 2010) and Madras Natarajan et al. (2019) conducted simultaneous laboratory and field investigations of RCA leachate pH, and both studies measure significantly higher leachate pH in the laboratory than in field monitoring experiments (Table 1). The concurrent investigations by Engelsen et al. (2006, 2009, 2010) and Madras Natarajan et al. (2019) illustrate a discrepancy between field and laboratory measurements of leachate pH, which indicates that the current laboratory methodology inadequately describes leachate conditions in the field. The many parameters that affect RCA in the field are difficult to encompass in laboratory methods and include pavement drainage design, frequency/duration of precipitation, degree of saturation, temperature, variation in subbase soil geology, and traffic loads, all of which vary in time and space. In designing laboratory investigations of RCA leachate chemistry and in providing guidance for the use of RCA as base course material, several factors must be considered: accurately modeling RCA carbonation, particle abrasion, contact time, and base course drainage.

Development of the protective carbonation layer on the surface of RCA is a result of intermittent wetting and drying cycles. This is a progressive process, such that carbonation depth increases with time and number of wetting and drying cycles of RCA. Utilization of an end-over-end tumbler to determine material pH causes particle abrasion and removal of the protective calcium carbonate layer, again exposing uncarbonated matrix with reactive portlandite (Fig. 2). Such effects are illustrated in the simultaneous laboratory and field investigations presented by Engelsen et al. (2006, 2009, 2010) and Madras Natarajan et al. (2019); these investigations employed batch reactor leaching experiments with end-over-end tumblers to characterize leachate pH in the laboratory. For experiments assessing leachate pH of stockpiled, aged, or otherwise carbonated RCA, particle abrasion should be limited to represent the development and preservation of protective carbonate layers on the surface of RCA as a result of intermittent wetting and drying.

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

Different pavement drainage designs (e.g., subbase layers, subsurface drains, and daylighting) result in variations in leachate interactions with soil acidity, and atmospheric and soil vapor carbon dioxide (Fig. 3). At the very least, the availability of carbon dioxide and soil acidity to neutralize high pH RCA leachate should be considered in the leachate fate and transport analysis. Gupta et al. (2017) investigate soil-RCA leachate interactions and found that soil acidity can neutralize small volumes of RCA leachate pH, such that 1 m of subgrade soil has the capacity to neutralize RCA leachate for 20 years, disregarding the additional factors that reduce leachate pH (Fig. 3) (Gupta et al., 2017). Additional subsurface processes that reduce leachate pH include carbonation, groundwater acidity from bicarbonate and other dissolved species, and soil vapor carbon dioxide (Gupta et al., 2017). Future research is required to evaluate the time-dependent leachate pH behavior after the leachate drains from the RCA base course layer.

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

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Characterization of Recycled Concrete Aggregate after Eight Years of Field Deployment

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Abstract: Recycled concrete aggregate (RCA) is a high-quality substitute for virgin aggregate as base or subgrade material in pavement construction. However, heavy metal leaching and/or production of high pH leachate are environmental risks commonly associated with the use of RCA. To characterize changes in physical and chemical properties after use, RCA base course and subgrade soil samples were recovered from the Minnesota road research (MnROAD) field site after eight years and compared to the original RCA physical and chemical characteristics. RCA samples were analyzed to determine their mineralogy, carbonate content, acid neutralization capacity (ANC), material pH, and trace element leaching potential. ANC was higher in the recovered RCA and higher for the fine-grained RCA particles than the coarse particles, which was confirmed by extensive carbonation of the fines fractions during field deployment. Material pH of RCA and subgrade soil samples were significantly higher than leachate pH measured in previous and current field investigations of this site, suggesting that conventional laboratory techniques do not represent field conditions and should be modified to better represent field conditions. **DOI: 10.1061/(ASCE)MT.1943-5533.0002708.** *© 2019 American Society of Civil Engineers.*

Author keywords: Recycled concrete aggregate (RCA); Leachate; pH; Minnesota road research (MnROAD).

Introduction

Reconstruction of highways in the United States is creating growth in the demand of virgin aggregate and in the energy required to process and transport aggregate materials (Lee et al. 2010). It is estimated that 76% of the 1.54 billion tons of crushed stone consumed in the US in 2016 was used as construction material, primarily for road construction and maintenance (Willet 2016). Meanwhile, more than 375 million tons of concrete waste was produced in 2014 from demolition of aging concrete structures (USEPA 2016). Due to environmental and sustainability concerns, concrete waste is increasingly being recycled in construction applications (Lee et al. 2010), especially in place of virgin aggregate in road construction. Despite the potential cost and sustainability benefits, acceptance of concrete waste recycling remains low in many municipalities (Engelsen et al. 2017).

Recycled concrete aggregate (RCA), also known as reclaimed concrete material (RCM), is generated from the demolition of portland cement concrete (PCC) in roads and other concrete structures. After demolition and excavation, the RCA is typically hauled to a stockpiling facility (e.g., aggregate supplier), landfilled, or reused on site. At the stockpiling facility or construction site, reinforcing steel is removed and the RCA is crushed to an engineered gradation for use as high-quality base or subgrade material (Chesner et al. 1998; Edil et al. 2012).

Because RCA is a potential source of environmental contamination, the physical and chemical properties of RCA leachate have been extensively studied (Butera et al. 2015; Chen et al. 2012, 2013; Engelsen et al. 2010; Galvín et al. 2014; Townsend et al. 2004). Characterization of heavy metal leaching from RCA has determined that hydrated cement paste is the primary source of heavy metals in RCA leachate and that heavy metal leaching is therefore characterized by the leaching patterns of binders commonly used in construction (e.g., portland cement, fly ash, and/or slag) (Engelsen et al. 2010, 2009; Galvín et al. 2014; Kosson et al. 2014). Leaching mechanisms are strongly dependent on leachate pH and degree of carbonation of the concrete material. Understanding the chemical and physical processes involved in the carbonation of RCA during its use is critical in understanding its potential environmental impacts. Recent field studies of RCA as a road subbase indicate that the leachate pH is initially elevated and then approaches neutral within a year after construction (Chen et al. 2013; Engelsen et al. 2017, 2012). However, laboratory studies report leachate pH values above 12 for extended periods of time, directly

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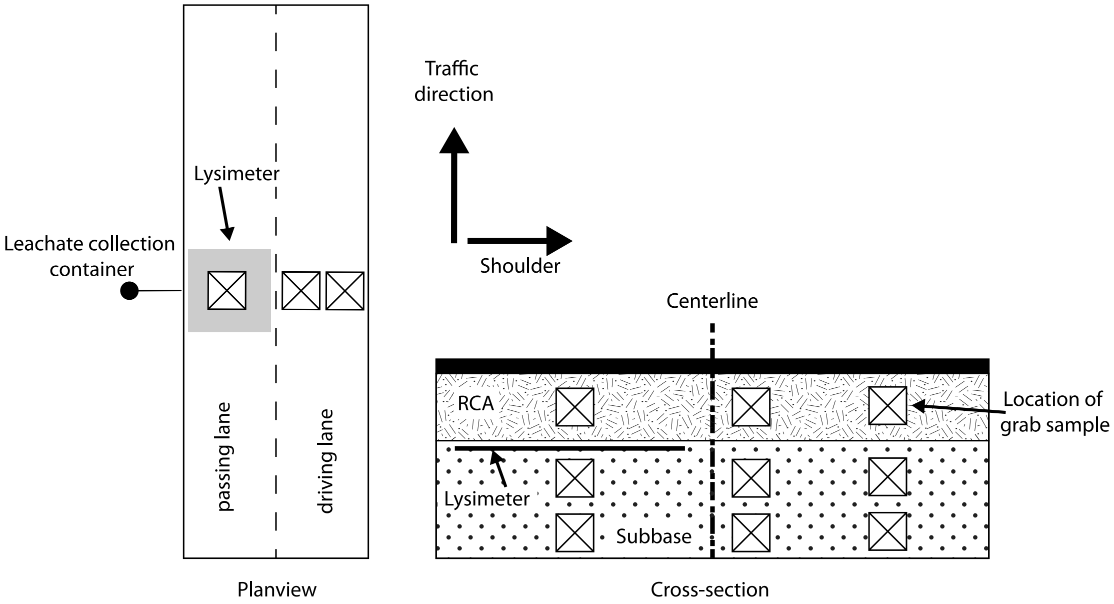

Fig. 1. Representative location of grab samples collected during the decommissioning of Cell 16 at the MnROAD research facility in July 2016.

contradicting the results of the field studies (Chen et al. 2013; Engelsen et al. 2017). These laboratory-based studies employ different methodologies to understand RCA leachate chemistry, including batch tests (Abbaspour et al. 2016; Engelsen et al. 2009, 2010), leached column tests (Chen et al. 2013; Qin and Yang 2015), and periodically saturated and drained experiments termed box tests (Mulligan 2002; ODOT 2002; Steffes 1999); however, they all report elevated leachate pH values in contrast to the near-neutral pH values measured in field experiments described by Chen et al. (2013) and Engelsen et al. (2017).

The purpose of this study is to examine the physical and chemical properties of recovered RCA from the Minnesota road research (MnROAD) highway field site to compare to the physical and chemical characterization of the original RCA by Chen et al. (2012, 2013). In addition to standard physical characterization, the degree of carbonation, acid neutralization capacity, material pH, and trace element leaching potential were analyzed after eight years of field deployment at MnROAD.

Materials and Methods

MnROAD Field Site Description

In September 2008, Chen et al. (2012, 2013) obtained RCA material from Minnesota Department of Transportation (MnDOT) to construct roadway test cells at the MnROAD test facility mainline on westbound I-94 between St. Cloud and Minneapolis, Minnesota. Experimental Cell 16 was constructed with RCA as the base course aggregate. The cell was paved with a 127-mm warm-mixed asphalt layer over the 305-mm base course layer, 305-mm Class 3 aggregate subgrade layer, and 178-mm select granular material layer above the clay subgrade. Cell 16 was designed to investigate high pH leachate from RCA, with a pan lysimeter (3 m × 3 m) installed under the RCA to collect percolated leachate. The original RCA material used for construction of the site was obtained from a stockpile maintained by the Knife River Corporation located at 7979 State Highway 25 NE in Monticello, Minnesota. All samples met the US Department of Transportation required gradation as base course, with a maximum grain size of 50 mm; the grain size distribution curves are shown in Chen et al. (2013). Additional details of site construction and RCA characterization are described by Chen et al. (2012, 2013).

After eight years, the test sections were deconstructed in July 2016, and aggregate samples were collected from the passing lane, centerline, and driving lane to include spatial variability across the roadway profile: Samples 16P, 16C, and 16D, respectively. Samples at each P, C, and D location were taken at three profile depths: (1) a base course material sample, (2) a subgrade soil sample just below the RCA (or pan lysimeters), and (3) a deeper subgrade soil sample below the pan lysimeters (Fig. 1). In total, nine material samples were obtained.

Leachate Chemistry

Leachate collected from Cell 16 had a pH between 6.5 and 8.0 in the second year after construction (Chen et al. 2013). In samples collected from April 2016 to July 2016, approximately eight years after construction, leachate pH consistently measured between 7.2 and 7.4 (Table 1).

Table 1. Summary of leachate pH observed during the final three months of an eight-year field deployment

Date	pH
May 3, 2016	7.3
June 8, 2016	7.2
July 7, 2016	7.4

Characterization of Physical Properties

The physical and hydraulic properties of the recovered MnROAD RCA materials were characterized using grain size analysis, moisture content, dry unit weight, absorption, specific gravity, compaction characteristics, and the unified soil classification system (USCS) (Table 2). All tests were conducted according to ASTM and AASHTO standards.

Grain Size Analysis

The grain size distribution of the recovered MnROAD RCA Samples 16 P-1, 16 C-1, and 16 D-1 was determined according

Table 2. Summary of physical properties

Property	Original RCA	16 P-1	16 C-1	16 D-1
Specific gravity	2.7	2.26	2.13	2.50
Moisture content (%)	3.0	8.69	9.30	8.83
Absorption (%)	4.9	7.62	7.95	6.29
Optimum water content (%)	11.2	12	11.70	13.50
Max dry density (kN/m^3)	19.5	21.4	21	21.7
USCS classification	GW	GW	GW	GW

to ASTM D422-63 (ASTM 2007). Bulk samples were oven dried at 105°C ± 2°C for 24 h prior to mechanical sieving, and samples were passed through a No. 4 sieve and No. 200 sieve to isolate the gravel, sand, and fine portions.

Moisture Content

The moisture content of the recovered MnROAD RCA Samples 16 P-1, 16 C-1, and 16 D-1 was determined according to the ASTM D2216 (ASTM 2010) standard for soil and rock. A representative bulk sample was taken for each material and oven dried for 24 h 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 according to (AASHTO 2012; ASTM 2015) the AASHTO T85 standard for specific gravity and absorption of coarse aggregate.

Maximum Dry Density and Optimum Water Content

Compaction characteristics for the recovered MnROAD RCA Samples 16 P-1, 16 C-1, and 16 D-1 were determined using the modified Proctor method according to ASTM D1557 (ASTM 2012). Maximum dry unit weight and optimum water content were derived from the compaction curve for each sample.

Characterization of Chemical Properties

Acid Neutralization Tests

The ability of the recovered RCA to neutralize acid was tested according to the methods outlined in Chen et al. (2012, 2013). One representative RCA batch sample was obtained from each sample location (16 P-1, 16 C-1, and 16 D-1), homogenized by hand mixing, and oven-dried overnight. A portion of the batch sample was analyzed as an unfractionated bulk sample, and the remainder was size-fractionated using dry mechanical sieving into three grain-sized fractions: fine particles (<0.075 mm), sand-sized particles (<4.75 mm and >0.075 mm), and gravel-sized particles (<75 mm and >4.75 mm). Samples were not crushed prior to fractionation to accurately assess the impact of the in situ surface properties on leachate chemistry. To prepare batch tests, 5 g of RCA fines, sands, or bulk sample was mixed with 50 mL of acid/base solution. Batch tests using gravel samples used 50 g of RCA in 500 mL of acid/base solution. The acid and base used in the batch tests were HNO_3 and NaOH, respectively. All samples were agitated in an end-over-end tumbler at 30±2 rpm for 24 h. The pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) of the solutions were measured using a Thermo Scientific (Waltham, Massachusetts) Orion Combination pH electrode, an Intellical (Loveland, Colorado) CDC401 Graphite Conductivity probe, and an Intellical MTC101 ORP/RedOx probe, respectively.

The acid neutralization capacity (ANC) curve of each material was determined from the relationship between the amount of acid/base added and the resulting pH of the solution. The EC and the ORP were similarly compared to the amount of acid/base added to each sample. Following the batch tests, aqueous samples were stored at 4°C for further analysis.

Determination of Material pH

Material pH is defined as the solution pH resulting from contact of a 10:1 mass ratio of deionized water to RCA after 24 h of end-over-end tumbling. Sample preparation for material pH experiments was the same as that used for batch tests.

Elemental Composition of Leachate

The concentration of elements in the leachate was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The elemental composition of each RCA specimen was determined by acid digestion according to ASTM D5198-09 (ASTM 2017). Prior to analysis, the leachate samples from the material pH batch tests were placed in a centrifuge for 10 min at 10X g, to isolate the solid phase. The supernatant was then collected and diluted to a 1:1 ratio with 5% nitric acid to preserve the samples. 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 100 ppm.

Continuing calibration verifications (CCV) and continuing calibration blanks (CCB) were analyzed every 10 samples, and a duplicate was analyzed every 20 samples. Quality control requirements outlined in USEPA (2014) 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 original sample.

Solid-Phase Composition of RCA

X-ray diffraction (XRD) was used to identify and quantify crystalline minerals in the recovered RCA in accordance with ASTM standard C1365 (ASTM 2018), which specifies the use of Reitveld refinement to quantify crystalline materials. The fine-fractionated samples were crushed to a fine powder using a mortar and pestle and packed into a small amorphous silica capillary. Data was collected using a Rigaku D/Max Rapid II (Tokyo, Japan) diffractometer. The results were displayed as intensity (counts per second) versus 2-theta angle and compared to a database of mineral XRD patterns. XRD patterns were collected from two samples for each material.

Thermogravimetric analysis (TGA) measures the change in mass of a sample with temperature. Bound and structural water are released at relatively low temperatures (200°C), whereas calcium carbonate ($CaCO_3$) degrades to form calcium oxide (CaO) and carbon dioxide (CO_2) around 700°C following Reaction 1

$$CaCO_{3(s)} \rightarrow CaO_s + CO_{2(g)} \text{ Reaction 1}$$

Measuring the change in mass of the solid sample as CO_2 is released yields the amount of calcium carbonate in the sample. The TGA procedure was conducted in accordance with ASTM standard E1131-08 (ASTM 2014). An empty crucible was placed in the furnace to tare the instrument and collect a blank curve of the experimental method. The experiment was performed using 50 to 100 mg of the fine size fraction packed into the crucible. The furnace was heated at a rate of 10°C/min from 25°C to 1,000°C.

Results and Discussion

Physical Properties

After eight years of field deployment, the physical properties of the recovered RCA were quite similar to the properties of the original

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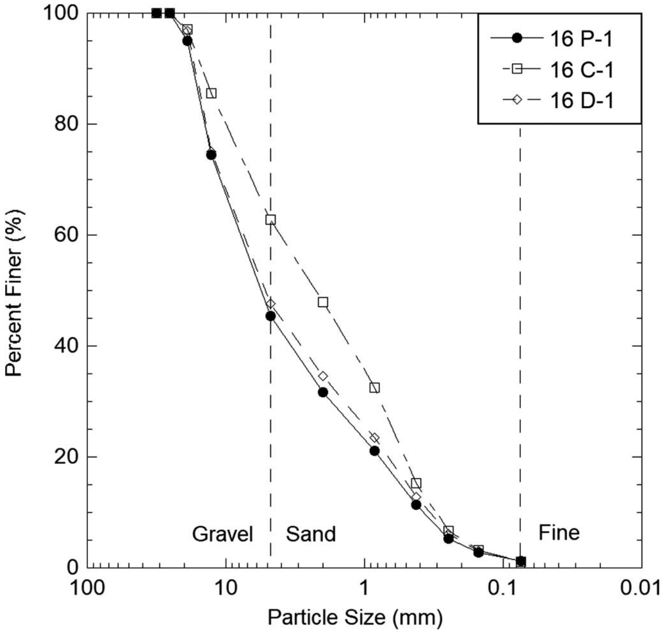

Fig. 2. Recovered MnROAD RCA particle size distribution curves for RCA Samples 16 P-1, 16 C-1, and 16 D-1.

RCA (Table 2). Specific gravities ranged from 2.1 to 2.5, moisture contents from 8.7% to 9.3%, optimum water contents from 12% to 13%, maximum dry densities from 21.0 to 21.7 kN/m^3, and water contents at maximum density from 11.7% to 13.5%. All three samples were classified as well-graded gravel (GW) (Table 2 and Fig. 2).

Chemical Properties

Oxidation-Reduction Potential and Electrical Conductivity

The material oxidation reduction potential (ORP) ranged from −8.5 to 173.5 mV (Fig. S1 in Supplemental Data). The data reveal a trend of increasing ORP with the addition of acid. This was due to the increase in the amount of dissolved ionic species as more acid reacts with the RCA. The material electrical conductivity ranged from 0.373 to 3.370 mS/cm (Fig. S2). Similarly to the trends in ORP, the electrical conductivity of the leachate increased with the addition of acid to the system (Fig. S2).

Acid Neutralization Capacity and Material pH

The bulk, sand, and gravel fractions of all three RCA samples exhibit similar ANC curves, in which a decrease in pH is observed with the first additions of acid and a plateau is observed between pH 4 and 7 (Fig. 3). The ANC curves for the fine fraction of all

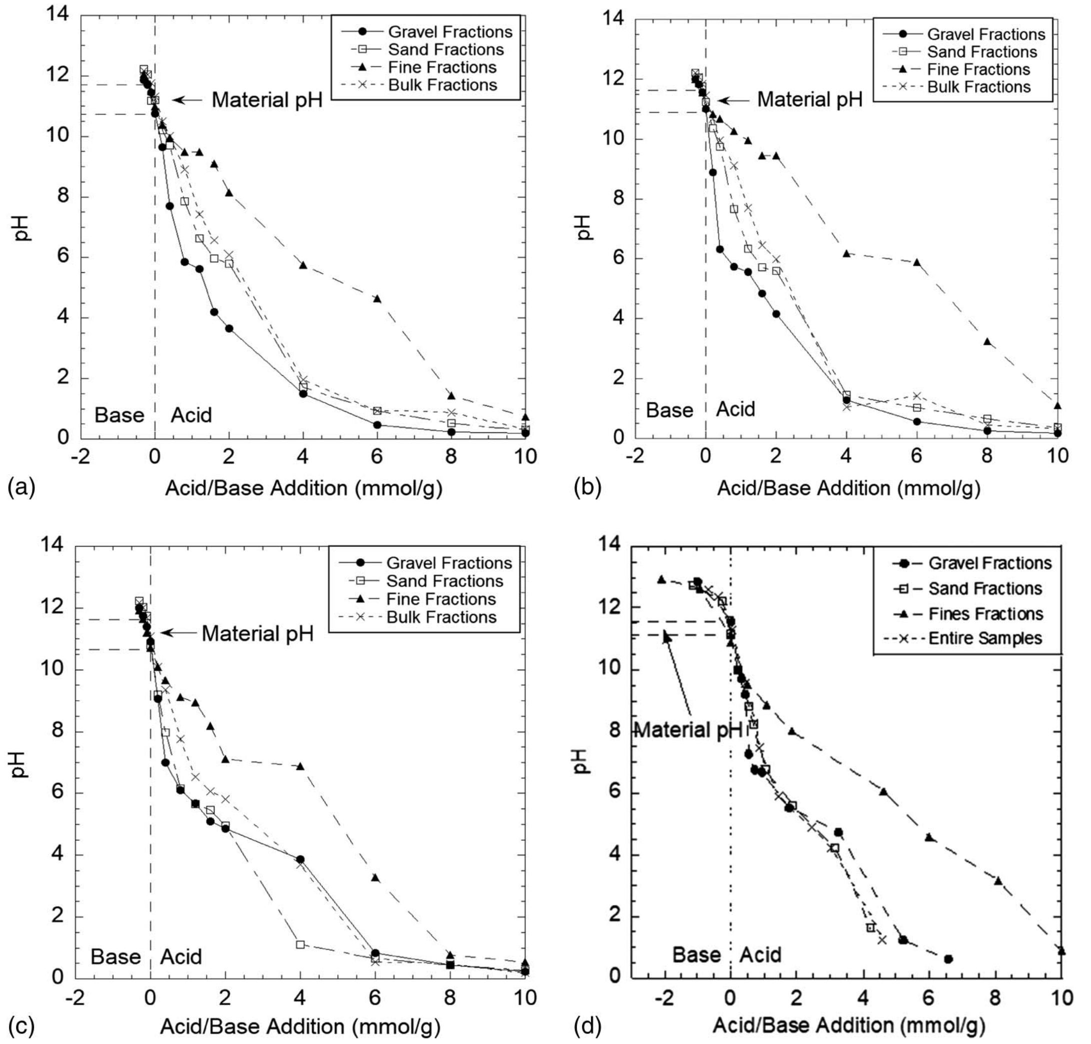

Fig. 3. ANC curves for recovered MnROAD RCA Samples: (a) 16 P-1; (b) 16 D-1; and (c) 16 C-1; and for (d) the original RCA (reprinted from Chen et al. 2012, © ASCE). Data includes bulk, fine, sand, and gravel fractions.

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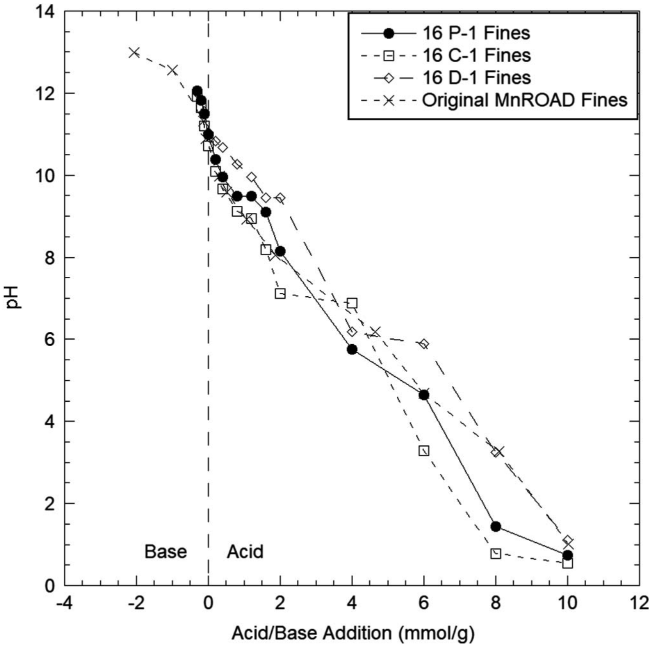

Fig. 4. ANC curves for recovered MnROAD RCA Samples 16 P-1, 16 C-1, and 16 D-1, and for the original RCA from Chen et al. (2012). Data includes only fine fractions.

three RCA samples exhibit two plateaus: (1) at a pH value above 9, and (2) between pH 5 and 7. The observed ANC trends indicate that the fine particles neutralize more acid per unit mass (Fig. 4) than the other size fractions.

The material pH for each of the RCA size fractions ranges between pH values of 10.7 and 11.4, while the material pH for the subgrade soils ranges between 10.1 and 10.9 (Table 3). In all cases, the material pH of the bulk and size-fractionated samples was between 0.5 and 1 pH units lower than the material pH of 12.3 of the original RCA (Chen et al. 2013). However, the material pH values of the subgrade soils were quite elevated compared to the material pH of 8 measured by Chen et al. (2013). The changes in RCA material pH were likely due to carbonation of the RCA surface, whereas the elevated material pH for the subgrade soils was indicative of the accumulation of basic compounds leached from the RCA. However, in all cases the material pH of the RCA and the subgrade soils (~12 and ~10.5, respectively) was elevated in comparison with the leachate pH (~7.4) measured prior to field-site deconstruction (Tables 1, 3, and 5).

Carbonation and Surface Chemistry

Garrabrants et al. (2004) and Chen et al. (2013) concluded that the plateaus in ANC for RCA samples are generally the result of dissolution of calcium carbonate from carbonation of the concrete. Carbonation in concrete is caused primarily by reactions between portlandite [$Ca(OH)_{2(s)}$] and calcium silicate hydrate (C-S-H), with atmospheric carbon. The double plateau observed in the fine fractions is the result of two-stage protonation of the carbonate anions in the system. ANC curves for the fine fractions resemble a carbonate base titration curve, showing a two-stage protonation. That the equivalence points observed for the RCA fine fractions are slightly different from two-stage protonation of carbonate is likely due to the additional ANC of other alkali materials in the concrete. The pK_{a1} and pK_{a2} of a carbonate base are 6.53 and 10.33, respectively, whereas the ANC curves for the fine fraction exhibit plateaus at pH 5 to 7 and at pH 9 to 9.5.

Evidence of extensive carbonate formation is observed only in the fine-grained fraction of RCA, indicating a greater degree of carbonation in the fine-grained RCA than in other size fractions. More carbonation per unit mass of sample is likely due to the availability of reaction surfaces on the fine fraction of RCA, allowing increased exposure of $Ca(OH)_2$ and C-S-H to atmospheric and/or dissolved carbon dioxide to form calcium carbonate. The acid neutralization behavior of the fine-grained material is consistent with this interpretation.

Spatial Trends in Chemical Properties

RCA collected from beneath the passing lane, 16 P-1, and the driving lane, 16 D-1, exhibit similar ANC plateaus at a pH near 6 for the bulk, sand, and gravel size fractions. The center lane sample, 16 C-1, exhibits a gradually sloping plateau over a pH range between pH 4 and 7. Additionally, 16 C-1 samples generally had shallower ANC curves than the 16 P-1 and 16 D-1 samples, with the exception of the sand-sized fraction, and the second plateau in the fine fractions occurred at pH 7 for 16 C-1 and at pH 6 for both 16 P-1 and 16 D-1. Titration end-points for all three fines samples were between 2 and 3 mmol/g of acid added.

Highways 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 likely drain faster, draining into the adjacent passing and driving lanes. Therefore, the center of the road experiences longer dry periods than under the passing and driving lanes and could accommodate additional carbonation of RCA mineral surface. The longer dry periods in comparison with the two adjacent lanes could also allow for less dissolution of alkali material over time. The slightly higher ANC observed in 16 C-1 (Fig. 3), specifically in the bulk and gravel fractions, suggests that shorter contact times with infiltrated water may increase RCA carbonation.

Solid-Phase Characterization

An increase in carbonate mineral content, particularly in fine fractions of the recovered RCA samples is also detected with both XRD and TGA (Table 4). TGA reveals an increase of approximately 5% in $CaCO_3$ content as compared to the original RCA (Chen et al. 2013). Overall, the amount of carbonate minerals observed with XRD is consistent with TGA. XRD analysis of the recovered materials confirms the presence of calcite ($CaCO_3$) and dolomite ($Ca_xMg_{1-x}CO_3$) in the recovered RCA samples, but portlandite

Table 3. Material pH for recovered MnROAD RCA samples

Unit	Fraction	16 P	16 C	16 D
1—RCA	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
2—Subgrade soil	Bulk	10.41	10.47	10.91
3—Subgrade soil	Bulk	10.15	10.53	10.61

Table 4. Major crystalline minerals in the fines fraction of the recovered MnROAD RCA sample observed using XRD

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

Table 5. Material pH for the original MnROAD RCA from Chen et al. (2012, 2013), and recovered MnROAD RCA samples 16 P-1, 16 C-,1 and 16 D-1

Fraction	Original RCA (Chen et al. 2012, 2013)	16 P	16 C	16 D
Bulk	11.3–12.1	11.3	11.1	11.5
Sand	11.1–11.9	11.2	10.8	11.2
Fine	10.9–11.8	11.0	10.7	11.0
Gravel	11.5–12.1	10.8	10.9	11.0

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$[Ca(OH)_2]$ is not detected in the any of the samples (Table 4). XRD methods tend either to underestimate or not to detect $Ca(OH)_2$ because in cement paste it may exist in an amorphous or cryptocrystalline form (Taylor 1997). On the basis of the XRD results, it can be inferred that the crystalline $Ca(OH)_2$ was not present above 5% by mass in this RCA, likely due to its leaching and carbonation during eight years of deployment.

Relationship between Solid-Phase Chemistry and Acid Neutralization

The largest difference in acid neutralization behavior between the original and recovered RCA was the development of the double plateau in the fines fractions (Fig. 3). All three fines samples exhibited a double plateau, indicating carbonation. Additional differences in the ANC for the coarse fractions between the original and recovered RCA indicated that carbonation had occurred during field deployment. The ANC curves for the original RCA (Chen et al. 2013) were quite similar for the gravel and sand fractions [Chen et al. 2013, Fig. 1(c)], but the ANC curves for the gravel and sand fractions in the recovered RCA are not similar (Fig. 3). The sand fractions demonstrate increased ANC in samples 16 P-1 and 16 D-1, from 0 to 4 mmol/g addition of acid. This change in trends indicates increased carbonation of the sand-sized fraction as compared with the gravel-sized fraction.

Base and Subgrade Material pH

The sand-sized particles (44%–62% by mass) have a higher material pH than the fine particles and gravel particles, whereas the pH of the unfractionated material is similar to the sand-sized particles (Table 5). The fine fractions have a lower material pH and greater carbonation, likely due to their large reactive surface area per unit mass. Conversely, the sand- and gravel-sized fractions have a higher material pH and have less carbonation. Carbonation uses the alkali phases from the cement and reduces the material pH. The sand-sized fraction likely controls the material pH of the bulk RCA because it accounts for the largest proportion of the bulk mass.

The recovered RCA samples have consistently higher inorganic carbon content than the original RCA, indicating that carbonation occurred during the eight-year placement at MnROAD (Table 6). This is also similar to the degree of carbonation in the RCA observed by Engelsen et al. (2009).

Table 6. Carbon content as a percentage of sample mass, for the original MnROAD RCA from Chen et al. (2012, 2013), and recovered MnROAD samples 16 P-1, 16 C-1, and 16 D-1

Sample	Inorganic carbon (%)	$CaCO_3$ (%)
MnROAD Sample 16 P-1	2.4	20.3
MnROAD Sample 16 C-1	2.3	19.4
MnROAD Sample 16 D-1	2.2	18.6
Original MnROAD RCA	1.6	13.3

Impact of RCA on Subgrade Materials

The material pH of the recovered subgrade soil, a clayey sand, provides understanding of the impacts of RCA leachate (Table 5). All subgrade soil samples had elevated material pH compared to the initial value of 8 (Chen et al. 2013), and the material pH decreased slightly with increasing distance from the RCA base layer. The elevated material pH values could be attributed to precipitation of hydroxide or carbonate phases on the particle surface; however, these phases were not at concentrations high enough to be detectable in XRD analysis. Additionally, bound ions might also have impacted the material pH, and they would not have been detected by XRD analysis.

Elemental Composition of Leachate

Quantification of leachate element concentrations ICP-OES analysis is provided in the Supplemental Data section (Table S1). In general, all three samples demonstrated elevated concentrations of Ca (maximum 237.7 ppm), Si (maximum 31.0 ppm), Na (maximum 72.1 ppm), and K (maximum 26.1 ppm), and relatively low concentrations of Cr (0.034–0.160 ppm), Zn (0.178 and 0.202 ppm), and Cu (not detectable). The leachate from the fine-grained samples generally had the highest dissolved trace elements, followed by the sand and the gravel fractions. Due to the low weight composition of the fine fractions (around 1% by mass), the leachate behavior of the bulk samples was likely controlled by the behavior of the sand fractions (44%–62% by mass).

A study of the original MnROAD RCA examined the leaching of Cr, Zn, and Cu from the bulk material and various size fractions (Chen et al. 2013). Cr and Cu concentrations in leachate from the recovered RCA were lower than those observed in the original sample for all three fractions, likely removed via leaching or sequestration as insoluble metal carbonates (Fig. S2 in Supplemental Data). Zn concentrations are higher in leachate from the recovered RCA than the original RCA. External sources of Zn, including tire and brake abrasion, combustion exhaust, and the application of road salt, likely added Zn to the system (Gunawardana et al. 2012; Shaw et al. 2012).

Conclusions

Potential for heavy metal leaching and high pH leachate are perceived environmental risks associated with RCA, and these risks are strongly dependent on pH and degree of carbonation of the concrete material. In many applications, the environmental impact of RCA is localized and quite limited; however, the potential for long-term production of high pH leachate is dependent on many environmental factors (Saeed et al. 2006). It is crucial to understand the chemical and physical processes that occur during field deployment of RCA in order to determine the time scale and magnitude of environmental risks in the wide variety of environments in which RCA is utilized. To characterize changes in physical and chemical properties of RCA after field deployment, RCA base course and subgrade soil samples were recovered from the MnROAD field site after eight years and compared to the original RCA characterized by Chen et al. (2012, 2013). In general, the ANC of the RCA increases over the eight-year field deployment. The fines fraction of the recovered RCA had a higher ANC than the coarse fractions, and the equivalence points observed in the ANC curves of the recovered fines fraction indicate extensive carbonation. The recovered MnROAD RCA was further characterized to determine its material pH, mineralogy, and carbonate mineral content. Inorganic carbon content found in the recovered RCA was higher than that of the original RCA characterized by Chen et al. (2012, 2013), providing further evidence for carbonation. X-ray diffraction analysis of the fine fractions highlighted the absence of crystalline portlandite in the recovered RCA, and the ICP-OES indicated a decrease in leachable Cu and Cr and an increase in Zn in leachate in contact with the recovered RCA.

Field monitoring of leachate pH indicated that it remained near neutral for the duration of field-site operation and did not concur with laboratory column leaching experiments performed using the same material (Chen et al. 2012), which indicated a leachate pH of at least 11.5. Furthermore, the material pH of the RCA base course and the subgrade soils was significantly higher than the leachate pH determined from the pan lysimeters at the MnROAD facility, which ranged between pH 6.5 and 8.0 within 7 months of installation (Chen et al. 2012, 2013) and between pH 7.2 and 7.5 eight years after installation. Discrepancies between the material pH measured in the laboratory and the leachate pH measured in the field indicate that conventional laboratory methods are not sufficiently representative of field conditions. In the case of the RCA, the use of an end-over-end tumbler to determine material pH may have resulted in particle abrasion and removal of the protective calcium carbonate layer that would otherwise have limited the material pH. In the case of the subgrade soils, the high water-to-solid ratio and extended contact time likely allowed more extensive dissolution of calcium carbonate minerals and the concomitant large increase in pH. This study focuses on RCA used in conjunction with warm-mix asphalt; future studies should also examine the effect of different types of surface courses on RCA chemistry.

Acknowledgments

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Supplemental Data

Figs. S1 and S2 and Table S1 are available online in the ASCE Library (www.ascelibrary.org).

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Running title: Neutralization of High pH and Alkalinity Effluent from Recycled Concrete Aggregate (RCA) by Common Subgrade Soil

Core ideas:

1) The reactive transport of high pH and high alkalinity discharge from recycled concrete aggregate through model subgrade soils was evaluated.

2) A reactive transport model incorporating advection, diffusion, and reaction is utilized to model the observations in laboratory-scale column experiments.

3) The rate at which the high pH front travels in the subgrade soil is directly related to a soil's clay mineral content and cation exchange capacity.

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Neutralization of High pH and Alkalinity Effluent from Recycled Concrete Aggregate (RCA) by Common Subgrade Soil

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Abbreviations:

CEC, cation exchange capacities; CH, high plasticity clay; CL, low plasticity clay; GWB, GeoChemist’s WorkBench; IC, ion chromatography; ICP-OES, inductively coupled plasma optical emission spectroscopy; LDPE, low-density polyethylene; ML, low plasticity silt；PI, plasticity index; PVF, pore volumes of flow; RCA, recycled concrete aggregate; SC, clayey sand; USCS, unified soil classification system; USEPA, United State Environmental Protection Agency; XRD, x-ray diffraction.

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ABSTRACT

Use of recycled concrete aggregate (RCA) as highway basecourse material conserves virgin aggregate, reduces energy consumption, CO_2 emissions and may also decrease costs during construction. However, concerns remain over possible negative environmental impacts associated with high pH (> 11) effluent from RCA in contact with water. This study examines the reactive transport of high pH and high alkalinity water, modelled on RCA leachate, through model subgrade soils. By developing an understanding of the reactions controlling effluent neutralization, this study aims to quantify the change in pH from the discharge site through surrounding subgrade soils. Four types of subgrade soils with a range of mineral composition, Atterberg limits, and cation exchange capacities (CEC) are examined. They include a clayey sand (SC10), low plasticity clays (M14, SC25) and a high plasticity clay (CH38). Batch reaction experiments are utilized to develop kinetic parameters describing the neutralization of high pH/alkalinity leachate by clay minerals through mineral dissolution and reprecipitation. Based upon this information, a reactive transport model incorporating advection, diffusion, and reaction is utilized to model the change in pH as a function of distance traveled through model subgrade soils and is applied to laboratory-scale column experiments. The rate at which the high pH front travels is directly related to a soil's clay mineral content. Soils with high CEC's effectively delay the propagation of hydroxide-front by the dissolution of clay minerals. This study demonstrates that common subgrade soils with moderate clay content will effectively neutralize high pH leachate initially produced by RCA.**Keywords:** recycled concrete aggregate; pH; alkalinity; subgrade soil; kinetic dissolution;

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INTRODUCTION

As road reconstruction expands due to aging highways, there is an increased demand for virgin aggregate for use in road construction (Ewell, 2004; Transportation of the United States, 2006; Carpenter, et al., 2007). The demand for aggregate in the United States is approximately 1.2 billion Mg per year, and 58% of the aggregate is used in roadway construction, of which 90% is virgin aggregate (Ewell, 2004). However, there are regions of the US where virgin aggregate is not readily accessible, thus the cost and environmental impact of the aggregate increases due to transportation (Carpenter et al., 2007). Concrete recycling reduces the need for mining of virgin aggregate, thereby conserving natural resources and often decreasing transport costs and environmental impacts (Carpenter et al., 2007; Soleimanbegi et al., 2014). Additionally, recycling concrete reduces the need for landfill space, stockpiles and waste concrete, as-well-as illegal concrete dumping. Most importantly recycled concrete aggregate has excellent mechanical properties (higher resilient modulus, and freeze-thaw durability) and its use reduces energy consumption and CO_2 emissions for use as base-course aggregate in pavement structures (Lee et al., 2010; FHWA, 2004; Edil et al., 2012).

During the recycling process, crushing or fracturing of concrete exposes fresh surfaces. Due to the solubility of hydroxide-bearing minerals and other chemical reactions, the pH and alkalinity of water that interacts with recycled concrete may become elevated (Chen et al., 2013). Concern about environmental threats associated with high pH water entering surface and/or groundwater bodies may lead to stricter regulations on RCA leachate water. Most laboratory studies and many field studies suggest that the leachate pH could be very high (e.g., > 9) for extended periods of time (Engelsen et al., 2010 and 2012); however, recent field studies reveal that the pH of discharges from RCA base course ranges from 7.0 to 12.5 (Chen et al., 2013; Roque et al., 2016; Natarajan et al., 2019). Therefore, developing an

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understanding of the pH change from the point of discharge through surrounding subgrade soils will help determine appropriate methods to protect sensitive environments.

Alkaline wastes, such as RCA, fly ash, red mud, have been extensively reused as engineering fills or additives in concrete in recent years (Gomes et al., 2016; Cetin et al., 2014; Abbaspour et al., 2016; Bestgen et al., 2016; Sun et al., 2019). Leachate generated from these wastes are often associated with the concerns of high pH (usually pH = 9-14) and elevated concentrations of hazardous elements, especially oxyanions [e.g., arsenic (As) and chromium (Cr)] (Chen et al., 2012; Sun et al., 2019). Attenuation options for the hyperalkaline leachate usually include active aeration (high partial pressure of CO_2) for carbonation, recirculation of drainage waters, and acid treatments (Mayes et al., 2009; Abbaspour et al., 2016). For example, Roadcap et al. (2005) stated that strong acid, including hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), can effectively neutralize the pH of discharges from the active processing plants but may not successfully remove other contaminants (e.g., heavy metals). However, the measures for pH attenuation mentioned above often require intensive capital or chemical input, and the discharge after treatments could remain toxic to the environment (Roadcap et al., 2005; Mayes et al., 2009). Natural attenuation could be a low-cost and passive method to attenuate the alkaline discharge by taking advantage of the properties of the soils. Studies have shown the feasibility of using natural bioprocesses (e.g., carbonation) and soil acidity, to reduce the pH of the discharge (Gupta et al., 2018). However, information on the capability of soils with differing mineralogy, especially, aluminum (Al)-bearing minerals and cation exchange capacity (CEC) remains scarce.

This study combines batch and column laboratory studies using representative saturation and geochemical conditions to determine the fate and transport of simulated high pH and alkalinity leachate through representative subgrade soils. A geochemical model is then

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developed using the results of the. laboratory studies to predict leachate neutralization in various scenarios.

MATERIALS AND METHODS

Subgrade Soils

The subgrade soils used in this study were selected from the University of Wisconsin-Madison (UW) Soil Bank (Benson and Trast, 1995; Benson and Gurdal, 2013), which contains more than 40 North American soils with a wide range of physical and chemical properties (Atterberg limits, grain size distribution, mineralogical constituent). Four soils were selected that span the range of soil classification in the Unified Soil Classification System (USCS). Their corresponding physical properties (e.g., Atterberg limits and standard Proctor compaction characteristics) and cation exchange capacities (CEC) of these soils are summarized in Table 1. Table 1 also includes the typical range of physical properties of RCA across the US. Each soil was assigned an alphanumeric designation with the first two letters corresponding to the USCS (CL – low plasticity clay, CH – high plasticity clay, ML – silt, SC – clayey sand) and the numeric designation corresponding to the plasticity index (PI). The cation exchange capacity was measured following the procedure in ASTM D7503 (ASTM, 2010). The CEC spans a broad range, from 3.3 to 31.2 cmol+/kg, which reflects the differences in mineralogy between the soils (see subsequent discussion). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were the predominant cations, comprising nearly the entire exchange capacity of each soil.

The mineralogical composition of the four soils was determined using X-ray diffraction (XRD) as described by Moore and Reynolds (1989) and Scalia et al. (2014). (Table S1). All of the soils contain a considerable quartz fraction. The fine-grained soils with higher PIs (CL25, CH38) tend to have a larger fraction of montmorillonite or mixed layer illite-smectite.

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Soils with lower PI (ML14) have a greater fraction of illite or kaolinite. The more plastic clayey sands (SC10) typically have lower PI (<18) and have mixed layer illite-smectite in the clay fraction with trace amounts of kaolinite and illite.

Table 1. Physical properties of subgrade soils (used in the current study) and RCA (typical ranges from literature)

Properties		Methods	Subgrade Soils				RCA^c
			ML14	CL25	CH38	SC10	
Source Location			Atlanta, GA	Omaha, NE	Denver, CO	Monterey, CA	U.S.
USCS		ASTM D2487 (ASTM, 2011)	MH	CL	CH	SC	GP, SP, SM
Optimum Water Content, w_{opt} (%)		ASTM D698 (ASTM, 2012)	19.6	18.3	22.5	13.4	9.2-11.2
Maximum Dry Unit Weight, γ_{dmax} (kN/m^3)		ASTM D698 (ASTM, 2012)	16.4	17.4	15.5	18.6	16.2-20.8
Specific Gravity, G_s		AASHTO T85 (AASHTO, 2015)	2.6	2.6	2.8	2.7	2.6-2.8
Atterberg Limits	Liquid Limit (LL)	ASTM D4318 (ASTM, 2017a)	42	49	50	27	N/A
	Plasticity index (PI)		25	28	14	10	
Particle Size Fractions (%)	Gravel	ASTM D6913 (ASTM, 2017b)	0	1	0	11.8	31.8-76.3
	Sand		1.1	15	36	57.7	21.6-64.9
	Fines		98.9	84	64	30.5	2.1-12.8
	2 μm Clay		31.4	30	23	14.1	N/A
Soil Activity (A)^b		-	0.80	0.93	0.61	0.71	N/A
Hydraulic Conductivity to Water^a, k_s (m/s)		ASTM D5084 (ASTM, 2016)	9.3×10^{-10}	1.3×10^{-11}	8.8×10^{-11}	1.7×10^{-7}	0.8×10^{-5} – 1.2×10^{-3}
Mole Fractions of Bound Cations	Na	ASTM D7503 (ASTM, 2010)	0.0	0.0	0.0	0.0	N/A
	K		0.0	0.02	0.01	0.0	
	Ca		0.46	0.84	0.93	0.60	
	Mg		0.53	0.14	0.06	0.41	
Soluble Cations (mol/kg)	Na	ASTM D7503 (ASTM, 2010)	0.09	0.16	0.95	0.25	N/A
	K		0.03	0.37	0.32	0.06	
	Ca		0.0	1.4	7.0	0.04	
	Mg		0.11	1.2	1.9	0.16	
CEC (cmol$^+$/kg)		ASTM D7503 (ASTM, 2010)	15.5	28.1	31.2	3.3	N/A

[a] Prepared with γ_{dmax} at w_{opt} per standard Proctor ASTM D698 (ASTM 2012).
[b] Activity (A) = PI/(weight percentage of 2 μm Clay).
[c] The typical ranges of physical properties of RCA were obtained from Chen et al. (2012) and Chen et al. (2013).

RCA Leachate

In this study, a synthetic RCA leachate was used to simplify the leachate chemistry in order to develop a better understanding of the buffering mechanism of subgrade soils. pH alone is not a sufficient indicator of the threat of a solution to the environment. The alkalinity, ability of the solution to resist changes in pH, is also considered when determining the threat

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posed by high pH leachate. Leachate that has a high pH but relatively low alkalinity can be easily neutralized in the environment, while leachate with both a high pH and high alkalinity may be an environmental issue.

The highest pH (12.6) of the RCA leachate from field studies conducted by Chen et al. (2013) and Engelsen et al. (2012) (pH = 6.5 – 12.6, with an average of 12.2) was selected for the synthetic RCA leachate. The alkalinity of the synthetic RCA leachate was selected based on the acid neutralization capacity (200 – 600 mEq, with an average of 300 mEq) of RCAs from laboratory studies in Chen et al. (2012) and Engelson et al. (2010). However, this alkalinity range overestimates the actual RCA leachate alkalinity since the minerals provide buffering of acid addition and cannot totally dissolve in the leachate. Therefore, the alkalinity of synthetic leachate (= 274 mEq) was adjusted to be within the highest electrical conductivity (EC ~2.2 S/m) of leachate observed during field and laboratory studies described by Chen et al. (2012) and Chen et al. (2013). The synthetic RCA leachate was prepared by mixing 9.9 g regent grade $NaHCO_3$ (Fisher Scientific Inc., MA, US) and 7.3 g regent grade NaOH (Fisher Scientific Inc., MA, US) in 1 L of ultrapure water (Milli-Q water, Millipore Corporation, MA, US). Additionally, 0.2 g/L of regent grade LiBr (Fisher Scientific Inc., MA, US) was included in the synthetic leachate as a conservative tracer.

Batch Reaction Tests

Batch reaction tests were conducted to investigate mineral dissolution kinetics of the four study soils in contact with synthetic RCA leachate. Soils were air-dried and reduced in size by grinding with a mortar and pestle to less than 2 mm, and 20-g of each soil was used for batch tests mixed with either ultrapure water or synthetic RCA leachate at a liquid to solid ratio (L/S) of 10:1. The mixtures were placed in 125 mL low-density polyethylene (LDPE) bottles and mixed for 24 hours in an end-over-end tumbler at 30 rpm. Aqueous samples were

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withdrawn after 24 hours for further characterization. Tests were run in triplicate and average values reported.

Column Tests

Column tests were conducted to investigate the neutralization of high pH/alkalinity leachate through a column of soil. The air-dried soil samples (i.e., CL25, ML14, CH38, and SC10) were packed by light tamping each soil in polyvinylchloride columns (diameter = 50 mm, height = 500 mm), respectively (Fig. S1). Table S2 describes packing information for each of the four soils. Four sampling ports were included on the side of the columns at 100 mm intervals, influent and effluent ports were included on the bottom and top of the column, respectively. All fittings in contact with RCA were nonmetallic. A continuous, upward flow of synthetic RCA leachate was generated by a peristaltic pump to maintain saturation during the entire testing period. Liquid samples were collected from the four sampling ports and column outlet twice during the first 2 pore volumes of flows (PVFs), and then once per PVF until either the pH and alkalinity from the top port are the same as with the synthetic RCA leachate (i.e., $\mathrm{pH_{in}/pH_{out}}$ and $\mathrm{alkalinity_{in}/alkalinity_{out}} = 1 \pm 0.01$), or after 30 days if this condition was not met. The goal flowrate was 1 PVF per day; however, a flow rate of 1 PVF per day could not be maintained in the tests with soils CL25 and CH38 due to low permeability. Therefore, the actual PVF of these tests was calculated based on the effluent volume during the test (flow rate $\approx$0.08 PVFs per day). Additionally, samples were not obtainable from sampling ports, and therefore only effluent data is presented for these two materials.

Chemical Analysis

Aqueous samples from column and batch reaction experiments were centrifuged at 6,000 rpm for 10 mins before chemical analysis. The pH and alkalinity of liquid samples were

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measured by bench pH meter (Orion 5-star, Thermo Scientific Inc., MA, US) and automatic alkalinity titrator (Potentiometric Compact Titrator, Mettler-Toledo LLC, OH, US), respectively. Major elements released by dissolution of minerals including Al, Ca, Mg, silicon (Si) and iron (Fe), were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Inc., MA, US) following the United State Environmental Protection Agency (USEPA) Method 6010 (USEPA, 1996). Anions, including sulfate (SO_4^{2-}) and chloride (Cl^-), were quantified by ion chromatography (IC, Dionex 2100, Thermo Scientific Inc., MA, US) following USEPA Method 9056A (USEPA, 2007).

Geochemical Modelling

Kinetic Batch Reaction Modelling

The react module of GeoChemist's WorkBench (GWB) 10.0 (Aqueous Solutions LLC, U.S.) was used to simulate batch reaction tests of the subgrade soils and synthetic RCA leachate (or ultrapure water) for 24 hours at 25 C^o. The initial chemistry of the RCA leachate was used as the basis of the model, while minerals in soils based upon their corresponding concentrations were used as the reactants. Other input values associated with the minerals include the mass, surface area, and dissolution rate constants, which are the critical parameters for the simulation of kinetic dissolution of minerals (Table S3). The surface area of each mineral was based on the values reported by Kazempour et al. (2012) and Savage (2012), which were calculated based on the grain diameter of 100 μm (assuming spherical grains). However, the soil samples used in this study generally have high clay content (percent of 2 μm clay = 14.1~34.1%), which has a general grain diameter around 2 μm for clays. Therefore, the surface areas of clay minerals were readjusted using the grain diameter of 2 μm. The rate constant of each mineral was calculated at corresponding pH conditions (e.g., pH = 12.6 for RCA leachate case) based upon the equation reported by Palandri and Kharaka (2004) (Eq. 1):

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$$\log(rate) = \log(A_{base}) - {E_{base}}/{(2.3025RT)} - n_{H+} * pH$$

(Eq. 1)

where A_{base} is the Arrhenius pre-exponential factor of base dissolution mechanism (mole • m^{-2} • s^{-1}), E_{base} is the activation energy of base dissolution mechanism (J/mole); R is the gas constant (8.314 J·mol^{-1}·K^{-1}); T is the temperature of reaction (298.15 K); n_{H+} is the reaction order with respect to protons.

Chemical Transport Modelling

The chemical transport model was constructed using the PhreeqcRM reaction module for transport models (one-dimensional transport) per the method described by Parkhurst and Appelo (2013). The 1D model simulates the chemical transport processes when RCA leachate permeates through the soils and models the propagation of hydroxide-front in different subgrade soil as well as compaction conditions (e.g., column tests with loosely packed conditions or field scenarios with standard Proctor compaction). The outcome of the model was aimed at determining pH at a specific location in the column as a function of the amount of simulated leachate introduced.

The model was constructed using the following assumptions: 1) the column was saturated during the testing period; 2) the soils were uniformly packed in the column; 3) the minerals were homogeneously distributed throughout the column; 4) the kinetic parameters, except dissolution rate, were constant during throughout the testing period, and the change in surface area and porosity by dissolution or precipitation were not considered in the model. In this study, the chemical transport model (with the same packing conditions as column leaching tests) was validated by comparison to experimental results from column leaching tests using the kinetic parameters listed in Table S3. Eq. 1 is built into the model so that the

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effect of pH on the dissolution rate can be calculated instantly with the change in pH as the hydroxide-front propagated.

A 1-D chemical transport model was developed and optimized using the results from the batch and column tests. The model was constructed with 50 cells and 0.01 m per cell (total length of 0.5 m). The dispersivity was set as 0.01. Diffusion of hydroxide within the soil matrix is also considered in the simulation. The self-diffusion coefficient of OH^- in water is 5.2×10^{-9} m^2/s (Li and Gregory, 1974), and the effective diffusion coefficient in the soil after considering tortuosity of the soil (0.19~0.30 for silty clay, and 0.25~0.35 for sandy soil; Barraclough and Tinker, 1981 and 1982) is less than 1.8×10^{-9} m^2/s. The diffusion is not significant in the column tests but may be significant in simulating the field applications where compaction may have lower permeability (e.g., K_s of M14 is 9.3×10^{-10} m/s under standard proctor). Therefore, a diffusion coefficient of 2×10^{-9} m^2/s was used in the model.

RESULTS AND DISCUSSION

Batch Reactor Tests

Batch reactions with ultrapure water or simulated RCA leachate are used to determine kinetic parameters controlling the dissolution of soil minerals in simulated RCA leachate. The average of the triplicate tests is reported in Table S4. Except for M14, the pH of the ultrapure water after 24 hours of contact ranges between 7.7 and 8.2. Soil M14 is quite rich in iron oxides (e.g., 3 % hematite), resulting in a slightly acidic pH of 5.7 after 24 hours of contact time. Water in contact with soils SC10 and M14 has low concentrations (< 10 mg/L) of all analyzed elements, while elevated concentrations of Ca and Mg (> 10 mg/L) are observed in water in contact with soils CL25 and CH38. In particular, soil CH38 releases 870 mg/L Ca and 111 mg/L Mg into the water. This observation is consistent with the soluble cations

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present in soils CL25 and CH38, where Ca and Mg are the major soluble cations at 1.2~1.9 mol/kg and 1.4~7.0 mol/kg, respectively (Table 1).

The pH of the simulated RCA leachate remains quite elevated (12.2~12.4) after 24 h of contact with the subgrade soils, even in the case of soil M14. This phenomenon is likely due to the high pH and high alkalinity (buffering capacity) of the synthetic leachate. In all soils, increased mineral dissolution is observed in the presence of RCA leachate (Table S4), likely due to hydroxide mediated mineral dissolution (Palandri and Kharaka, 2004; Welch and Ullman, 1996). Mineral dissolution results in a large increase in the release of Al and Si from the soils. In particular, the dissolved Si concentration for soils M14 and CH38, increase by more than 100 times (0.3 to 43.6 mg/L and 1.5 to 157.6 mg/L, respectively). Contact with RCA leachate leads to much lower concentrations of dissolved Ca^{2+} (<5.9 mg/L) and Mg^{2+} (non-detectable), likely due to the formation of $Mg(OH)_{2(s)}$ and $CaCO_{3(s)}$ precipitates.

Batch Reaction Modelling

The kinetic dissolution model of the batch reactions indicates that although most of the minerals present in each soil undergo a small amount of dissolution, clay minerals including kaolinite (0.2~0.3%), illite/mica (0.7~1.2%) and montmorillonites (16.4~13.9%) underwent the most dissolution (Table S4). This is due to their large reactive surface area and high dissolution rate at elevated pH values. The modeled pH (12.4-12.6) and alkalinity values (238.3-262.1 mEq) are 1.0-1.02 times to the experimental values (pH = 12.2-12.4, alkalinity = 262.1 mEq) obtained from the batch reaction tests. The Al and Si concentrations obtained from the experimental tests and model are within a factor of 3 (Fig. 1). The results of batch modelling indicate the selected kinetic and physical parameters and are a reasonable basis for chemical transport modelling.

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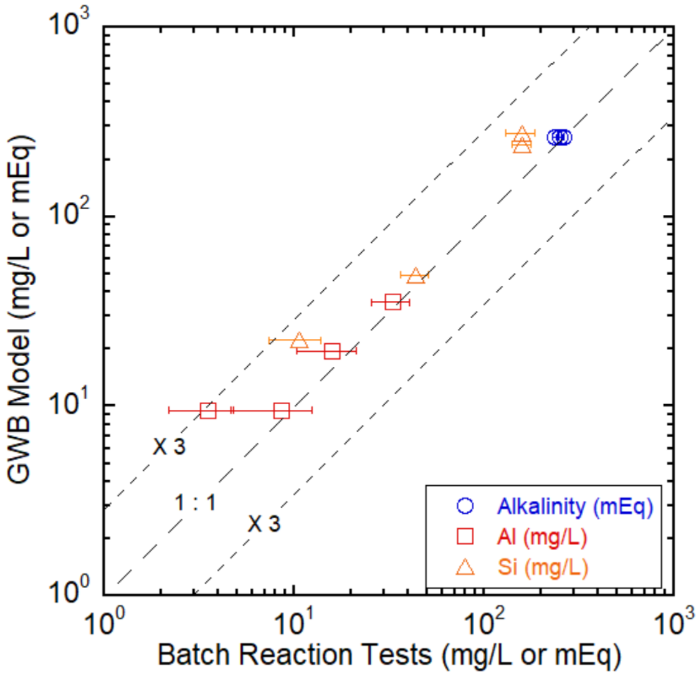

Figure 1. Comparison of alkalinity, Al, and Si concentration between measurements from batch tests and GWB modelling.

Column Tests

Soils SC10 and M14

Soil SC10 is predominantly quartz sand (59% of quartz) with only small amounts of Al-bearing clay minerals (Table S1). After 1 PVF into the column containing soil SC10, the pH is above 12, and the alkalinity is similar to the synthetic leachate at the first sampling port (0.1 m from the bottom); however, the pH and alkalinity of effluent from the column were 7.8 and 140 mEq, respectively. However, after 2 PVFs, the effluent pH and alkalinity at the end of the column reach 12.5 and 230 mEq, respectively, which indicates a complete breakthrough of both hydroxide and alkalinity. Compared with the breakthrough of the conservative Br$^-$ tracer (at 1.4 PVF, Fig. 2a), the breakthrough of the pH and alkalinity front is retarded by about 0.6 PVF, which indicates there is reaction between the soil and the leachate.

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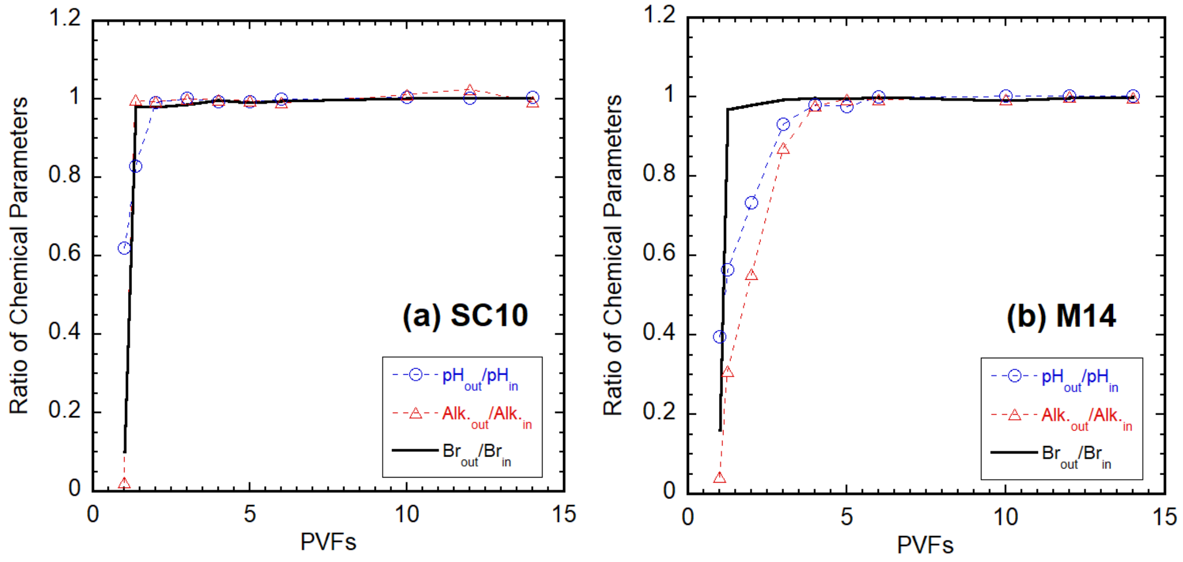

Figure 2. Breakthrough curves of pH, alkalinity, and Br tracer from the end of the column (at 0.5 m) prepared with (a) soil SC10 and (b) soil M14 as a function of PVFs.

The hydroxide and alkalinity fronts propagate more slowly through the column packed with soil M14, indicating that this soil is more reactive with respect to the high pH/alkalinity solution than soil SC10 (Fig. 2b). Hydroxide and alkalinity breakthrough is greatly retarded in column M14, likely due to the presence of exchangeable acidity and reaction of the leachate with the soil, as indicated by the relatively low pH when contacted with water (pH = 5.7, Table S4) and the presence of large quantities of kaolinite in the soil. This results in a pH of 5 and alkalinity of 10 mEq in the first 50 mL of leachate to elute from the column. Hydroxide and alkalinity do not breakthrough until 4 pore volumes of leachate has been introduced, at which point the pH is 12.3, and the alkalinity is 230 mEq in the column's eluent.

Relatively low dissolved Al concentration is observed upon introduction of synthetic RCA leachate into the column containing soil SC10 (Fig. S2a). This is attributed to the low amount (~22 wt.%) of soluble Al-bearing minerals (e.g., with a dissolution rate > 10^{-18} mol g^{-1} s^{-1}), which include high surface area clay minerals (e.g., illite and kaolinite) and albite feldspar. After 2 PVFs, dissolved Al and Si in the effluent reached steady state at ~ 70 mg/L

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and 80 mg/L, respectively (Figs. S2a and S3a). Additionally, the Al and Si concentrations are within the range of 63.2~70.3 mg/L and 76.3~86.7 mg/L, respectively, throughout the entire column. The Al/Si ratio in the column effluent is approximately 0.33 (i.e., Al:Si = 1:3) at pH < 12 and is likely to be controlled by the dissolution of albite ($KAlSi_3O_8$) and K-feldspar ($(Na_{0.82}Ca_{0.17})AlSi_3O_8$) (Fig. S4a). These minerals also have high dissolution rates at 25°C at pH 7, for example, albite's dissolution is $10^{-12.04}$, and K-feldspar is $10^{-12.4}$ mole m^{-2} s^{-1} (Table S3). At pH 12, the dissolved Al:Si ratio increases to 1:1 which is when the dissolution rate of albite increases to $10^{-10.1}$ mole m^{-2} s^{-1}, while the dissolution rate of K-feldspar decreases to $10^{-15.6}$ mole m^{-2} s^{-1}.

In the column containing soil M14, elevated Al (100-200 mg/L) is detected in sampling ports 1, 2, and 3 (0.1, 0.2 and 0.3 m, respectively) after the introduction of one PVF of simulated leachate into the column. As additional simulated leachate is introduced, the peak dissolved Al concentration moves up through the column to sampling port 3 after 2 PVF, port 4 after 3 PVF and to the final effluent port after 4 PVF (Fig. S2b). The concentration of dissolved Al decreases rapidly after the high pH front passes, indicating that dissolution primary Al-bearing minerals and reprecipitation of secondary Al-bearing minerals is likely occurring. For example, the Al concentration in port 3 (0.3 m from the bottom of the column) decreases from 262.8 mg/L at the 2nd PVF to 100 mg/L at the 4th day and lags the change in pH by approximately 1 PVF (Figs. 2b and S2b).

Dissolved Si in columns containing soils SC10 and M14 follows a different trend than Al and does not appear to directly correlate with changes in pH (Fig. S3). The peak Si concentration in the column containing soil SC10 after 1 PVF occurs within the first 20 cm of the column. Continued leachate introduction results in elevated Si (~60-80 mg/L) throughout the column. In the case of the column containing soil M14, the peak Si concentration remains near the 0.1 m sampling port for the duration of the experiment and is lower throughout the

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remainder of the column, for example at 0.2 m, the concentration ranges from 10 – 40 mg/L while it decreases to 0 – 15 mg/L at the top of the column (Fig. S3b).

The dissolved Al-Si ratio in the column containing soil SC10 is nearly 1:1 after the breakthrough of hydroxide-front (2nd PVF). This reflects the high quartz (SiO_2) content of the material and indicates that the concentrations of dissolved Al and Si are likely being controlled by the dissolution of a combination of minerals that result in higher Si:Al ratios such as quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), and/or illite $KAl_2(Si_3AlO_{10})(OH)_2$. In the column containing soil M14, the Al:Si ratio ranges from 1.0 to 3.9 at the first sampling port (0.1 m) for the duration of the testing period but increases from 5.0 to 43.8 at the top of the column. The increasing ratio of dissolved Al:Si is likely due to either the continuous precipitation of insoluble silicates (e.g., calcium silicate, Ca_2SiO_4) or possibly the formation of silicone rich Si-Al minerals, such as analcime ($NaAlSi_2O_6$•H_2O) (Labrid and Bazin 1993).

The highest concentrations of Ca, Mg, and Fe were observed in the first pore volume of flow for through both columns (Fig. S5), and their concentration decreases to less than 10 mg/L (or method detection limit) as hydroxide-front propagates along the column (Fig. 2). The low concentration of dissolved of Ca, Mg and Fe is expected due to their propensity to precipitate in the presence of high carbonate concentrations and at elevated pH.

Soils CL25 and CH 38

The breakthrough of hydroxide and alkalinity fronts does not occur in columns containing soils CL25 or CH38 during a 30-d testing period (Fig. 3). The low permeability of both soils to the synthetic RCA leachate is observed during the testing period likely due to high smectite (or montomorillonite) content. Soils CL25 and CH38 had lower initial hydraulic conductivities (1.3 to 8.8 x 10^{-11} m/s) compared to soils SC10 and M14 (9.3 x 10^{--10} to 1.7 x 10^{-7} m/s). Additionally, the introduction of simulated RCA leachate with its high pH

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and dissolved Na^+ likely results in the dispersion and/or swelling of the clay minerals, which would further limit the hydraulic conductivity (Jo et al., 2001).

Relatively high pH (pH = 10.5) is observed in the effluent of a column packed with soil CL25 after the introduction of the first PVF of leachate, the pH of the effluent then decreases to 7.9~8.6 after 1.5 PVF. The initial high pH of the leachate is likely due to preferential flow paths, before the dispersion/swelling of the clay minerals in the column. The pH of effluent from the column packed with soil CH38 is consistently low (7.8 – 8.1) for the duration of the experiment (~ 2.6 PVF). The alkalinity of effluent from both tests are consistently low and within the range of 10 – 50 meq L^{-1}.

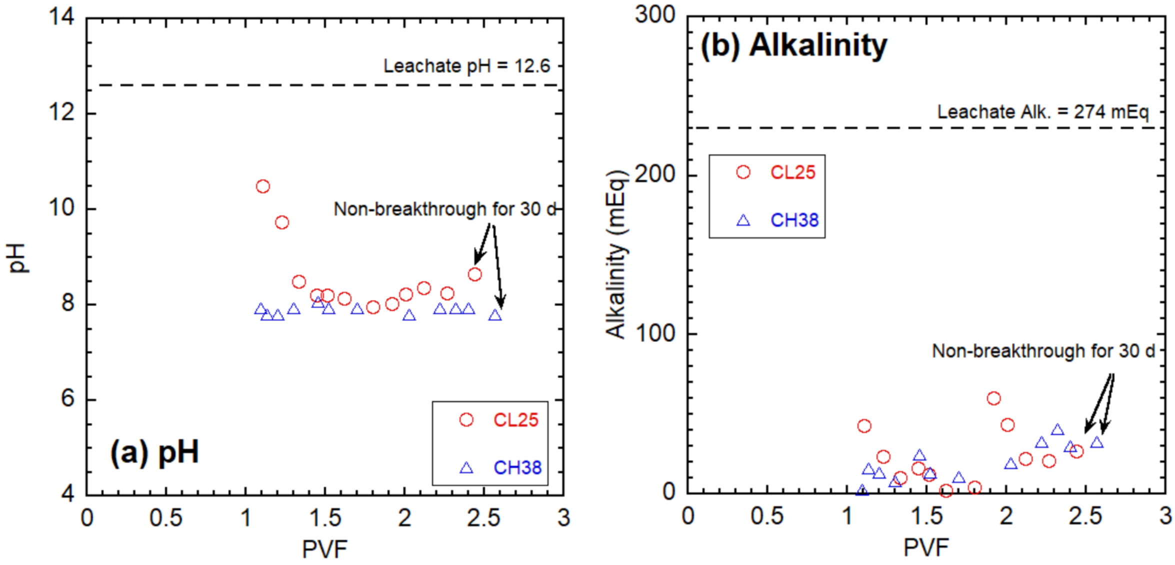

Figure 3. pH and alkalinity of effluent when RCA leachate permeated through the 0.5-m soil columns packed with soil CL25 and CH38 as a function of PVFs (flow rate ≈ 0.08 PVF per day due to the low permeability of the soil).

Low dissolved Al (< 4 mg/L) and Si (< 20 mg/L) are present in both column's effluent, which when considered with the relatively neutral pH of the system indicates minimal dissolution of Al and Si – bearing minerals (Figs. S6a and b). However, dissolved Ca^{2+} and Mg^{2+} (Figs. S6c and d) are observed in both column's effluent, reaching concentrations of up to 700 mg/L for Ca^{2+} and 220 mg/L for Mg^{2+}. This is likely related to the high amounts of bound Ca and Mg in cation exchange complexes in soils CL25 and CH38. Both soils have

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high CECs (>28.0 cmol$^+$/kg), and the major bound cations are Ca^{2+} and Mg^{2+}. The high dissolved Na^+ concentration (0.3 M) in the RCA leachate could replace the bound Ca^{2+} and Mg^{2+} by cation exchange and transform the Ca/Mg-smectite into Na-smectite. Although this cation exchange process is in reverse order of lyotropic theory (naturally Ca/Mg replaces bound Na), the exchange is likely due to the high osmotic pressure exerted by the RCA leachate (Chen et al., 2018). The release of Ca^{2+} and Mg^{2+} likely results in the precipitation of $CaCO_3$ and $Mg(OH)_2$, which would provide a sink for hydroxide and carbonate in the system, thereby lowering the pH and alkalinity of the column effluent.

Reactive Transport Model

Model Validation using Column Leaching Tests

Application of the kinetic parameters derived from the batch experiments to a reactive transport model of hydroxide and alkalinity transport through a column packed with soil SC10 are quite accurate. The model predicts the distribution of pH values throughout the column after 1 PVF and the complete breakthrough of hydroxide after 2 PVF (Fig. 4a). However, the model's prediction of dissolved Al and Si are not in good agreement with the experimental results (Fig. S7).

The model predicts increasing concentrations of both of these elements as a function of distance from the column input, while experimental results reveal that dissolved Al remains relatively constant at ~ 60 mg L^{-1} throughout the column and over the course of the experiment (Fig. S7a). Experimental and modelled results for Si exhibit a similar pattern with the model predicting increasing Si concentration as a function of distance in the column, while the experimental results reveal that Si concentration throughout the column is relatively constant at ~80 mg/L (Fig. S7b). Additionally, the concentration of both Si and Al exhibit a marked decrease in sampling ports 1 and 2, during the introduction of the fourth PVF of simulated leachate, the model does not accurately describe this trend. The molar ratio of Al:Si

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is approximately 2:3, indicating that the congruent dissolution of illite ($KAl_2(Si_3AlO_{10})(OH)_2$), is the likely source of dissolved Al and Si to the solution. Additionally, the calculated dissolution rate constants for illite in basic environments are ~4 orders of magnitude larger than the rate constants for Feldspar (Table S3). The decrease in Si and Al concentration in the third and fourth PVF introduced into the column indicates a lack of base soluble clay minerals, possible due to their complete dissolution, which would indicate that the minerals are dissolving faster than predicted. While there are several possible explanations for the differences between the measured and modeled Si and Al concentrations, errors in assumptions about the size of the clay minerals in this soil seem most likely cause and would explain the trends observed in the experimental data.

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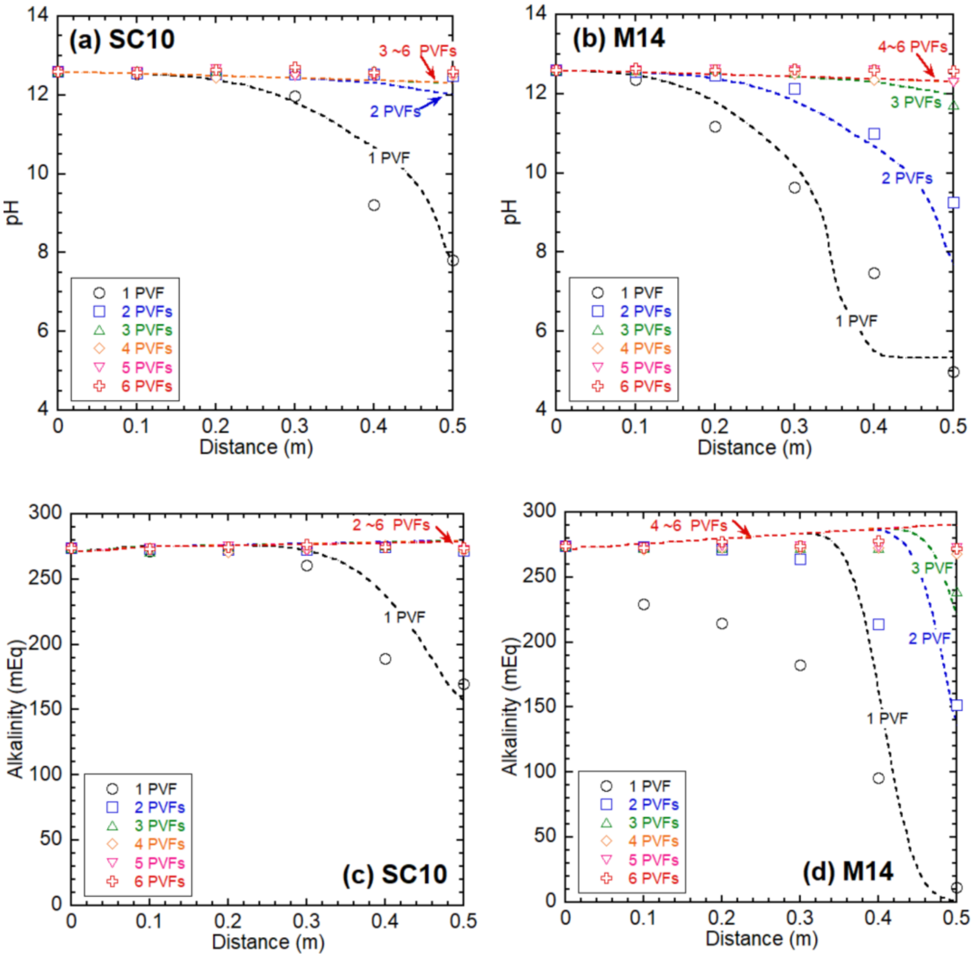

Figure 4. pH and alkalinity of porewater as a function of distance from the continuous source (RCA leachate was introduced at 0 m) in the Phreeqc modelling (dashed lines) and column leaching tests (points) prepared with (a) soil SC10 and (b) soil M14.

In the case of the column containing soil M14, the modeled pH and alkalinity are quite similar to the experimental results (Figs. 4b and d), with the complete breakthrough of hydroxide and alkalinity occurring after 4 PVF. During the first three PVFs the model predicts the general trend in dissolved Al concentrations; however, the actual concentration of dissolved Al is underpredicted across the entire column for the first two PVF and is overpredicted in the third and fourth PVF (Fig. S8a). As with soil SC10, the underprediction of Al concentration in the first two PVF is likely due to incorrect clay particle size distribution. In the second two PVFs, the model overpredicts the concentration of Al,

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indicating that there is a process actively removing Al from solution, such as the precipitation of analcime ($NaAlSi_2O_6•H_2O$) or other Al-rich minerals, that is not incorporated into the reactive transport model. Unfortunately, kinetic parameters for the precipitation of these minerals under conditions relevant to the current study are not presently available. In the case of Si, the shape of the modeled data is generally representative of the experimental data with little systematic variation between the two (Fig. S8b). The decreasing trend of Si, as mentioned previously, is likely due to continuous precipitation of insoluble silicates (e.g., calcium silicate, Ca_2SiO_4) or forming Si-Al minerals, such as analcime ($NaAlSi_2O_6•H_2O$) in Na-rich environment (Labrid and Bazin 1993).

APPLICATION AND CONCLUSIONS

In this study, the reactive transport model developed to model the migration of hydroxide and alkalinity through the columns packed with soils SC10 and ML14 can be applied to determining the length of time that the hydroxide front will take to reach a specific distance from the discharge location (Fig. S9). Based on the findings of this study, the following applications and conclusions are drawn:

- By using a typical saturated hydraulic conductivity for compacted clayey soils of 1×10^{-7} m/s one can directly compare the ability of soils SC10 and M14 to neutralize high pH leachate. The comparison is conducted by calculating the migration of the pH front through 5-m deep subgrade soils for 10 PVF (~1.87 years), using pH 8.5 as the pH of concern.
- The simulation indicates that the hydroxide front propagates much slower in soil M14 than soil SC10. After the introduction of 10 PVF leachate water with a pH of 8.5 has only traveled 0.25 m from the discharge source in 1.87 years. Extrapolation of the linear trend indicates that it will take ~37 years for the pH to exceed 8.5 at a distance of 5 m, which is longer than the typical 30-year design life of the highway. However, if a

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subgrade soil with chemical properties similar to SC10 is used, the hydroxide front will migrate much more rapidly, and after less than one year the pH of the soil's pore water may exceed pH 8.5 at a distance of 5 m.

- It should be noted that this simulation includes several worst-case assumptions including saturated soil media, continuous discharge of high pH leachate, lack of mixing of other fluids and does not include the effect of atmospheric CO_2 on reducing leachate pH. Changes in any of these factors could decrease the speed at which the hydroxide front migrates and would depend on field conditions.
- In the case of soils SC25 and CH38, which have a very high ability to attenuate hydroxide, one can safely assume that amount of time to reach a pH considered environmental deleterious (e.g., pH >8.5) is quite long (> 50 years).

In general, low hydraulic conductivity, as well as a high content of clay minerals, will be beneficial in attenuating high pH leachate associated with RCA used in roadbed construction. Clayey sands with CEC > 15.5 cmol^+/kg (e.g., M14, CL25, and CH38) or higher effectively delay the propagation of hydroxide through clay mineral dissolution and/or precipitation of carbonate. Therefore, in the highway construction with RCA as basecourse, the properties (especially, hydraulic and mineralogical properties) of subgrade soil should be determined for safely and environmental-friendly use of recycled material.

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