

pH-dependent Leaching of Trace Elements from Recycled Concrete Aggregate

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ABSTRACT: Recycled concrete aggregate (RCA) has excellent mechanical properties and is often used as base course in pavement construction. However, highly alkaline leachate from RCA has been observed in laboratory studies. The associated high-pH leaching patterns can be of concern, especially when compared to the neutral pH environment observed in actual road sections using RCA as base course. In this study, the pH-dependent leaching concentrations of trace elements copper (Cu) and zinc (Zn) and the oxyanion chromium (Cr) were investigated on unfractionated RCA samples and fractionated RCA samples (i.e., 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). A pH-buffering plateau was observed between pH 4.9 and 7.0 in the acid neutralization capacity curve. Cu and Zn showed the highest levels of leaching at $\text{pH} \approx 2$, and the lowest leaching at $\text{pH} > 7.5$. Cr showed the lowest level of leaching between pH 5.0 and 6.5, and higher leaching concentrations towards the acid and alkali directions. The fine particles tended to leach more Cu and Zn than sand- and gravel-sized particles at $2 < \text{pH} < 13$, while leaching of Cr from the fine fraction was not elevated except at $\text{pH} < 2$.

INTRODUCTION

Ever-increasing road reconstruction due to aging infrastructure in the United States (U.S.) is causing increased demand for virgin aggregate. The production of virgin aggregate constitutes one of the greatest costs in highway construction. The demand for aggregate in the U.S. increased from 58 million tons in 1900 to 2.3 billion

tons in 1996, and is estimated to reach 3.0 billion tons by 2020 (USGS 1997). Additionally, approximately 123 million tons of waste is generated annually from building demolition (FHWA 2004), which adds to the cost of waste handling and disposal. Currently, the construction industry is moving towards beneficial use of recycled waste materials in construction in lieu of virgin aggregate. Specifically, recycled concrete aggregate (RCA) provides excellent mechanical properties (e.g., lower specific gravity, higher resilient modulus, and freeze-thaw durability) for use as base course aggregate in pavement structures (ACPA 2009). Moreover, use of RCA has significant life-cycle benefits, such as reducing greenhouse gas emissions, energy and virgin aggregate consumption, and costs of pavement construction. In the U.S., an average of 140 million tons of RCA is produced annually (ACPA 2008), and at least 41 states recycle concrete pavements (FHWA 2004). However, wise use of recycled materials also requires their safe use. Since RCA is a cement-based material, there are concerns related to potentially elevated leaching patterns due to the inherent high alkalinity of RCA. In practical applications using cement-based material, wide pH ranges $7.5 \leq \text{pH} \leq 12$ due to both weathering of material and material alkalinity have been observed (Van der Sloot et al. 2008). pH-dependent leaching patterns from contaminated soil and waste materials also have been reported (Dijkstra et al. 2006, Dijkstra et al. 2004 and Engelsen et al. 2010).

In this study, the pH-dependent leaching characteristics of trace metals and minor elements from four samples of RCA collected from a wide geographic area (California, Colorado, Minnesota and Texas) were investigated. The effect of grain size of the RCA on leaching was also considered. Since the chemical constituency and exposed surface area of finer and coarser particles may be different, grain size is expected to strongly influence the leaching of trace metals from RCA. pH-dependent testing along with consideration of grain size is considered to be a more realistic approach for the prediction of metal leaching in a field scenario.

MATERIALS AND METHODS

pH-dependent batch tests were conducted according to methods outlined in Kosson et al. (2002) using four RCA sources: California (CA), Colorado (CO), Minnesota (MN) and Texas (TX). Physical properties and chemical compositions of the four RCAs are shown in Table 1. One representative sample was taken from each source and homogenized by hand mixing. The representative samples were separated into two specimens: one used to represent the entire sample and the other for grain-size fractioning. The fractionated samples were sieved into three grain-size fractions: fine particles (<0.075 mm), sand-sized particles (<4.75 mm, >0.075 mm), and gravel-sized particles (<75 mm, >4.75 mm). All fractions were then reduced to less than 2 mm-size with a steel jaw crusher (50 mm \times 152 mm opening high Mn-steel jaw crusher by Sturtevant Inc., MA, USA).

The total elemental composition of each RCA specimen was determined by acid digestion according to ASTM D 5198-09. A 1:1 nitric acid digestion of 5 g of solid sample was performed at 90 to 95°C for 2 h. The total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC) were determined with a SC144 DR sulfur and carbon analyzer (LECO Inc., St. Joseph, MO, USA). The batch tests were performed with unfractionated (entire) samples and fractionated samples at

a liquid to solid ratio of 10:1 by weight. Samples were agitated in an end-over-end tumbler at a speed of 30 ± 2 revolutions per min (rpm). A pH range of 2 to 13 was used for the pH-dependent leaching tests, with target pH of 13, 12, 10.5, 9, 8, 7, 5.5, 4 and 2. A pre-test titration was conducted to determine the contact time to equilibrium and the acid/base addition required for each batch. pH, electrical conductivity (EC), and oxidation-reduction potential (Eh) were determined after testing. The acid neutralization capacity (ANC) curve of each material was also derived from the pH-dependent batch test by the quantity of acid/base addition to each batch and the corresponding final pH reading of the eluate. Development of the ANC is an important step in conducting pH-dependent leaching tests on cement-based materials, since the acid buffering ability of the material will affect the leaching characteristics of the contaminants by both controlling the pH condition and maintaining the integrity of solid matrix when acid attacking (Giampaolo and Mastro 2001).

Table 1. Physical properties and chemical compositions of RCAs

Location (State)		CA ¹	CO ²	MN ¹	TX ³
Physical properties					
	Method				
Moisture Content (%)	ASTM D2216	4.5	3.9	3.0	2.1
Optimum Water Content (%)	ASTM D1557	10.9	11.9	11.2	9.2
Max Dry Unit Weight (kN/m ³)	ASTM D1557	19.8	18.9	19.5	19.7
Specific Gravity	AASHTO T85	2.6	2.6	2.7	2.6
Absorption (%)	AASHTO T85	5.0	5.8	4.9	5.5
Particle size distribution					
75-4.75 mm (wt%)		50.6	40.9	31.8	76.3
4.75-0.075 mm (wt%)	ASTM D2487	47.1	46.3	64.9	21.6
<0.075 mm (wt%)		2.3	12.8	3.3	2.1
Hydraulic Properties					
Hydraulic Conductivity (m/s)	ASTM D5856	1.9×10^{-5}	1.6×10^{-5}	1.8×10^{-5}	7.7×10^{-6}
Chemical composition					
Total Carbon (%)	LECO carbon analyzer	1.9	1.9	1.6	3.2
Total Organic Carbon (%)		1.4	0.3	0.4	0.4
Total Inorganic Carbon (%)		0.5	1.5	1.2	2.8
Copper (Cu) (mg/kg)		16.5	10.0	13.6	6.1
Zinc (Zn) (mg/kg)	ASTM D5198	32.4	58.8	30.4	20.4
Chromium (Cr) (mg/kg)		20.2	7.5	11.5	8.9
Material pH					
Entire Sample	Accumet	12.1	12.1	11.3	12.0
Gravel-sized Particles	AR50	12.1	12.1	11.6	12.1
Sand-sized Particles		11.9	11.9	11.2	11.7
Fines Particles	pH meter	11.9	11.8	10.9	11.1

Note: ¹Stockpile of single demolition, ²Various demolitions, ³Commercial source with special aggregate and material characteristics.

All Samples were then filtered using 0.45- μ m filter paper, preserved with nitric acid, and stored at 4°C. Trace elemental concentrations and oxyanion concentrations in the eluate were determined with inductively coupled plasma optical emission spectrometry (ICP-OES, Vista-MPX CCD Simultaneous ICP-OES, Varian

Inc., CA, US). Two trace elements, Cu and Zn, were chosen to be evaluated in this study because acid digestion showed Cu and Zn to be the most concentrated trace elements in the RCAs (Table 1). One oxyanion, Cr, was chosen for analysis because previous leaching studies (Sadecki et al. 1996, Engelsen et al. 2006) showed relatively high Cr released concentration from RCA.

RESULTS AND DISCUSSIONS

Acid Neutralization Capacity – Acid/Base Addition and pH

Figure 1 shows the ANC curve of the unfractionated (entire) RCA samples and their fractionated subsets. Negative values in Figure 1 represent base additions. pH data from the ANC for fractionated RCA and unfractionated RCA are shown in Table 1. The material pH (no acid or base added) of the RCAs ranged from 11.3 to 12.1, with CA, CO, and TX RCA having similar pH, and relatively low pH from MN RCA. Similar ANC curves were observed for CO, TX, and MN RCA – rapid drop of pH followed by a plateau around pH 4.9 to 7.0. Garrabrants et al. (2004) concluded that the plateau in the ANC can be explained by dissolution of calcium carbonate (carbonation) in concrete, which is caused by a reaction between portlandite and calcium silicate hydrate with carbon dioxide from the environment. Carbonation conditions may occur during the concrete service life and in stockpile storage. In comparison, the CA RCA showed a pH plateau that was less obvious. The TIC results showed that the CA RCA had much less inorganic carbon (0.4% of mass) compared with the CO RCA (1.5% by mass), TX RCA (2.7% by mass), and MN RCA (1.2% by mass).

The gravel-sized and sand-sized particles (87.2% to 97.8% of total RCA mass fraction) presented an ANC curve similar to the unfractionated RCA. Moreover, the gravel-sized particles had higher material pH (11.5 to 12.1) than sand particles (11.1 to 11.9) and fine particles (10.9 to 11.8), and likely control the pH of the bulk (unfractionated) pH (11.3 to 12.1). Carbonation is the most probable reason for this pH difference among fractions, since all fractions are sourced from the same monolithic concrete and treated using the same procedure. Carbonation begins on the surface of the concrete and slowly penetrates the interior of the concrete (Houst and Wittmann 2002 and Garrabrants et al. 2004). After crushing, the fines have a much higher surface area than gravel-sized particles, which results in more reactive surface for carbonation, consuming more cement and leading to a lower material pH. The higher carbonation degree in the fines can also be shown by comparing the ANC curve of the fine fraction with the other fractions. The fines fraction had a higher resistance of acid attack than other fractions. In general, the acid neutralization capacity decreased as the particle size increased.

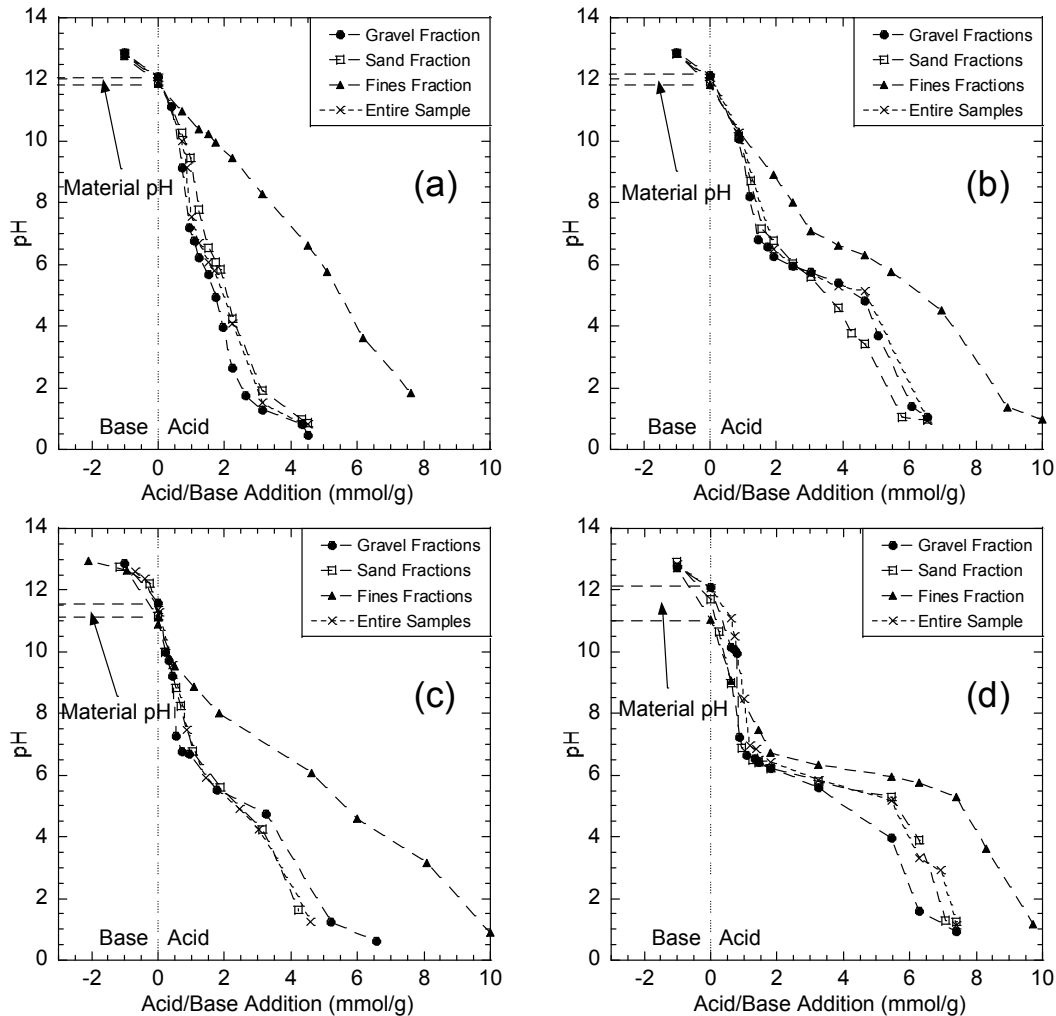


Figure 1 ANC curves of (a) CA RCA (b) CO RCA (c) MN RCA (d) TX RCA

Leaching of Trace Elements Cu and Zn from Recycled Concrete Aggregate

Figure 2 shows pH-dependent leaching of Cu and Zn from the unfractionated RCAs. Cu and Zn showed similar leaching trends, with maximum leached concentrations at $\text{pH} \approx 2.0$ and minimum leached concentrations at alkaline or near-neutral pH (7.5–13.0). An increase in leaching concentration with decreasing pH was observed for each element, with Cu starting at $\text{pH} \approx 6.5$ and Zn at $\text{pH} \approx 7.5$.

The concentrations of leached Cu and Zn were not directly related to the total elemental content of the RCA (Table 1). CO RCA tended to leach more Cu and Zn than the other RCAs within the pH range of 2.0 to 13.0, even though the total elemental composition had lower quantities of Cu and Zn available to leach compared to the other three RCAs tested. This trend in leaching behavior was also observed in waste material leaching studies performed by Van der Sloot et al. (1997) and Kosson et al. (2002).

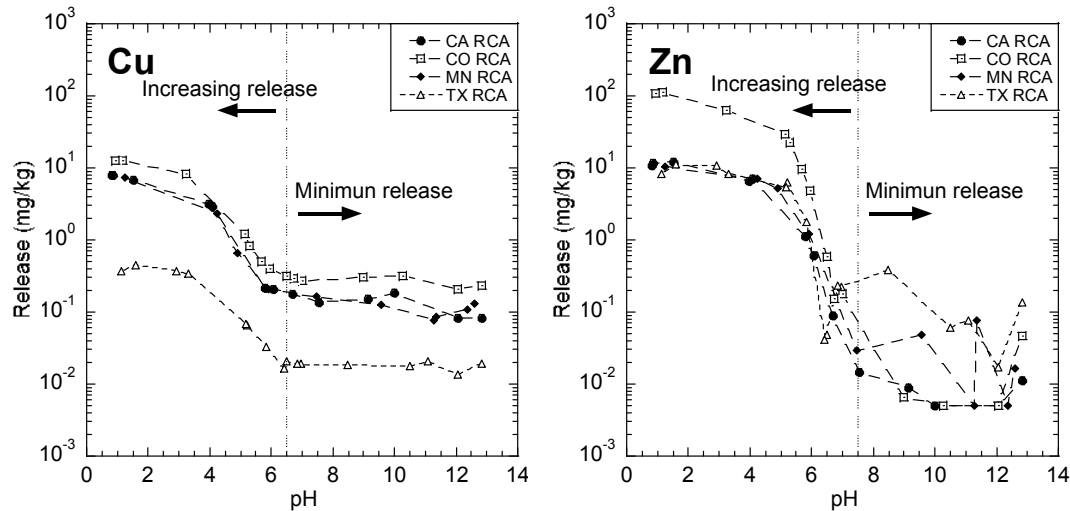


Figure 2 pH-dependent leaching of Cu and Zn from unfractionated RCAs

Figure 3 shows the pH-dependent leaching patterns of Cu and Zn from three fractions. The grain-size specific fractions showed a similar leaching trend for all RCA sources. In the pH range of 2 to 13, fine particles showed a higher leaching concentration than coarser-sized particles, and the leaching was enhanced as particle size decreased. At pH > 12, slightly enhanced leaching of Cu and Zn were observed from fines, while gravel-sized particles showed no obvious difference in leaching behavior. Previous studies with field road base have shown that this alkaline effluent usually occurs in the first few flushes from field road base and has been observed in previous studies (Sadecki et al. 1996, Engelsen et al. 2006). At pH typical of field-scale studies (6.5~8.0), leaching of Cu and Zn from smaller sized fractions increased, with the fine fraction having leached concentrations of Cu and Zn up to an order of magnitude higher (MnDOT 2010).

Leaching of Oxyanion Cr from Recycled Concrete Aggregate

Chromium, which usually forms negative-charge oxyanions (e.g., CrO_4^{2-}), showed a V-shaped pH leaching pattern. The minimum release of Cr occurred between pH 5.0 and 6.5, and increasing concentrations were observed towards both pH=2 and pH=13. The most acidic region (pH \approx 2) showed higher leaching levels (3.2 to 6.1 mg/kg) relative to the most alkaline region (pH \approx 12) where concentrations were between 0.9 and 1.2 mg/kg (Figure 4). The leaching amount was also independent from the total elemental content. All RCAs showed similar Cr levels at pH \approx 2 and pH \approx 13, while Cr contents in solid samples showed notable differences, ranging from 7.5 to 20.2 mg/kg. Figure 5 shows the various Cr species across the range of pH and Eh conditions (Cornelis et al. 2008). The Eh data of the unfractionated RCAs are also plotted in Figure 5. At high pH (pH > 11.0), CrO_4^{2-} (hexavalent chromium) is the dominant form of Cr, whereas various tri-valent chromium forms occur at pH < 11.0.

A similar V-shaped leaching pattern was also observed among each grain-size fraction (Figure 6). There is no obvious differences in Cr leaching among the three fractions at pH 2.0 to 13.0. Finer particles showed a slightly higher leaching ability than gravel-sized and sand-sized particles at pH < 2.

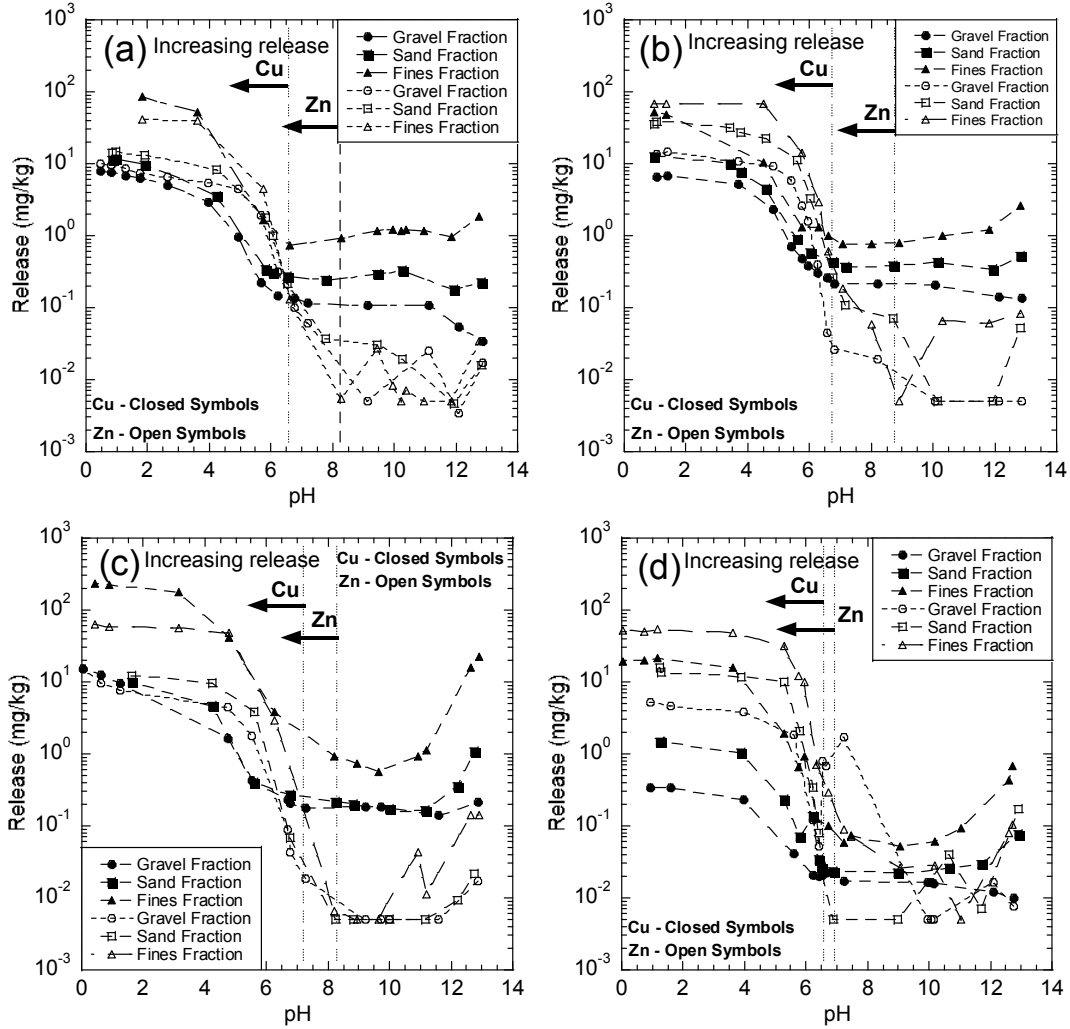


Figure 3 pH-dependent leaching of Cu (closed symbol) and Zn (open symbol) from (a) CA RCA (b) CO RCA (c) MN RCA (d) TX RCA

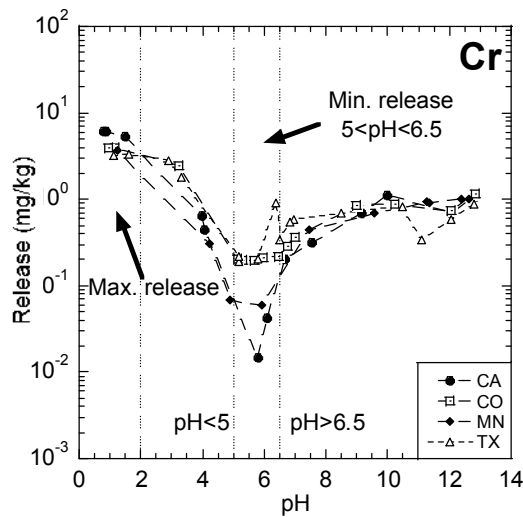


Figure 4 pH-dependent leaching of Cr from four unfractured RCAs

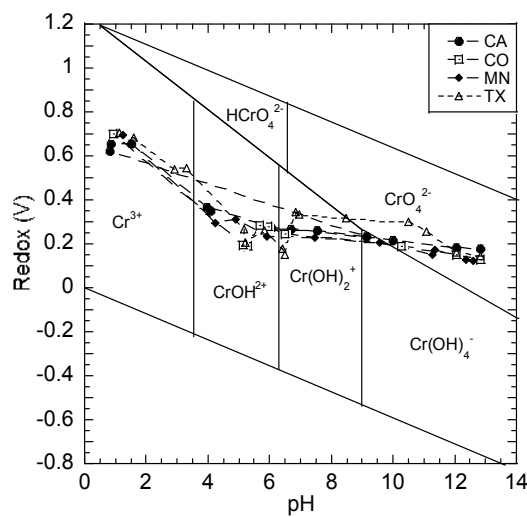


Figure 5 Cr species as a function of pH and Eh (Cornelis et al. 2008)

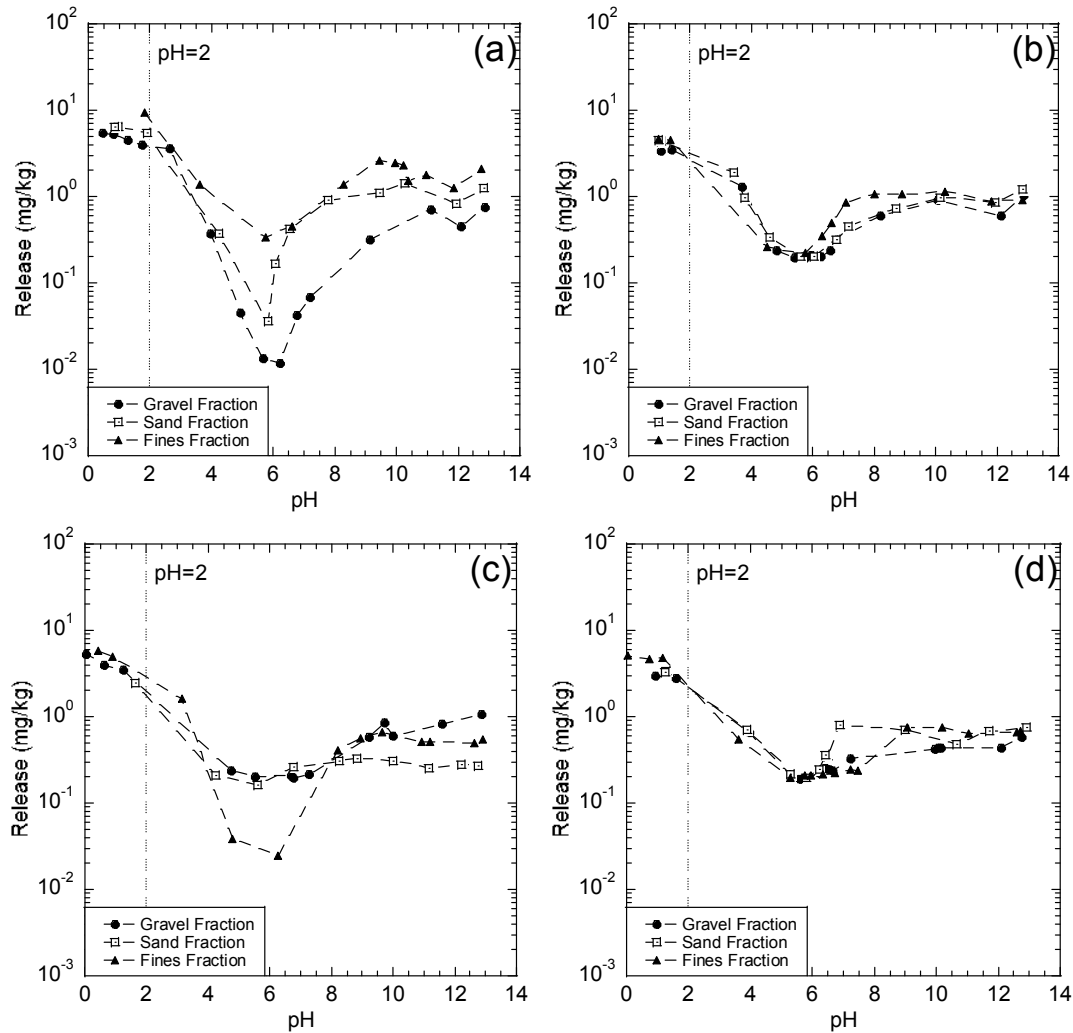


Figure 6 pH-dependent leaching of Cr from fractionated (a) CA RCA (b) CO RCA (c) MN RCA (d) TX RCA

Discussion

As background to this study, leaching observations were made from both field and lab tests. A field road section using MN RCA as the base course was constructed in a separate, ongoing study, and parallel column tests that used all four RCA sources were conducted. Leachate pH and metal concentrations from the laboratory column tests have been noticeably different from leachate samples collected from a pan lysimeter installed under the RCA base course layer in the field. The column tests and field test results indicate that pH-dependent leaching behavior can occur and be used to interpret the leaching differences. pH from column leaching tests ranged between 11.0 and 12.5 and showed no decline over 100 pore volumes of flow (PVF), while pH of field samples decreased to near neutral and remained between 6.5 and 8.0 after 1.2 PVF and 7 months. Trace elements (Cu and Zn) in the field leachate peaked at 10.3 and 73.3 $\mu\text{g/L}$, respectively, whereas column test leachate had a maximum Cu and Zn concentration of 10.8 $\mu\text{g/L}$ and 2.4 $\mu\text{g/L}$. Oxyanion Cr in the field leachate peaked at

16.7 µg/L, compared with oxyanion concentrations of 80.8 µg/L from the column leaching tests (MnDOT 2010).

Finer particle sizes have higher trace metal leaching potential and ANC than gravel-size particles, even though all particles are sourced from the same monolithic concrete. However, given the duration of stockpiled conditions or other exposures to the environment, the chemical composition of each fraction is likely to change. Carbon dioxide exposure and carbonation change the cement hydrate phase, enhancing the leaching of trace elements. Enhanced trace element leaching may be avoided if fine particles of RCA can be minimized along with avoiding exposure to carbon dioxide in stockpile conditions. Moreover, at high pH (pH>12), leaching of Cr(VI) is pronounced and the impact to the environment should be considered.

CONCLUSIONS

Acid neutralization capacity curves of Colorado, Minnesota and Texas RCA showed significant acid neutralization capacity, while RCA sourced from California had an lower acid neutralization capacity. When RCAs were fractionated (i.e., 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) finer particles showed a higher acid neutralization capacity than coarser particles. Different leaching patterns of trace elements (Cu and Zn) and the oxyanion (Cr) were observed from the pH-dependent batch tests. Cu and Zn showed highest leaching concentrations at pH≅2 and lowest leaching at pH>7.5. An elevated leaching concentration was also observed for each element at pH 6 to 7.5. Cr showed a V-shaped leaching pattern, with the lowest leaching concentrations occurring between pH 5.0 and 6.5, and higher leaching concentrations in the more acidic and alkaline regions (pH<5 and pH>6.5). Fine particles leached more Cu and Zn than coarser grains at pH 2 to 13. However, the difference in leaching based on grain size alone is relatively small for Cr at pH 2 to 13. When pH<2, finer particles tended to leach more Cr than coarser grains, but this extremely low pH environment is unlikely in any field scenario. pH-dependent tests along with consideration of grain size and leachate pH-Eh states can be used to assess metal leaching in a field scenario.

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