



Heavy metal removal capacity of individual components of permeable reactive concrete



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ABSTRACT

Permeable reactive barriers (PRBs) are a well-known technique for groundwater remediation using industrialized reactive media such as zero-valent iron and activated carbon. Permeable reactive concrete (PRC) is an alternative reactive medium composed of relatively inexpensive materials such as cement and aggregate. A variety of multimodal, simultaneous processes drive remediation of metals from contaminated groundwater within PRC systems due to the complex heterogeneous matrix formed during cement hydration. This research investigated the influence coarse aggregate, portland cement, fly ash, and various combinations had on the removal of lead, cadmium, and zinc in solution. Adsorption, adsorption, precipitation, co-precipitation, and internal diffusion of the metals are common mechanisms of removal in the hydrated cement matrix and independent of the aggregate. Local aggregates can be used as the permeable structure also possessing high metal removal capabilities, however calcareous sources of aggregate are preferred due to improved removal with low leachability. Individual adsorption isotherms were linear or curvilinear up, indicating a preferred removal process. For PRC samples, metal saturation was not reached over the range of concentrations tested. Results were then used to compare removal against activated carbon and aggregate-based PRBs by estimating material costs for the remediation of an example heavy metal contaminated Superfund site located in the Midwestern United States, Joplin, Missouri.

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1. Introduction

The immediate risks of metal-laden waters to the general public were recently shown in the release of mining residuals and heavy metal contaminants near the Animas River, USA and Rio Doce, Brazil (Egler et al., 2014; Gobla et al., 2015; Mariuzzo and Barata, 2016). The severe impact to human life and the high cost of environmental cleanup for related damages has been largely at the expense of the companies and agencies that manage the sites, while the burden of enduring the acute and long-term effects of contamination is placed on the public. Advances in treatment technologies are of high interest especially ones minimizing environmental risks, while remaining cost effective for remediating a majority of the RCRA 8 metals. Cadmium, lead, and zinc were chosen as representative metal contaminants due to their mobility and toxicity especially present in local, Midwestern, groundwater (Carroll et al., 1998; Environmental Protection Agency, 1990). Several methods are available for the remediation of groundwater, however the EPA-preferred method of treatment is with permeable reactive barriers (PRBs), as these typically provide the best cost to benefit ratio (Powell et al., 1998). PRBs are passive systems simply constructed

by cutting a vertical trench downgradient of the contaminant plume, filling the trench with baffles, and installing a reactive medium to intercept and treat the groundwater (Bartzas and Komnitsas, 2010; Collins et al., 2010; Morar et al., 2012; Mulligan et al., 2001; Paul et al., 2003; Wilkin et al., 2008). Typical reactive media components include permanganate, persulfate, activated carbon, or zero-valent iron, all of which remove metals through adsorption or oxidation (ITRC, 2011). Each material is generally toxin specific and costly to produce or regenerate (Bartzas and Komnitsas, 2010; Watts and Teel, 2006). Permeable concrete as a reactive medium, called permeable reactive concrete (PRC), is a potential alternative with benefits to both cost and simplicity of design as compared to traditional PRBs (Knox et al., 2012). Contributions to removal of heavy metals by aggregate or some cement components are known; however, the combined or bulk removal, related to the individual components, has not been previously studied.

Permeable concrete, also termed pervious concrete, Portland Cement Pervious Concrete (PCPC), no fines concrete, or enhanced porosity concrete, is a best management practice used for stormwater reduction and water quality improvement (American Concrete Institute Committee 522, 2010; Kevern, 2015; Kevern et al., 2008; Sañudo-Fontaneda et al., 2014). Permeable concrete has been shown to remove some metals (copper and zinc), nutrients (nitrogen and phosphorus), organics, and suspended solids from surface waters primarily through physical filtration and adsorption, although stormwater

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volume reduction has been the primary focus of application (Haselbach et al., 2014, 2006; Luck and Workman, 2007; Newman et al., 2002). Permeable concrete typically contains single-sized coarse aggregate bound by sufficient cement paste to coat each aggregate particle and provide load transfer between the cement-coated pieces. Permeable concrete hardens into a highly porous material distinguished from conventional concrete by a high degree of interconnected and tortuous voids (>10% voids by volume) (American Concrete Institute Committee 522, 2010). The two most fundamental components of permeable concrete are cement paste and aggregate, and both have the individual capacity to remove contaminants from solution. Portland cement is well-known as a soil stabilizer or solidifier for use in sequestering heavy metals in soil mixing (Mulligan et al., 2001). Portland cement hydration produces highly alkaline conditions >12.0 S/U and causes metals in solution to precipitate or sorb with the cement hydration products such as calcium-silica-hydrate (CSH) gel (Aziz et al., 2008; Chen et al., 2007). Supplementary cementitious materials (SCMs) such as class C fly ash and natural zeolites have been used in PRBs or water treatment facilities to remove heavy metals through precipitation and adsorption. Removal by fly ash is attributed to the high specific surface area, formation of additional CSH gel, and increased zeta potential as alkalinity increases to improve metal sorption (Bayat, 2002; Czurda and Haus, 2002; Petersen et al., 1996; Purnomo et al., 2008; Wang et al., 2004; Weng and Huang, 1994, 2004).

A wide variety of coarse aggregate materials are used to produce pervious concrete such as crushed limestone, mixed river gravel, high pressure-nonfoliated metamorphics, and cemented sedimentary, well indurated, materials (Kevern et al., 2008, 2010). In general, local-sourced aggregates are used unless chemical, physical, or mechanical properties do not meet prevailing specifications or ASTM C33 (ASTM, 2003). Adsorption by aggregate or soils is also a well-known process generally applied to evaluate the environmental impact risk derived by the natural attenuation of native soils to remove contaminants. Limestone, granite, and silica aggregates have been shown to remove heavy metals from solution in both surface and groundwater applications (Bradl, 2004; Demirkan, 2008; Elliott et al., 1986; Ernst et al., 2016; Lu and Xu, 2009). Calcite contained in powdered limestone, waste sludge, and synthetic sources can adsorb individual metals such as lead, zinc, or cadmium (Ghazy and Ragab, 2007; Merrikhpour and Jalali, 2012; Sibrell et al., 2007). Reaction kinetics and removal rates for calcite with lead or zinc are reported in the literature; however, a combined removal for lead, zinc, and cadmium is not well known (Papadopoulos and Rowell, 1988). This research investigates the removal of lead, zinc, and cadmium from an aqueous solution by three different aggregates (limestone, Kansas River-sourced pea gravel, and inert soda-lime distillation glass beads) used with two cementitious mixtures (100% Portland cement and Portland cement with 25% replaced by Class C fly ash). The results expand the current knowledgebase for PRC, providing the background for design to move the technology into mainstream applications.

2. Methods

2.1. Materials

Three coarse aggregates were tested (Gravel-G, Limestone-L, Soda-lime glass beads-GB) with two cementitious mixtures: 100% Type I/II ordinary Portland cement (labeled PC) conforming to ASTM C150/C150M-16e1 (2016) or with 25% replacement of Type I/II cement with Class C fly ash (labeled CA) conforming to ASTM C618-15 (2015) with chemical properties measured according to ASTM C311/311M-13 (2013) (ASTM, 2016; ASTM, 2010, 2005). Chemical and physical properties of the materials are summarized in Table 1. Aggregates had a uniform gradation with a maximum nominal size for the pea gravel and limestone of 9.5 mm (3/8 in.) and soda glass beads of 6.0 mm (1/

Table 1
Composition of components.

Chemical	Portland cement (%)	Class C fly ash (%)	Limestone (%)	Gravel (%)	Glass beads (%)
SiO ₂	20.49	40.71	3.75	34.90	74.00
Al ₂ O ₃	4.26	18.99	0.50	3.32	1.30
Fe ₂ O ₃	3.14	6.05	0.18	0.79	0.04
CaO	63.48	20.10	51.88	0.75	10.50
MgO	2.11	4.82	1.33	0.70	0.20
SO ₃	2.90	0.83	0.00	0.00	0.20
Na ₂ O	0.18	1.46	0.00	1.98	13.00
K ₂ O	0.47	0.65	0.00	1.17	0.30
CO ₂	1.48	0.00	0.00	0.00	0.00
CaCO ₃	3.41	0.00	92.60	56.39	0.00
LOI	2.20	0.08	0.00	0.00	0.00

4 in.). Absorption of the gravel and limestone was approximately equal at 1% as determined using ASTM C127-14 (2014) (ASTM, 2014). Pea gravel consisted of subrounded to subangular grains while crushed limestone consisted of angular grains. The specific gravities of Portland cement, class C fly ash, limestone, pea gravel, and glass beads are 3.15, 2.69, 2.65, 2.62, and 2.50 respectively. Soda-lime glass beads were used as an assumed nonreactive scaffold for the cement paste to identify the cement's role in removal. The beads were required to provide a similar macro-pore distribution and paste thickness to adequately compare paste with limestone or pea gravel concrete. Soda-lime glass beads are commonly used in distillation columns and were assumed to be nonreactive.

Limestone aggregate was sourced from the lower ledge of the Callaway-Cooper-Mineola facies of Cedar Valley Limestone. The Callaway-Cooper-Mineola is a Devonian calcitic-magnesia limestone which covers about 58% of Missouri, U.S., with about 30% surficially exposed and 28% below grade. The pea gravel aggregate was sourced from the Kansas River drainage basin and procured from aggregate dredging operations located in Bonner Springs, Kansas. The Kansas River flows about 275 km (170 miles) from the confluence of the Smoky Hill and Republican rivers, at Junction City, eastward to its mouth in Kansas City, Kansas. The drainage basin covers just over 155,000 km² (60,000 miles²). Sediment within the Kansas River reflects the geologic composition of its drainage basin with approximately 160 geologic bedrock units contributing to the sediment of the Kansas River. Most of the coarse materials obtained are of various limestones, dolomites, chert, sand or mudstone, or crystalline calcite (Scott and Hambleton, 1965). A potassium feldspar bearing metamorphic rock also appears in sufficient mass within the sample used for this study. Some gravel contains both potassium feldspar and dolomite, effervescing very weakly in dilute hydrochloric acid. Metamorphic rocks exposed at the surface in Kansas are associated with the Riley and Woodson county igneous intrusives. Granite or granitoid igneous rocks are found in Woodson County and are medium to coarse-grained with intrusions into Pennsylvanian shales (Franks, 1965, 1966). Lower Permian limestones and shales have been slightly altered by contact metamorphism in Riley County which explains the dolomite encased potassium feldspar. Quartzite is apparent within lesser percentages, is more than likely "Silver City" in origin, and derived from Woodson and Wilson counties. Limestone and dolomite fragments are most likely Late Pennsylvanian or Early Permian (270–300 million years ago) in origin but not distinguished from each other as they tend to react similarly in the presence of dilute hydrochloric acid which indicates similar calcium response and therefore a similar effective reactivity with metals. Chert or flint, as known regionally, is a hydrate amorphous silica that occurs along east facing cuestas that form the dominate physical landform of the region, locally termed "The Flint Hills" (Fowler et al., 1935). The Kansas River cuts through the cuestas to transport the chert, sandstone, and

mudstone downstream. Lithology of the pea gravel consisted of a wide array of different geologic strata with multiple depositional environments or formation origins.

2.2. Sample preparation

PRC samples were proportioned using the mixtures specified in Table 2. All mixtures were proportioned to have a designed void content (DVC) of 25%. Fresh concrete was mixed according to ASTM C192/C192M-16a (2016) (ASTM, 2007). Especially when evaluating pollutant removal between mixtures, maintaining identical void content is of utmost importance. In order to achieve identical void contents, the amount of fresh material was determined from the mixture proportions to achieve 25% voids in the 50 mm by 100 mm cylinders. Fresh concrete was weighed within ± 0.1 g and placed in the cylindrical molds using the combination of hand pressing and vibration. The minimum energy and vibration time required to consolidate all of the material into the molds was used to minimize segregation. Specimens were then sealed and placed in a curing chamber (23 °C and 100% relative humidity) for 3 days before demolding. After demolding the samples were placed in an environmental chamber set at standard laboratory conditions (23 °C and 50% relative humidity) until tested with a minimum limit of one week and a maximum hold time of two months.

2.3. Jar testing

Three reagent grade stock solutions were prepared with Type I ASTM D1193-06(2011) (2011) deionized water (18.0 Mega-ohms) and certified ACS quality heavy metal salts (CdCl_2 :142892, PbCl_2 :MKBS4048V, ZnCl_2 :152361) (ASTM, 2006). Three concentrations of 1.00, 0.10, and 0.01 millimolar of cadmium, lead, and zinc were used for jar testing. An additional control solution using DI water alone was also prepared to measure background and residual metals within the testing apparatuses and to account for other laboratory contaminants such as atmospheric lead or residual metals on probes (Caravanos et al., 2006). Control solutions were used to provide quality control for the results obtained during specimen testing. Continuously stirred, batch reactors similar to ASTM C1733 were utilized to ensure available pore space was constantly mixed and in contact with solution (ASTM, 2010). One liter HDPE wide-mouth bottles containing magnetic stir bars were filled with 750 mL of solution and then placed on a magnetic stir table for 72 h. Continuous solution mixing was performed at 500 rpm to provide thorough vortex mixing until equilibrium. Concrete samples were wrapped with nylon thread and suspended in the solution by securing the ends of the thread under the compression seal of the bottle lid to hold the samples within the solution vortex as shown in Fig. 1. For aggregate testing a nylon mesh bag was used to hold an aggregate mass equivalent of one concrete cylinder in a similar shape and position as the concrete samples.

After testing samples were removed and approximately 200 mL of solution from each reactor was acidified with nitric acid as a preservative. Equilibrium concentration of the individual metals was measured by ICP-MS using EPA method 200.8 (Environmental Protection Agency, 1994). Remaining solution was preserved by freezing.

Table 2
Mix designs and proportioning.

Mixture	Cement (kg/m^3)	Fly ash (kg/m^3)	Aggregate (kg/m^3)	Water (kg/m^3)
PC-G	267	0	1462	107
CA-G	200	67	1453	107
PC-L	267	0	1479	107
CA-L	200	67	1469	107
PC-GB	267	0	1395	107
CA-GB	200	67	1386	107



Fig. 1. Jar testing apparatus with aggregate or concrete.

Completed solid materials were wrapped in plastic and dried in the environmental chamber (23 °C and 50% humidity) to suspend any on-going chemical reactions. Each mixture had three replicates for each solution concentration, including the control set, for a total of 12 samples tested per mix or per aggregate. One additional reactor containing stock solution was prepared without concrete or aggregate for each concentration as a reference. The reference also provided a quality control measure to account for systematic contaminants within the experimental design including potential residual metals from the bottles or nylon thread. The reference stock solution was used as the baseline for removal calculations. Final pH and conductivity were measured after the concrete or aggregate specimens were removed.

2.4. Leach testing

Batch leach testing using deionized water (Type I ASTM D1193-06(2011) (2011) water at 18.0 Mega-ohms) was performed on the concrete samples (ASTM, 2006). The purpose of using deionized water was to create similar initial pH conditions as groundwater (pH of 6.0–6.5 S/U) while producing the maximum leaching potential of surface ions sorbed during jar testing. The method was developed after reviewing other standard and regulatory procedures to appropriately reflect anticipated conditions (ASTM, 2004). The batch leach testing method would not be applicable for surface water conditions based on the suitability of leach testing methods performed by Tiwari et al. (2015) for SCMs (Tiwari et al., 2015). Remobilization of metals was expected to be greatest for the highest tested pollutant concentrations; therefore, concrete specimens from the 1.0 mM batch were used. Leaching jar tests were performed identically to the batch jar testing, except 750 mL of DI water was used instead of a solution containing heavy metals. An additional blank solution without a specimen was used as a quality control to account for background metals from the jars or nylon thread. Approximately 200 mL of each sample solution was acidified and tested using EPA 200.8 standard method. Percent recovered for leached metals due to DI mobilization was calculated by dividing the concentration of metals recovered in the solution after 72 h by the total metals removed during initial jar testing.

2.5. Scanning electron microscopy

Precipitates and concrete cross sections of the jar testing samples were analyzed for heavy metals under Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) according to ASTM C1723 to provide a qualitative estimate of physical removal and

chemical distribution of the metals within the precipitates or concrete matrix (ASTM, 2010). Concrete samples were fractured with approximately 1 g of material mounted by double-sided carbon tape onto an imaging peg. Samples were then imaged at both medium and high magnification with a corresponding EDX analysis of the high magnification sample for the relative distribution of elements by location to provide qualitative composition estimates.

3. Results

Average replicate percent removal of heavy metals for each concentration is shown in Fig. 2 with one standard deviation used for error bars. At the highest concentration of 1.0 mM (Fig. 2A), concrete containing pea gravel aggregate (PC-G, CA-G) had the highest removal for all three metals, followed by concrete containing limestone aggregate (PC-L, CA-L), and then concrete containing glass beads (PC-GB, CA-GB). Lead removal at 1.0 mM was comparable for all concrete mixtures except CA-GB. Fly ash did not significantly decrease removal in the concrete mixtures except for CA-GB (fly ash with glass bead aggregate). Removal by aggregate-only samples (limestone or pea gravel) did not have removal with a consistent one-to-one relationship to the concrete counterparts. Between the two aggregate types, limestone had the highest removal and was comparable to PC-G and CA-G (Pea gravel with cement). Pea gravel had comparable removal to CA-GB for zinc and cadmium but increased lead removal similar to PC-GB. Pea gravel as aggregate alone or with cement (PC-GB, CA-GB) did not remove cadmium or zinc well unless combined together in PC-G or CA-G where removal was better than limestone aggregate alone.

At 0.10 mM metal concentration (Fig. 2B), concrete containing glass beads (PC-GB, CA-GB) had the highest removal with nearly 98% for all metals. Lead in CA-GB was an exception and had only 88% removal. Lead removal was comparable between CA-GB, PC-G, CA-G, PC-L, and CA-L at between 80 and 90%. Concrete containing limestone had the lowest removal of zinc and cadmium at the 0.10 mM concentration with between 50 and 60%. Limestone as an aggregate alone had the highest removal for all metals above all the other concrete mixtures, with 98–99%. Pea gravel alone had 90–97% removal and was much more comparable to the concrete with pea gravel mixtures of PC-G, CA-G. Although aggregate alone and cement-coated glass beads (PC-GB, CA-GB) had the highest removal at a 0.10 mM concentration, the combined mixtures of aggregate and cement in PC-G, CA-G, PC-L, and CA-L did not have similarly high removal.

At 0.01 mM (Fig. 2C), aggregate alone (limestone and pea gravel) removed 80–99% of all three metals with limestone consistently removing >98% for lead, cadmium, and zinc. Pea gravel incorporated in portland cement mixture (PC-G) performed with an almost one-to-one removal as pea gravel aggregate alone. Limestone incorporated in concrete (PC-L, CA-L) had 55–90% removal which was significantly lower than removal by limestone aggregate alone. Similar to the phenomenon at 0.1 mM, the 0.01 mM solutions showed high removal when individual

Table 3
Average pH.

Mixture design	Average pH (S/U)
PC-G	11.5
CA-G	11.4
PC-L	11.6
CA-L	11.6
PC-GB	12.2
CA-GB	11.7
Gravel	6.6
Limestone	7.2
Reference	5.6

aggregates or cement-coated glass beads were used, but removal tended to decrease when the materials were combined.

The final pH for each jar test is shown in Table 3. All concrete mixtures had a final pH between 11.5 and 12.0 S/U and the aggregates alone were between 8.5 and 6.0 S/U. Although the reference samples contained only DI water and metal chlorides, residual acid from the metals reduced the initial pH to approximately 5.6 S/U. Since pH for all samples was significantly greater for each jar test, all samples showed some buffering capacity.

Percent metals recovered by DI leaching of the original 1.0 mM specimens are shown in Fig. 3. Notice the y-axis scale has been expanded to observe the low level of leached material. <5% of any metal was recovered from pea gravel or limestone in concrete (PC-G, PC-L, CA-G, CA-L). The highest percent recovered was from individual pea gravel and limestone aggregates. Although initial removal for some concentrations was similar between the concrete and the aggregate specimens, Fig. 3 shows the combination of both aggregate and cement provides more permanent removal than either material individually, with less than half a percent of metals recovered.

Freundlich isotherms for each jar test are shown in Fig. 4. A log scale was used for the x and y axis therefore negative values indicate very small numbers, not leaching. Lead isotherms are linear for all mixes. Zinc and cadmium removal in PC-G and CA-G (Fig. 4A, B) as well as PC-GB and CA-GB (Fig. 4E, F) appear to have a weakly linear relationship, collinear with lead. Zinc and cadmium removal in PC-L and CA-L (Fig. 4C, D) have an upward curvilinear relationship similar to a type III isotherm (Hill, 1949). Isotherms of zinc and cadmium in limestone and gravel (Fig. 4G, H) have a curvilinear relationship to the right corresponding to a standard type I isotherm. Freundlich isotherm variables for each mix design and metal are presented in Table 4.

SEM imaging of a cement coated aggregate piece is presented in Fig. 5–6 to determine the means of transport and ultimate location of metals within the concrete. The bulk material image presented in Fig. 5 shows a cement coated aggregate piece with the viewing area approximately 1 mm in width. EDX was performed on the area to show distribution of zinc, cadmium, and lead. In general, all three metals were well distributed except for the central feature, labeled “A” in the backscatter image.

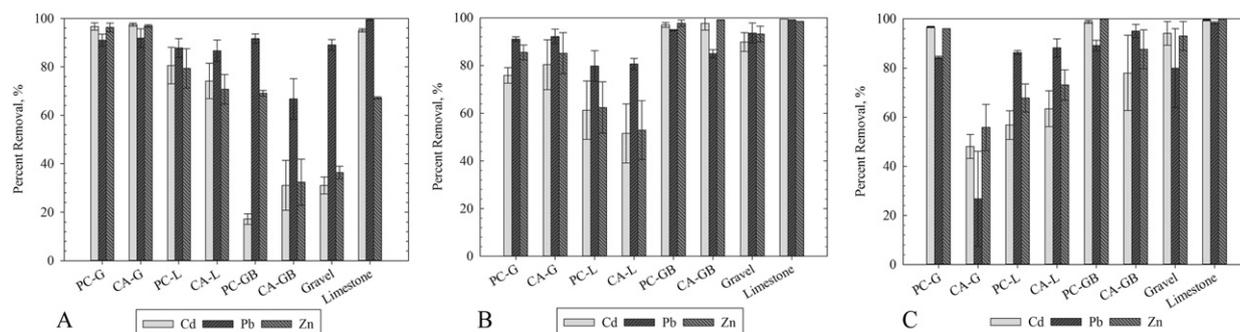


Fig. 2. Percent removal of heavy metals at A) 1.0 mM, B) 0.10 mM, C) 0.01 mM.

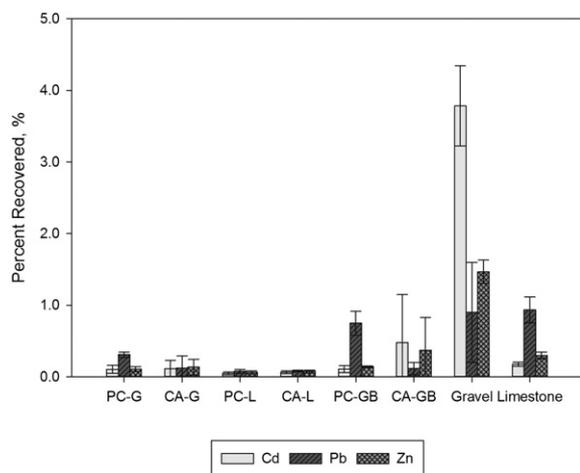


Fig. 3. Percent recovered of heavy metals by DI leaching.

Other white or highlighted areas in the backscatter view indicate higher concentrations of cadmium and zinc, whereas lead is more diffuse. The feature, labeled “A”, is a crack formed in the concrete sample prior to jar testing and is presented in detail in Fig. 6. Higher concentrations of zinc, cadmium, and lead appear near the surface aperture. A mild diffuse gradient is apparent as concentrations reduce to the bulk metal concentrations within 25–50 μm from the center of the crack.

4. Discussion

Removal of metals within PRC is complex with many components and conditions influencing the outcome. Removal occurs through absorption, adsorption, precipitation, coprecipitation, and diffusion. Adsorption, as a fundamental mechanism, is supported by the strong correlations to the linear or type I Freundlich isotherms for the aggregate-only samples (Fig. 4G, H) and limestone aggregate concrete (Fig. 4C, D). Type I response is related to the natural attenuation and saturation of materials to a contaminant (Singh and Prasad, 2015). At low concentrations (Fig. 2C), adsorption is the primary source of removal with limestone aggregate alone having the highest removal followed by cement coated glass beads (PC-GB), cement-coated limestone (PC-G), and then the pea gravel aggregate alone. The aggregate and cement contain available reactive calcium including either calcium carbonate, calcium hydroxide (portlandite), or calcium silica hydrate gel (CSH). CSH and portlandite reactions are especially seen in the reactivity within the crack of cement (Fig. 6). The adsorptive capacity of heavy metals on cement and limestone is known and related to the displacement of calcium ions on the material surface corresponding to the specific surface area (Shively et al., 1986; Xue et al., 2009). Limestone and pea gravel aggregates were tested in the as-received condition to mimic realistic material for application as a PRB. Therefore, aggregate fines (<75 μm) were present and likely the source for removal at lower concentrations in aggregate-only samples (limestone and pea gravel). Any surface fines present during concrete mixing were incorporated into the cement matrix for all concrete samples and may contributed to removal in the bulk cementitious paste. The incorporation of surface fines into cement potentially accounts for the lower removal with PC-L and CA-L as compared to limestone aggregate alone at the medium and low concentrations (Fig. 2B, C). The additional sorption sites present in the aggregate alone samples (limestone, pea gravel) were overwhelmed at the highest concentration of 1.0 mM (Fig. 2A) and can be seen by a reduction of removal in the pea gravel or limestone as compared to the lower concentrations (Fig. 2B, C). For applications as a PRB, the results imply increasing specific surface area for aggregate (especially limestone) would provide higher removal at lower concentrations. With a smaller grain size, long-term removal may be limited as the surface

bound metals could be readily remobilized by pH changes of the influent water (see leach testing Fig. 3) especially if the self-buffering capacity of the limestone is exceeded. The limit of self-buffering is approximately shown in Table 3 as the difference in pH between aggregate and concrete mixtures.

Aggregate bonds also play a major role in adsorption due to their influence on porosity and reactive surface area. Glass beads and smooth gravel would produce the thickest interfacial transition zone with the concrete thereby having the greatest overall reactive surface area as shown by the relatively high adsorption at lower concentrations (Fig. 2B, C). Conversely limestone bonds well with the cement reducing the interfacial transition zone thickness and minimizing aggregate surface reactive sites within the concrete mixture as demonstrated by the lower percent removal at the lowest concentration in Fig. 2C. The adsorption bond is strongly pH dependent as shown by the low permanency of removal onto pea gravel (Fig. 3). In contrast, the combination of limestone aggregate and cement provides the greatest permanency. The self-buffering capacity of the pore solution in cement mixtures would likely minimize pH change and prevent sorbed metals from leaching throughout multiple pore water volumes and at larger scales. Larger standard deviations were observed in pea gravel aggregate specimens (with or without concrete) and may be due to the random distribution of minerals in gravel and the small size of the samples. The large standard deviations represent the importance of chemistry on removal by adsorption and indicate potential scaling concerns for future testing.

Inconsistencies within the glass bead results indicated the nonreactive assumption may be incorrect and necessitated the testing of glass beads as an individual aggregate. Glass bead-only revealed zinc leaching at a constant amount of approximately 0.82 $\mu\text{g/g}$ of glass and average removal of lead to be 5.74 $\mu\text{g/g}$. The glass beads had no influence on the cadmium removal. Glass removal of lead can be explained by simple single layer physiosorption of the positive lead ions to the negative hydroxide ions positioned at the interface between the surface silica and bulk water. The glass beads have a density of 2.52 g/cm^3 and a diameter of 6 mm, giving a surface area of approximately 400 mm^2/g . There is an average of 0.014 μg lead per mm^2 of glass bead surface translating to about 4.20×10^{13} atoms per mm^2 . Standard bond lengths between silica and oxygen, or lead and oxygen ions are well known (Kumpf et al., 2001; Powers et al., 2012). Assuming saturation occurred, a bond length of 154 pm would satisfy the 4.20×10^{13} atoms per mm^2 and is nearly the same as the Si-OH bond length of 164 pm (McCarthy et al., 2008). The discrepancy can be resolved by remembering this calculated length is the distance of the lead atom to the surface and not an actual bond length. Furthermore, the calculated length is an average of all available distances and incorporates all three-dimensional configurations between lead and other atoms. The length of lead to oxygen bond is approximately 221 pm and given standard pyramid configuration with 90 degrees between O-Pb-O, the distance to the surface can be calculated as approximately 157 pm (Trinquier and Hoffmann, 1984). Since no one-to-one relationship between the glass beads as aggregate alone or when incorporated into concrete can be made, no error correction was performed on the percent removal for concrete containing glass beads. Practically, the results indicate the cement paste may have additional zinc removal capacity not demonstrated in the jar testing on glass beads with cement (PC-GB, CA-GB).

At high concentrations, precipitates formed in freely dispersed flocs and were not present at lower concentrations. Therefore, precipitation and co-precipitation are likely the primary initial removal mechanisms at the highest concentrations of metals (1.0 mM). These removal processes are more than likely near-instantaneous as noted by the poorly formed crystal mineralogy present in both the flocs and the surface deposition noted in SEM imagery (Fig. 6). Precipitation and co-precipitation are the primary removal mechanisms in a well understood process typically used in water treatment to remove heavy metals with calcium sources, such as in lime flocculation (Dean et al., 1972). Type III isotherms present in Fig. 4C, D may also support precipitation

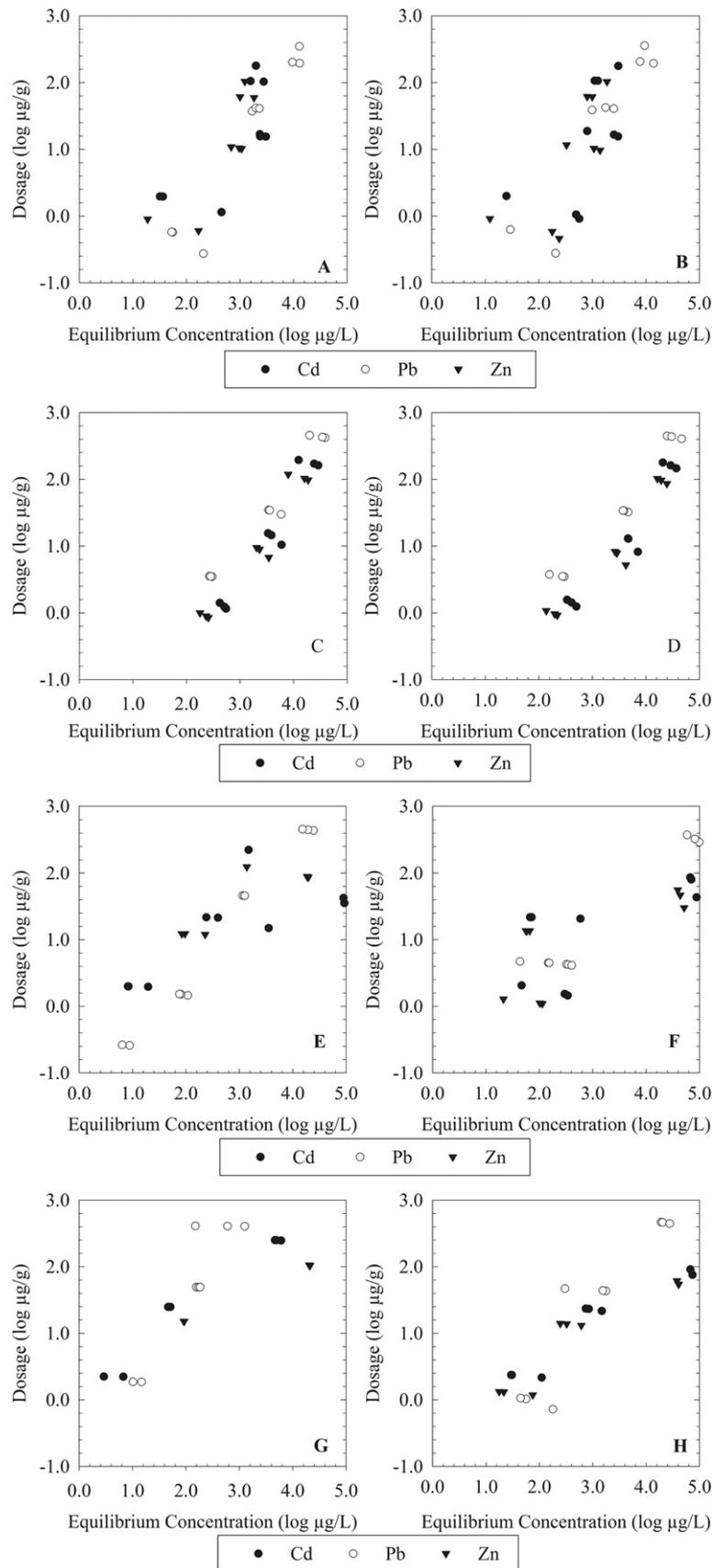


Fig. 4. Freundlich isotherms for: A) PC-G, B) CA-G, C) PC-L, D) CA-L, E) PC-GB, F) CA-GB, G) Limestone, 4 H) Gravel.

Table 4
Freundlich isotherm slope, intercept and R-squared.

Mixture design	Metal	1/n	Log k_f	R ²
PC-G	Cadmium	0.75	−1.00	0.54
	Lead	1.23	−2.61	0.93
	Zinc	0.94	−1.46	0.72
CA-G	Cadmium	0.81	−1.23	0.35
	Lead	1.34	−3.04	0.76
	Zinc	0.97	−1.65	0.52
PC-L	Cadmium	1.26	−3.31	0.94
	Lead	1.01	−1.98	0.97
	Zinc	1.10	−2.67	0.94
CA-L	Cadmium	1.07	−2.73	0.93
	Lead	0.95	−1.74	0.97
	Zinc	0.93	−2.19	0.93
PC-GB	Cadmium	0.34	0.19	0.57
	Lead	1.05	−1.76	0.98
	Zinc	0.40	0.35	0.75
CA-GB	Cadmium	0.35	0.05	0.46
	Lead	0.68	−0.87	0.94
	Zinc	0.35	−0.01	0.52
Limestone	Cadmium	0.62	0.15	0.95
	Lead	1.25	−0.97	0.86
	Zinc	0.36	0.48	1.00
Gravel	Cadmium	0.46	−0.26	0.91
	Lead	1.01	−1.66	0.88
	Zinc	0.49	−0.41	0.88

or co-precipitation as a primary removal mechanism, since an increase in metals from the dosage removed did not drastically increase the equilibrium concentration. The type III curvilinear response is likely due to the solubility limits of all three metals at a high pH and is expressed in Fig. 4C, D by the large increase in dosage (μg of metals removed per g of concrete) with minimal increase to equilibrium concentration (Chuan et al., 1996). Since the solubility of heavy metals decreases with increasing pH, interstitial water within the concrete provides a significant source of alkalinity and self-buffering capacity to cause precipitation in the pore space and then capture those precipitates. Competition for reactive surface sites between ions in free solution is also a well-documented phenomenon; however, with the abundance of calcium sites for nucleation, lead, zinc, or cadmium with calcium in

co-precipitation can readily occur (Lu and Xu, 2009; Mahdavi et al., 2015). Removal at high concentrations does not decrease with changes to calcium content of the mixture, further justifying the likelihood that co-precipitation between metal ions is occurring. Visible evidence of coprecipitation is visible in the concrete crack shown in Fig. 6. Theoretically pore infilling occurred as solution containing the three metals entered and initially reacted with some unhydrated cement. Rapid increases in pH within the pore solution occurred, forcing precipitation and additional reactions, likely including coprecipitation. Precipitates accumulated in the dead-end pore space and then formed a diffuse front into the surrounding cement. In general, this suggests that any locally sourced aggregate may provide removal given sufficient portland cement is used to increase pore pH, and sufficient dead-end pore space is provided, or tortuous pathways to serve as a physical reactive media for precipitation or co-precipitation.

Diffusion into the cement, while not directly measured, can be inferred from the general bulk distribution of metals into the paste (Fig. 5) and by the concentration gradient of zinc, cadmium, and lead into the crack area shown in Fig. 6. Diffusion is also supported by the extremely high permanency of removal for limestone based concrete (Fig. 4C, D). Once heavy metals were removed, only the samples with cement or limestone had <1% recovery. Diffusion and adsorption have been observed for lead and other +2 valence metals when used in waste immobilization with hydrocalumite or calcite (Chrysochoou and Dermatas, 2006; Elzinga and Reeder, 2002; Zhang and Reardon, 2003). Efflorescence of at the surface of pervious concrete systems is indicative of calcium build up along the pore surface as observed in Fig. 5. Metals are then attracted to the surface available calcium where they precipitate or sorb. Accordingly, since not all calcium sites were completely coated with metals, this cement region shown in Fig. 5 may not be fully saturated and additional removal is likely.

In comparison to other materials used in the removal of heavy metals from solution such as activated carbon, PRCs have equal or potentially greater removal. Further isotherm testing is necessary for verification of the type III trend and comparing PRC with carbon isotherms at higher concentrations. Preliminary isotherms provide a benchmark to reference and allow for comparison of existing removal data. They are, however, intended as a best-fit method with potential

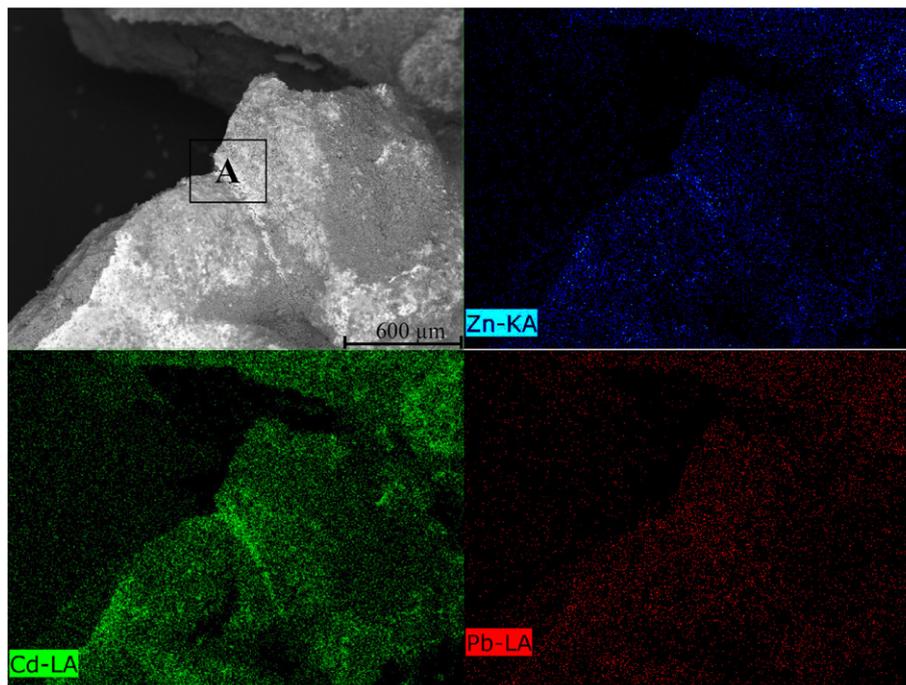


Fig. 5. Concrete coated aggregate piece with SEM and EDX showing metal deposition.

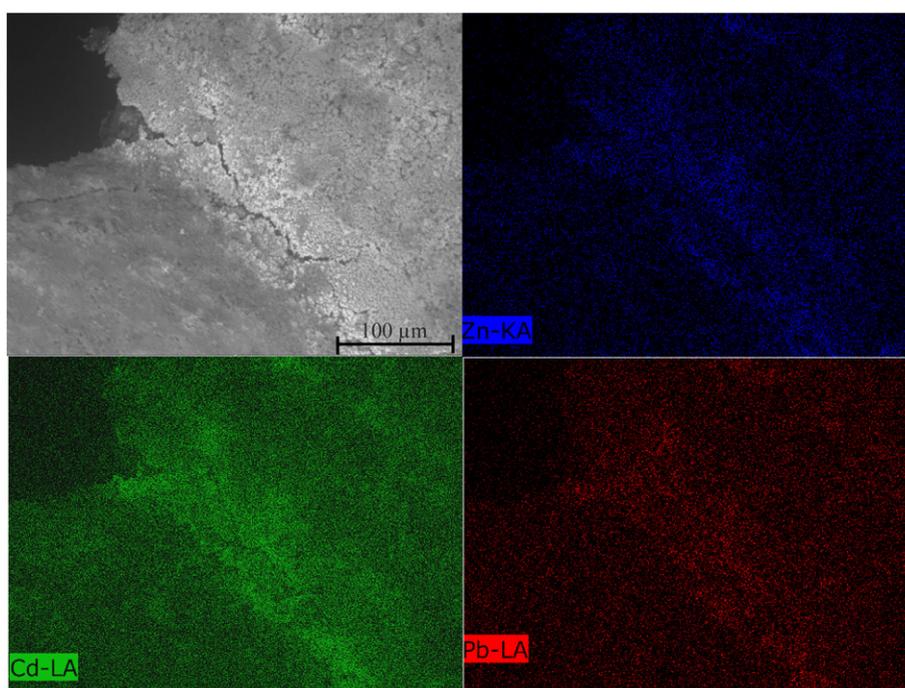


Fig. 6. Crack within cement showing precipitates and diffusion.

thermodynamic implications once kinetics have been investigated. The isotherms from Fig. 4A–F show a linear correlation suggesting that PRC had not approached surface reactivity saturation. When compared to similar dosages of activated carbon over the range of concentrations tested in this study, activated carbon from either commercial or organic sources reactivity would be saturated within this range (Kouakou et al., 2013; Mulligan et al., 2001; Senthil Kumar and Gayathri, 2009). The lack of a plateau within the PRC isotherms also supports the multi-layer deposition, indicating further justification for co-precipitation at the highest concentrations. Typically, adsorption isotherms have a pH dependence; however, removal in PRC or limestone was not adversely affected by the initial solution pH. Previous investigations using synthetic solutions with different initial pHs, showed similar removal for lead, cadmium, or zinc (Ernst et al., 2016; Liu et al., 2005; Sansalone, 1999; Scholz and Grabowiecki, 2007; Solpuker et al., 2014).

The SEM images shown in Figs. 5 and 6 show uniform distribution of heavy metals except around a discontinuity, a crack. The crack was most likely formed either through chemical shrinkage or from the sample demolding process and occurs from the surface into the cement hydration products. Cracks in concrete can exhibit some autogenous healing when exposed to water. As water permeates the crack and reaches the newly exposed unhydrated cement grains, secondary cement hydration commences and is able to fill the crack with new hydration products (Aldea et al., 2000). The secondary hydration follows the same step-wise process as primary hydration which first involves dissolution of calcium ions into solution. When exposed to heavy-metal contaminated solution the crack morphology and chemistry become a preferential zone of deposition which was observed first for cadmium, then zinc, and to a much lesser extent Lead. Some diffusion is shown as the concentration of cadmium and zinc decreases from the center of the crack to the bulk paste.

4.1. Application

One prospective site for application of PRC technology would be zone 4 of the Oronogo-Duenweg Mining Belt, an EPA Superfund site in Jasper County, MO. Contaminants of cadmium, lead, and zinc average to approximately 0.01, 0.016, and 1.6 mg/L, respectively, with

maximums of 0.22, 0.29, and 21.8 mg/L. The overall volume of contamination plume for the confined aquifer is estimated at 6.2 billion L. There are approximately 600 homes and 100–200 wells affected and current remediation techniques will cost \$60–90 million (Environmental Protection Agency, 1990). Although isotherms are essentially a best-fit method and should not be used for calculations beyond the scope of laboratory condition, in lieu of field testing, isotherms may provide a baseline of minimal removal for estimating costs for PRCs as novel technology.

Assuming the total plume volume will be treated with a single method of PRC or aggregate, the total required mass of metals to be treated would be 1300, 1740, and 104,000 kg of cadmium, lead, and zinc, respectively. Freundlich isotherm values from Table 4 and isotherms for commercial (Carbon 1) (Kouakou et al., 2013) or bael tree leaf (Carbon 2) (Senthil Kumar and Gayathri, 2009) sourced activated carbon were used to calculate the approximate mass of material needed to remediate the entire contaminant plume based on current market prices. Approximate market price for concrete, limestone, gravel, and activated carbon per kilogram are approximately \$0.70, \$0.02, \$0.05, and \$4.40, respectively. The metal requiring the maximum amount of material with an estimated corresponding cost is shown in Table 5. Lead is the limiting metal in pea gravel based PRC and cadmium in limestone PRC. The only material providing comparable removal to carbon is limestone aggregate alone and requires ten to one hundred times more material than

Table 5
Cost estimates for remediation of Oronogo-Duenweg Mining Belt.

Mixture design	Metal	Mass (kg)	Cost (\$)
PC-G	Lead	4.12×10^{10}	\$2,700,000,000
CA-G	Lead	8.57×10^{10}	\$5,700,000,000
PC-L	Cadmium	3.56×10^{11}	\$24,000,000,000
CA-L	Cadmium	1.26×10^{11}	\$8,400,000,000
PC-GB	Lead	8.92×10^9	\$590,000,000
CA-GB	Zinc	5.50×10^9	\$360,000,000
Limestone	Zinc	1.65×10^9	\$35,000,000
Gravel	Lead	7.86×10^9	\$390,000,000
Carbon 1	Zinc	4.98×10^7	\$220,000,000
Carbon 2	Lead	3.00×10^7	\$130,000,000

activated carbon; however, limestone is a significantly lower cost material. PRC has the highest cost however breakthrough and other kinetics data not discussed in this study would be required to provide sufficient data for complete lifecycle analysis or full-scale dose measurements. As metals precipitate from solution into the pore space and begin to reduce permeability and increase tortuosity, physical removal of contaminants may increase over time, as well as additional chemical removal not noted in this study. Leaching calcite from the concrete will tend to coat co-precipitates and additionally increase reactive surface sites thereby increasing service life significantly.

5. Conclusions

Removal of lead, cadmium, and zinc by PRC or aggregates is a complex process with removal shown to be largely dependent on the concentration of the contaminant. At high concentrations, the cement hydration products sufficiently alkalinized the water to cause high removal through precipitation. At low concentrations limestone provided the best removal, followed by portland cement-coated glass beads; however, the combination of limestone in cement did not result in comparable high removal. SEM evaluation of the cement and aggregate showed uniform distribution of all metals indicating a large potential for sorption. Some corresponding preference was observed between zinc and cadmium sorption; however, lead was more homogeneously distributed across the entire concrete samples. Diffusion and precipitation was observed within crack generated prior to jar testing, and indicates the significance of concrete reactivity for metal removal from solution. Isotherms for concrete samples indicated saturation did not occur over the considered range, but isotherms of aggregate alone began to approach saturation at the highest concentration. Locally available aggregate, such as pea gravel, could be used with a high level of success since removal and permanency of removal depended only on the use of cement and not on the aggregate material. Pea gravel alone would not be successful as a PRB as leaching may be excessive for lead or cadmium once saturation is reached or self-buffering capacity was exhausted. While a preliminary cost evaluation for materials based on isotherms showed limestone to be the preferred reactive media and PRCs to be more expensive, the actual cost may be significantly less especially with the development of breakthrough models. Additionally, type III isotherm observed for PC-L and CA-L indicated increased removal would require less material as contaminant concentrations increase. More rigorous evaluation of kinetics will establish when saturation is likely to occur and how extensive the type III isotherm depends on pH, especially over the service life of the concrete. Calcium mobilization and diffusion measurements into the cement paste would provide additional information on permanency and long-term removal. As a novel technology, a PRCs or limestone reactive barrier provides the traditional benefits of permeable concrete but designed to optimize the chemical reactivity between the calcium and heavy metals.

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