

Enhancing the Ability of Pervious Concrete to Remove Heavy Metals from Stormwater

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Abstract: Catastrophic release of heavy metals from the King River mine in Colorado and the Minas Gerais dam in Brazil have brought to the forefront the importance of contaminant stabilization and remediation in surface waters. Permeable reactive materials are currently utilized for the remediation of heavy metals and other pollutants by employing reactive media to remove contaminants. This research investigated the use of fly ashes with loss on ignition or sulfur trioxide exceeding ASTM C618 limits to enhance pollutant removal in pervious concrete. The high carbon and sulfur contents of the noncompliant fly ashes provide additional capacity to remove lead, cadmium, and zinc. High-sulfur and high-carbon fly ashes were less effective in metal removal at higher metal concentrations but improved removal at lower concentrations. These results suggest pervious concrete can be designed as an effective remedial technique for use in many infrastructure applications, including beneath permeable pavement, permeable asphalt, revetment, permeable shoulders, gabions for slope stability, mine tailing dams, and emergency surface water cleanup. DOI: 10.1061/JSWBAY.0000823. © 2017 American Society of Civil Engineers.

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Introduction

Pervious Concrete

Pervious concrete is a known and accepted low-impact development (LID) technology with the ability to reduce stormwater volume, improve water quality, and help mitigate urban heat-island effects [American Concrete Institute 522 (ACI 2010); Anderson et al. 2013; Haselbach et al. 2011]. Pervious concrete mixtures utilize open-graded aggregate containing little to no fine aggregate while balancing cementitious binder volume so that only the surface of individual aggregate granules is completely coated, allowing a significant portion (~20%) of permeable voids to remain. Pervious concrete normally contains ordinary portland cement (OPC) and may contain supplementary cementitious materials (SCMs) such as fly ash, slag cement, and silica fume. Cement hydration produces a hardened matrix possessing substantial interconnected macroscale void space capable of rapidly conveying water. Size, distribution, and tortuosity of the pores can be modified to promote physical filtration of contaminants and provide sufficient contact time for passing water to interact with the relatively high pH [>12.0 standard units (S/U)] of the cement paste (ACI 2010; Gerhardts 2005; Komastka et al. 2003). The high specific surface area coupled with tortuous pathways provide a vast array of available sites for physical and chemical reactions to occur. Additionally, hardened concrete contains crystalline and amorphous calcium silicates and calcium aluminosilicates, which compose the

actual hardened structure. These hydration products also possess interconnected microscale pores which provide additional sites for physical and chemical reactions. In conventional concrete the paste microstructure permeability is minimized to limit unwanted ion ingress and chemical attack which may lead to durability distresses (Ababneh et al. 2003; Wang et al. 2014; Williamson and Isgor 2016). Fortunately, the microstructure permeability can be oppositely modified to further increase porosity and thereby sites for removal reactions. Over time some of the calcium leaches from the hydrated structure and/or reacts with carbon dioxide in the air to lower the pH (Komastka et al. 2003). In all but the most extreme conditions, even at older ages pore solution pH remains above 9.0 S/U (Kuang and Sansalone 2011; Morgenroth et al. 2013). The high pH, large surface area, porous microstructure, and high-permeability macrostructure are ideal for using pervious concrete as a water-quality treatment strategy.

This research investigated the use of pervious concrete enhanced for pollutant removal to create permeable reactive concrete. Pervious concrete was produced using OPC and various acceptable and unacceptable fly ashes [according to ASTM C618 (ASTM 2015a)] for the removal of lead, cadmium, and zinc from solution. Bench-scale batch reactor testing was performed to measure removal enhancement and leachability.

History and Use of Pervious Concrete for Water-Quality Improvement

Surface water-quality improvements from pervious concrete have been shown for metals, acids, and nutrients. Conventional pervious concrete has demonstrated 90% removal of zinc and copper and 50% removal of nitrogen, and acid rain (pH 6.7 S/U) has been alkalized to 9.2 S/U (Calkins et al. 2010; Collins et al. 2010; Haselbach et al. 2014; Lee et al. 2014; Luck et al. 2008). While not all surface-water contaminants are in the aqueous phase, suspended solids are well removed by pervious concrete through filtration (Anderson et al. 2013; Kevern 2015; Kevern et al. 2008; Saáudo-Fontaneda et al. 2014). In successive stormwater loading simulations aqueous zinc and copper removal were consistently greater than 90%, indicating substantial capacity for simultaneous

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removal of both metals (Haselbach et al. 2014). Water-quality improvements from pervious concrete interacting with a solution is not limited to surface-water applications but may also be applied below grade when installed as a filter material below other permeable pavements or as permeable reactive barrier (PRB). If pervious concrete can effectively remove metals from solution, then it may offer an efficient technology to replace currently expensive groundwater treatments (e.g., activated carbon) (Erto et al. 2011) or provide a specific method to intercept heavy metals from urban stormwater or industrialized stormwater prior to infiltration to the groundwater.

Current Metals-Treatment Technologies

Current metals-remediation techniques include solidification/encapsulation treatment with activated carbon, resins, or other ion-exchange systems, or installation of reactive materials which passively filtrate water to remove contaminants (USEPA 2013). Such passive filtration systems are made using reactive media such as activated carbon, zero-valent iron, or persulfate and are designed to target and chemically treat specific aqueous contaminants (Mulligan et al. 2001; Paul et al. 2003; Wilkin et al. 2008). While up-front costs of materials and installation of reactive materials are substantial, they are the preferred U.S. Environmental Protection Agency (EPA) remediation method (Hyman and Dupont 2001; USEPA 1998). Most systems are designed to either promote oxidation, which reduces toxicity, or actively sorb contaminants to bind onto a granular media (Dwivedi et al. 2008; Mohan and Singh 2002; Ross et al. 2005; Thiruvengatachari et al. 2008; Watts and Teel 2006).

In theory, pervious concrete may function as a permeable reactive material or passive filtration media through the same mechanisms as traditional systems: (1) sorption, (2) precipitation, and (c) diffusion due to concrete's composition a second step of removal may occur as contaminants diffuse from the surface into the hydrated cement paste-aggregate matrix allowing for additional long term removal (Fig. 1). Instead of being a single-step reactive

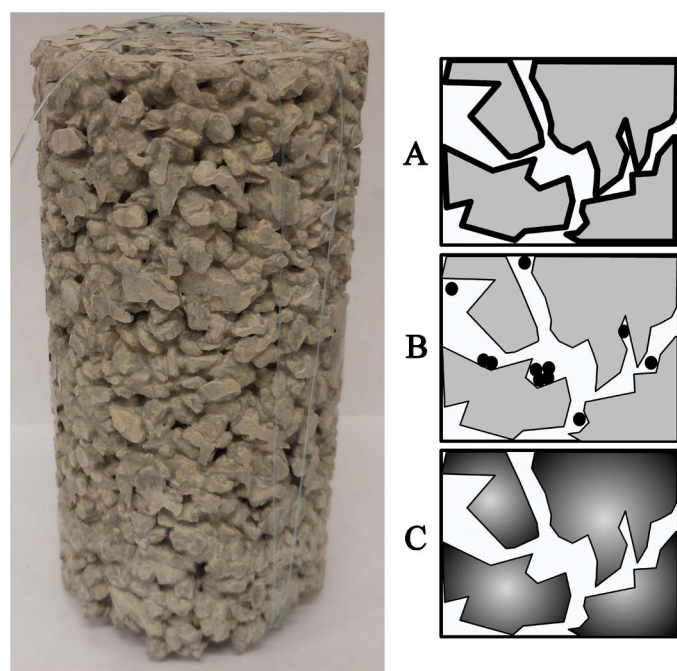


Fig. 1. Mechanisms of removal for pervious reactive concrete (image by Ryan R. Holmes)

filter, cement-based filters first create reducing conditions within the high-pH pore solution capable of lowering the solubility of most heavy metals to promote significant precipitation. Portlandite leaching from the cement paste provides significant sources of colloidal calcium to react and bind with heavy metals or to increase the pH of the pore solution (Mulligan et al. 2001). Similarly, zeolites, crushed concrete, and other alkaline materials have successfully been used to remove heavy metals due to heavy metal insolubility at high pH (9–12 S/U). The precipitated metals are then physically removed through filtering action (Borhade et al. 2015; Coleman et al. 2005; Czurda and Haus 2002; Iqra et al. 2014).

Amendments to Enhance Removal

Sustainable use of concrete includes the use of SCMs to lower the CO₂ footprint associated with Portland cement manufacturing along with diversion of waste from landfills. Recent enforcement of EPA air regulations on emissions for power plants requires upgrades to the best available technologies (BATs) for emission controls of mercury and SO_x. BATs typically inject activated carbon into the production stream to reduce mercury and sulfur dioxide. Fly ashes are then produced with carbon and sulfur in excess of acceptable limits for use in concrete, structural fills, or soil stabilization [Hower et al. 2010; ASTM C618, ASTM C311 (ASTM 2013)]. For both Class F fly ash and Class C fly ash (CA), loss on ignition (carbon content) is limited to a maximum of 6%, and sulfur trioxide to under 5% (ASTM C618). When fly ash containing excessive sulfur is used in soil stabilization or concrete, durability is reduced or heaving may occur due to extensive ettringite formation (Komastka et al. 2003). Carbon levels exceeding 6% in fly ash also deleteriously impact durability by increasing the variability of air entrainment, thereby increasing susceptibility to freeze-thaw failure (Triano and Frantz 1992). These fly ashes are therefore unusable in traditional applications and the majority are landfilled as waste industrial byproducts (USEPA 2016).

Though valorization of potentially landfilled fly ash is limited, fly ash has many applications for water quality as an adsorbent material. ASTM-compliant CA and high-carbon (HC) fly ash have been successful media for removal of contaminants in permeable reactive media applications with minimal leachability (ASTM 2011b; Czurda and Haus 2002; Demirkan et al. 2008, 2014; Graham et al. 1996; Morar et al. 2012; Rostami et al. 2001). Additionally, ASTM-compliant fly ash has been used as an effective adsorption media for industrial wastewater containing zinc and cadmium (Ahmaruzzaman 2010; Weng and Huang 1994). Given the current direction of Clean Air Act regulations for coal-fired power plants, production of fly ashes containing high amounts of carbon and/or sulfur will increase with further restrictions on mercury and sulfur dioxide emissions. Additional research into these fly ashes is needed especially for technologies that take advantage of these otherwise deleterious chemical components in order to valorize this material waste stream. Incorporation of these waste fly ashes into pervious concrete may increase removal capacity.

Methods

Four pervious concrete mixtures were tested to evaluate the dose response effectiveness at removing lead, cadmium, and zinc from solution and the influence of fly ash inclusion/composition. The mixtures were 100% portland cement (PC) and 25% cement replacement with either CA, HC fly ash, or high-sulfur (HS) fly ash. The experimental plan was designed to determine (1) if pervious concrete can remove heavy metals, (2) the level of removal for batch reactors of various initial concentrations of heavy metals

in order to develop an isotherm for comparing effectiveness of removal to other known reactive media, (3) permanency of removal by leaching, and (4) the effectiveness of fly ash with high carbon or sulfur to provide additional removal. Experimental factors included pH of the batch solution and heavy metals concentration to the dose of OPC, fly ash, or a combination.

Materials and Mixture Proportions

A simple pervious concrete mixture which contained limestone coarse aggregate, OPC, and water was used as a baseline. Type I/II OPC conforming to ASTM C150/C150M was used with a Blaine fineness of 373 m²/kg (1,821 ft²/lb) and a Bogue composition of 55% C3S, 17% C2S, 8% C3A, and 10% C4AF (ASTM 2016b; Cao and Kevem 2015). Uniformly graded limestone obtained from the Cedar Valley ledge and mined from Randolph, Missouri was used as coarse aggregate. The nominal maximum size of the aggregate was 9.5 mm (3/8 in.). X-ray diffraction (XRD) results indicated the aggregate was composed primarily of calcite, with quartz and ankerite as minor constituents. The bulk dry specific gravity was 2.65 and the water absorption was 0.9% (ASTM 2015b).

Chemical constituents of the portland cement, fly ashes, and aggregate are shown in Table 1 [ASTM 2016b; ASTM C311, ASTM C25 (2011b)]. No reportable amounts of mercury, lead, cadmium, or zinc were present in the fly ashes prior to testing. Concrete mixture proportions are shown in Table 2. All mixtures were designed for 25% voids and produced with a water:cementitious materials (*w/cm*) ratio of 0.40. Concrete containing only OPC served as the fundamental control mixture. Class C fly ash served as an additional experimental control in order to compare results against mixtures containing naturally occurring HC or HS fly ash.

Analysis

Analysis was performed using Eqs. (1)–(3). Percent recovered was calculated by Eq. (1). Dosage for metals removed per mass of concrete was calculated by Eq. (2) and then used in the subsequent

Freundlich isotherms. Isotherms were calculated by the linearized form of the Freundlich isotherm, Eq. (3)

$$\%L = \frac{(C_e - C_L)}{C_e} \times 100 \quad (1)$$

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

$$\text{Log}Q_e = \text{Log}k_f + \frac{1}{n}\text{Log}C_e \quad (3)$$

Concrete Placement Procedure

Pervious concrete samples were prepared using the mixture proportions specified in Table 2. The mixing procedure, while containing small-sized coarse aggregate, followed ASTM C305 (ASTM 2014). The prepared concrete was placed in 50 × 100 mm (2 × 4 in.) cylindrical molds. Fresh concrete was weighed prior to placement in the molds so that each mold contained a specified mass of concrete ±0.1 grams to achieve exactly 25% void space and was placed in the mold in a single lift. Finally, each mold was vibrated for approximately 20 s using a cushioned impact vibrating table with an operation frequency of 3,600 revolutions per minute (rpm). Specimens were sealed within plastic molds and allowed to cure for 3 days prior to removal. After initial curing was completed, the samples were maintained in a controlled environmental chamber with 50% humidity at 23°C until batch tested.

Batch Jar Testing

Three reagent-grade stock solutions were prepared from Type I ASTM D1193 (ASTM 2011a) deionized (DI) water (18.0 MΩ) thoroughly vortex mixed using high-rpm bench-scale mixing tables with certified American Chemical Society (ACS)-quality reagents (CdCl₂: 142892, PbCl₂: MKBS4048V, ZnCl₂: 152361) (ASTM 2011a). Each stock solution contained uniform concentrations of cadmium, lead, and zinc at concentrations of 1.00, 0.10, and 0.01 mM. Batch testing was performed by suspending cylinders using inert nylon thread and submerging in a 1 L high-density polyethylene (HDPE) wide-mouth bottle with continuously stirred stock solution for 72 h (Fig. 2). All bottles were acid washed in a 5% nitric acid solution for 12 h and rinsed with 3 volumes of DI water prior to testing. Each concrete mixture was tested with three replicates for each stock solution concentration (1.00, 0.10 and 0.01 mM), totaling nine cylinders tested per concrete mixture. Background levels of metals within the concrete, bottles, or nylon thread were accounted for by additional batch testing with a fourth concentration of DI water only. To account for removal by the bottle or nylon thread, one additional stock solution batch reactor was prepared for each concentration as a reference without concrete. Electrical conductivity, pH, and temperature were recorded for each batch reactor at the beginning and end of testing. After 72 h, the concrete cylinders were removed from solution, allowed to drip dry, loosely cover with cellulose-based plastic wrap, and permitted to dry in the environmental chamber at 50% humidity at 23°C to prevent cracking and preserve surface reactions. Immediately after the cylinders were removed from the testing solution, 200 mL of solution from each jar was acidified with 1 mL of 18.8% nitric acid and sent to a certified environmental lab for inductively coupled plasma mass spectrometry (ICP-MS) testing using EPA Method 200.8 for residual metals concentrations (USEPA 1994). The remaining solution was frozen to preserve samples in the event that repeated testing was necessary.

Table 1. Chemical Composition of Pervious Concrete Components

Item	OPC	CA	HC	HS	Limestone
SiO ₂ (%)	20.49	40.71	31.09	18.82	4.32
Al ₂ O ₃ (%)	4.26	18.99	17.03	7.97	0.61
Fe ₂ O ₃ (%)	3.14	6.05	4.22	5.43	0.18
CaO (%)	63.48	20.10	30.51	25.74	52.47
MgO (%)	2.11	4.82	3.31	3.65	1.33
SO ₃ (%)	2.90	0.83	8.43	9.89	—
Na ₂ O (%)	0.18	1.46	0.86	5.44	<1
K ₂ O (%)	0.47	0.65	0.50	—	<1
CO ₂ (%)	1.48	—	—	—	—
CaCO ₃ (%)	0	0	0	0	92.60
LOI (%)	2.20	0.08	6.84	5.23	—
Specific gravity	3.15	2.69	2.51	2.39	2.65

Table 2. Design of Mixtures

Mixture	Portland cement [kg/m ³ (lb/yd ³)]	Fly ash [kg/m ³ (lb/yd ³)]	Aggregate [kg/m ³ (lb/yd ³)]	Water [kg/m ³ (lb/yd ³)]
PC	270 (450)	—	1,480 (2,495)	110 (180)
CA	200 (340)	65 (115)	1,480 (2,480)	110 (180)
HC	200 (340)	65 (115)	1,470 (2,470)	110 (180)
HS	200 (340)	65 (115)	1,460 (2,465)	110 (180)

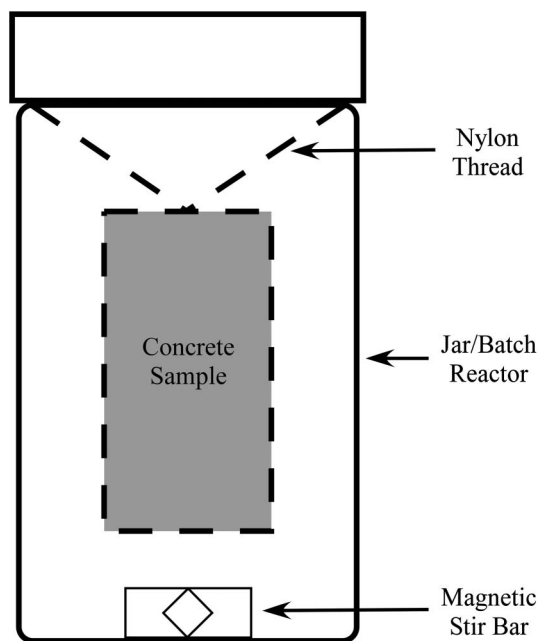


Fig. 2. Batch reactor setup

Leach Testing

Batch leach testing was performed on samples from each mixture previously batch tested in the 1.00 mM heavy metals solution to quantify removal as permanent, semi-permanent, or reversible. Type I ASTM D1193 DI water (18.0 M Ω) batch leach testing was selected over toxicity characteristic leaching procedure (TCLP) as a simplified research method with the intended purpose of determining the maximum desorption potential to leach available surface or free ions weakly bonded or sorbed during batch testing. This method was developed after reviewing other standard and regulatory procedures to appropriately reflect anticipated conditions (ASTM 2011a, 2014). Concrete specimens from the highest (1.0 mM) heavy metal solution were selected as most likely to have the greatest available surface and/or free ions. Cylinders were submerged using inert nylon thread and suspended in 750 mL of continuously mixed DI water for 72 h in acid-washed soda-lime glass jars. As with the batch jar testing, to control for background metal

levels a blank solution using DI water and nylon thread was prepared for each leach testing group of samples. Approximately 200 mL of each sample solution was acidified in 0.1% nitric acid and sent to a certified environmental lab for ICP-MS for heavy metal testing using EPA Method 200.8 (USEPA 1994).

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used as a qualitative approach to determine if removal was permanent and to determine where the metals were sorbed within the complex matrix. Precipitates formed during batch testing and the concrete matrix from the jar tests were both investigated using SEM according to ASTM C1723 (ASTM 2016a). One sample of residual solution from each of the concentrations was filtered and desiccated for at least 24 h before blotting with double-sided carbon tape to affix the precipitate crystals for analysis. Concrete samples were fractured into roughly 10 $\times$ 10 mm pieces and affixed with carbon tape onto a mounting peg for imaging. Samples were then imaged at low magnifications to evaluate regional distributions and at high magnifications at points of interest, such as unique crystal formations and/or metal deposits.

Results and Discussion

Percent removal of individual heavy metals from solution is shown in Fig. 3 and grouped by initial concentration. Each histogram bar represents the average of three replicates with one standard deviation as error bars. In general, all mixtures showed high levels of metals removal. At 1.0 mM concentrations [Fig. 3(a)], comparable removal of all metals is shown for PC, CA, and HS fly ash; however, HC fly ash removed less cadmium and zinc but demonstrated comparable removal of lead. HC fly ash similarly removed less cadmium at 0.1 mM [Fig. 3(b)] than the other three mixtures, but all mixtures removed comparable levels of zinc and lead. At 0.01 mM [Fig. 3(c)] both HS and HC fly ashes demonstrated comparable or higher removal of lead, cadmium, and zinc than the control. Removal did not appear to be pH dependent, because all batch reactors with concrete had a pH between 11.4 and 12.4 S/U as shown in Table 3 and did not vary largely with initial metal concentrations. When comparing three concentrations within a mixture, less removal occurred at the 0.1 mM concentration for all mixtures.

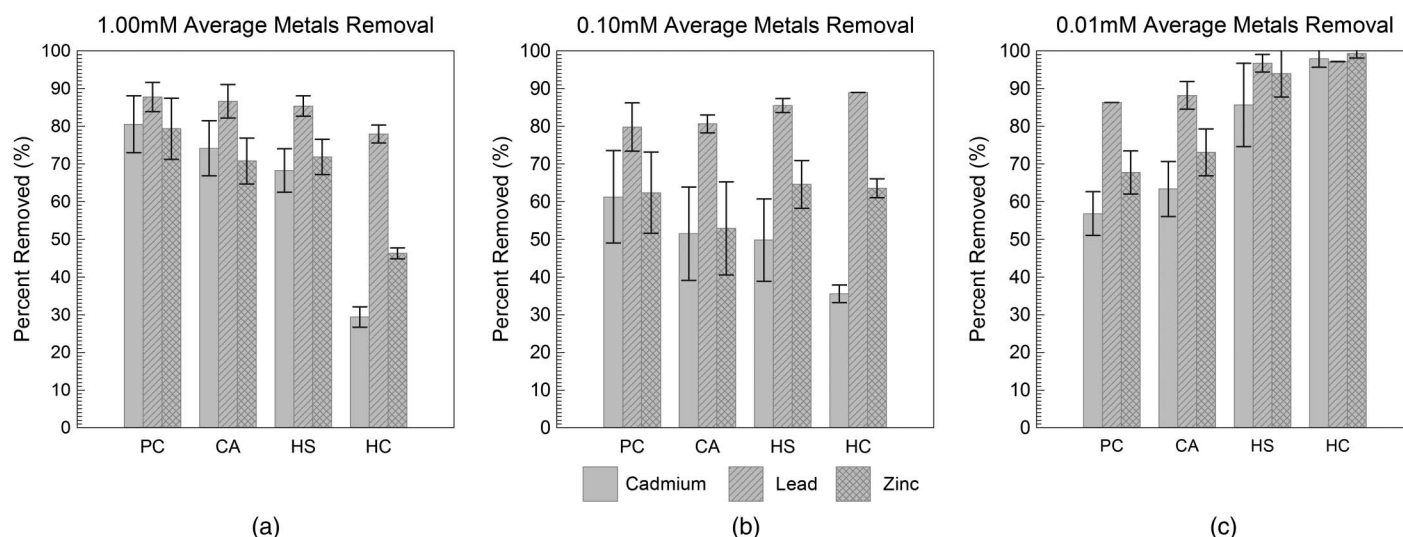


Fig. 3. Percent removal at (a) 1.0 mM; (b) 0.1 mM; (c) 0.01 mM

Table 3. Average Final pH

Mixture	Average final pH, S/U
PC	11.5
CA	11.4
HS	11.9
HC	12.4
Stock	7.5

Expected behavior and visual observation helps provide an explanation of removal mechanisms. At the lowest concentration of 0.01 mM, adsorption into the hydrated cement paste is the primary removal mechanism as the metals are drawn toward the calcium ions in the unhydrated cement, followed by precipitation within the pore structure. The solution remained completely clear and free of precipitates throughout testing. At the highest concentration adsorption remained a mechanism, but the samples quickly became coated with a large quantity of loosely attached precipitates forming like snowflakes in the solution of the 1.0 mM specimens (Fig. 4). Precipitates accumulated on the pervious concrete structure and more loosely within the large void spaces. At the high concentration, precipitation and coprecipitation likely dominated. Precipitates were quickly destroyed during removal of the concrete from the jars, which also indicates that the structures were formed rapidly with weak internal bonding as opposed to strong crystalline bonds formed over a longer timeframe. However, at the intermediate concentration (0.1 mM) no precipitates were observed, again indicating that the adsorption removal pathway dominated. Although total removal in terms of mass was higher in the 0.10 mM solutions, the percent removal was lower due to the limited surface reaction sites. Precipitates formed during reduction then can be physically removed within the tortuous voids and dead-end pore space in a similar fashion to suspended solids removal within permeable concrete systems (Deo et al. 2010; Haselbach et al. 2006; Kevern 2015). Cement paste is highly porous at the mesoscale and microscale, which provides the void space for physical removal and high specific surface area (Lafhaj et al. 2006; Neithalath 2006).

**Fig. 4.** Heavy metal precipitate deposition on concrete in batch reactor (image by Ryan R. Holmes)

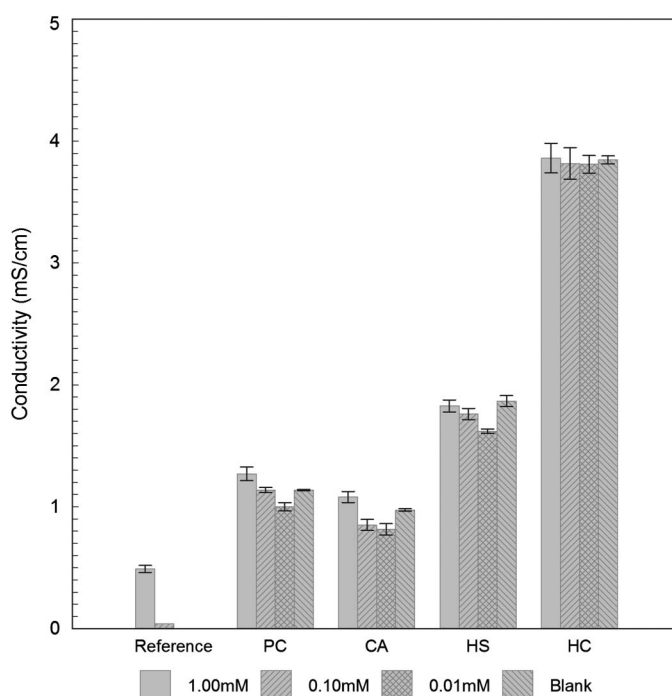
Accordingly, residual dissolved metals may adsorb to the concrete surface or potentially migrate from the pore space by diffusion to the internal concrete matrix, resulting in high metals removal.

Percent removal also indicates sulfur and activated carbon do not contribute greatly to the reactivity of the bulk cement paste, and potential sorption abilities therefore are quickly overwhelmed by other removal mechanisms. Additional evidence for this assertion can be observed from the HS and HC results, which had the highest removal at 0.01 mM, likely the result of the additional sorption sites from the sulfates or activated carbon. This may potentially also be a physical transport phenomenon because the fly ash may provide additional micropores, thereby increasing the sorption sites, but which may easily foul, as indicated by the low sorption at 1.0 mM. Because reactivity may be ion dependent, conductivity could provide a useful metric to estimate which mechanism(s) may provide the greatest removal. No direct correlation was observed between either electrical conductivity or pH and percent removal. However, higher electrical conductivity was shown for HS and HC in Fig. 5 for all concentrations, indicating additional dissolved ions from these concrete specimens.

Average percent recovered after a single rinse with DI water is shown in Fig. 6 as calculated by Eq. (1). Heavy metals recovered were less than 0.30% of the initial stock solution, indicating a high level of permanent removal for sorbed metals; this does not include precipitated flocs. HS and HC demonstrated higher leaching of lead than the OPC and CA controls, indicating a possible reversible sorption mechanism and furthering the initial hypothesis that there may be additional adsorption sites present from which additional metals could leach.

Estimating Dose

Freundlich isotherm relationships for each of the mix designs were prepared and are presented in Fig. 7 to compare standard dose between each mixture. Equilibrium concentrations are plotted on the horizontal axis in log micrograms per liter; the vertical axis is the

**Fig. 5.** Final conductivity of jar test samples

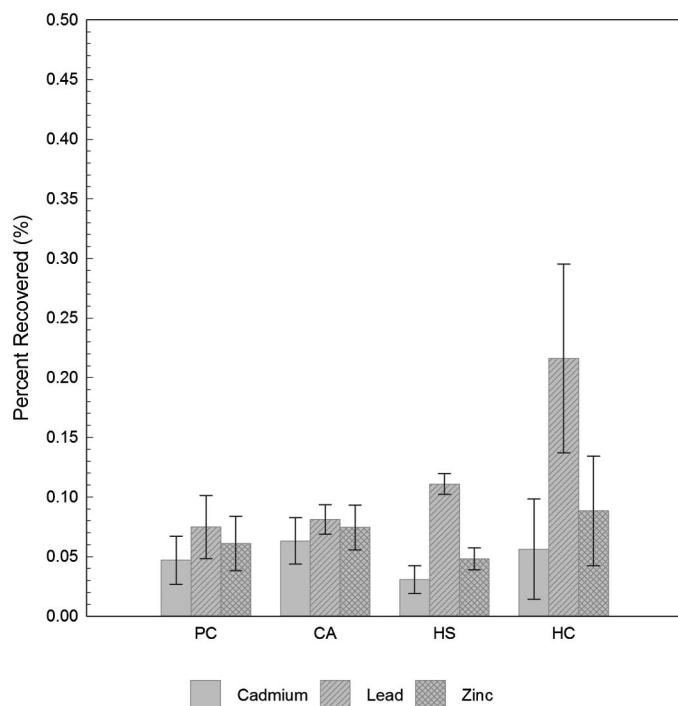


Fig. 6. Percent of mobilized metals after column leach testing

mass of heavy metals removed per mass of concrete in micrograms per gram, as described by Eq. (2).

As fit using Eq. (3), the Freundlich exponents indicate linear or curvilinear up relationships for all mixtures with values for the Freundlich constants presented in Table 4. Fundamentally, the isotherms are a method of determining a best-fit equation for the sorption data. The slope of a Freundlich isotherm theoretically describes the deposition of the adsorbate onto the adsorbent and the intercept describes the minimum removal (Weber and DiGiano 1996). Practically, this means that the lower the intercept, the lower will be the residual adsorbate, and the steeper the slope, the less adsorbent will be a material required to remove the same amount of adsorbate. Typically, three types of isotherm depending on the Freundlich exponent n are prevalent—linear ($n = 1$), curvilinear up ($n > 1$), and curvilinear to the right ($n < 1$) (Toth 2002). The heterogeneity factor n relates to the strength of the sorption bond, with the strongest being $n > 1$ for constant C_e and k_f values.

Slopes for PC and CA are mostly linear and approximately equal for each corresponding metal and have similar intercepts. HS and HC have much lower $1/n$ values and correspond to lower removal levels at high concentrations. For all samples, lead had a strong linear correlation, indicating a reversible but preferred bond. Zinc had a weaker linear relationship, but cadmium in HS and HC had the most curvature, indicating the weakest bond strength of the three metals, which was also reflected in the lower percent removal of cadmium at higher concentrations for these two mixtures. The

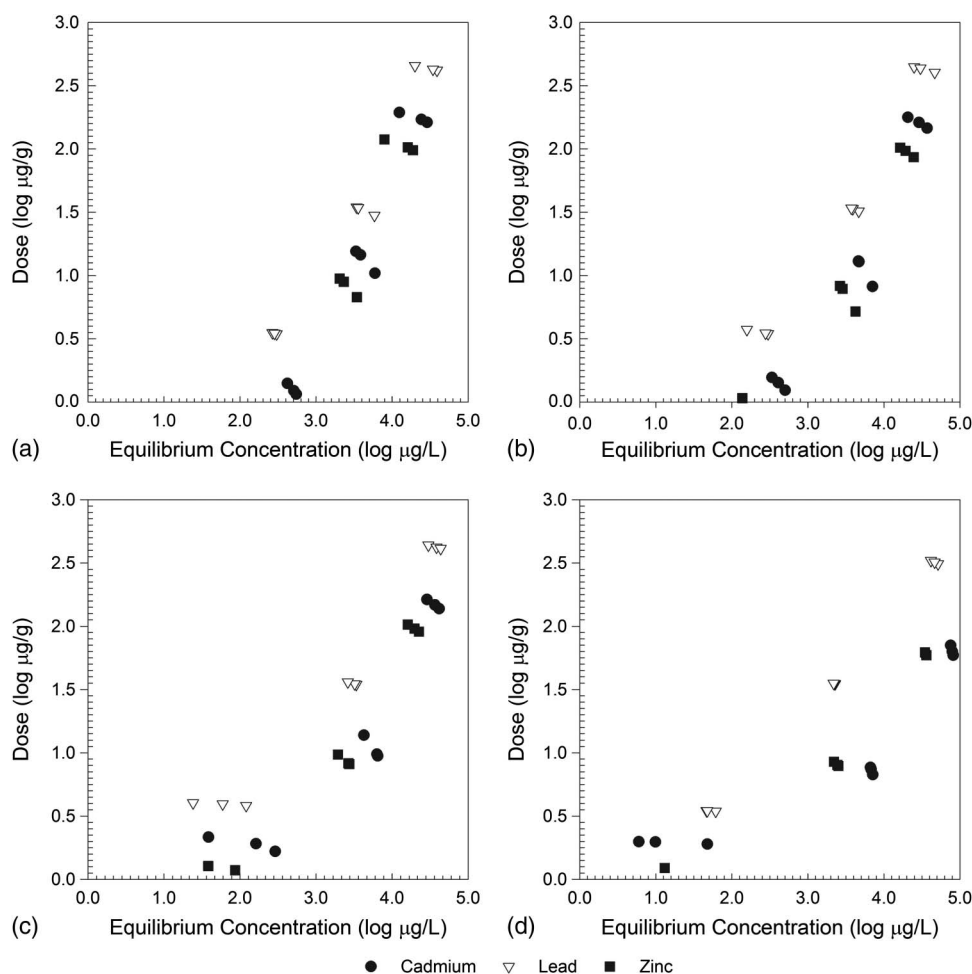
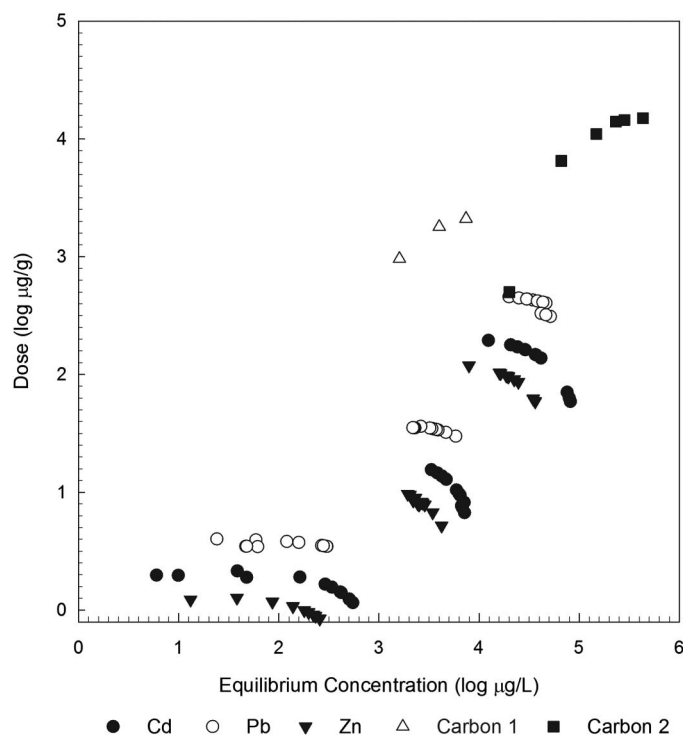


Fig. 7. Freundlich isotherms for (a) PC; (b) CA; (c) HS; (d) HC

Table 4. Freundlich Isotherm Equation Constants

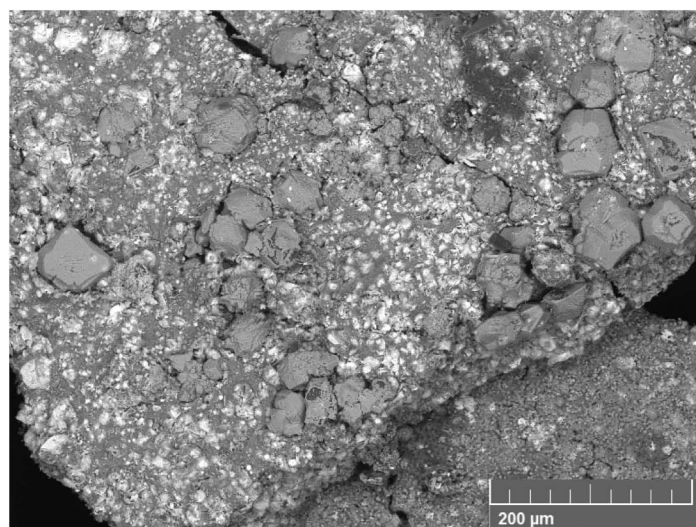
Mixture	Metal	1/n	Log k_f	R^2
PC	Cd	1.26	-3.31	0.94
	Pb	1.01	-1.98	0.97
	Zn	1.10	-2.67	0.94
CA	Cd	1.07	-2.73	0.93
	Pb	0.95	-1.74	0.97
	Zn	0.93	-2.19	0.93
HS	Cd	0.68	-1.20	0.84
	Pb	0.69	-0.66	0.95
	Zn	0.73	-1.30	0.93
HC	Cd	0.36	-0.20	0.84
	Pb	0.66	-0.62	1.00
	Zn	0.51	-0.65	0.94

**Fig. 8.** Combined Freundlich isotherm with activated carbon data

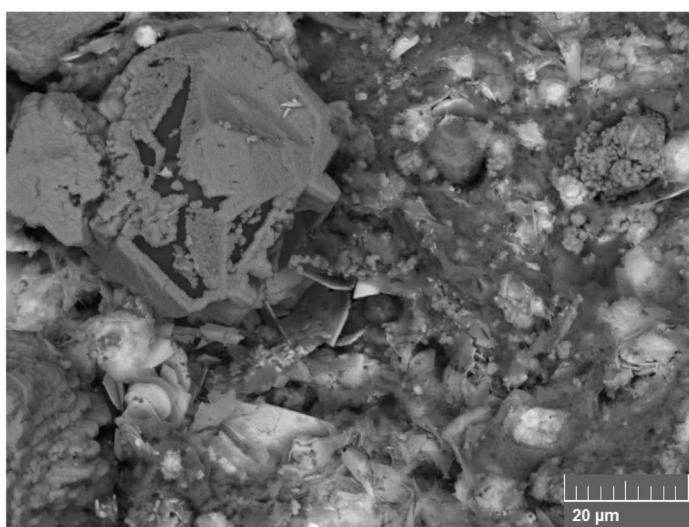
HS and HC fly ashes had the lowest $\log k_f$ values, indicating the highest capacity for sorption of any of the mixtures, especially HC for cadmium, which further reinforces that the HC and HS fly ashes have additional sorption sites. A combined plot of all isotherm data for all mixtures is shown in Fig. 8, including zinc adsorbed onto activated carbon (Carbon 1) (Kouakou et al. 2013) and lead adsorption by activated carbon (Carbon 2) produced from bael tree leaf (Kumar et al. 2009). Lead adsorption had one constant process throughout all mixtures, but cadmium and zinc had one or more removal reactions or transport mechanisms that influenced the slope/bond strength. Comparing any investigated pervious concrete mixture with activated carbon in the literature, the activated carbon clearly needed less material to sorb equal or greater amounts of zinc, but lead removal is comparable with activated carbon from bael tree leaf, although the bond is less permanent.

Sorption Mechanisms

Figs. 9–12 show SEM backscatter emission images of precipitates formed in the highest-concentration (1.0 mM) heavy metal solution for each mixture. Multiple forms of precipitates were formed with crystalline and amorphous components irrespective of mixture. Primary precipitates describe the general conglomerate of different precipitates that were most common and appeared to be mostly crystalline. Alternative precipitates describe a second type of cluster which formed less frequently and was more amorphous. Both groups of precipitates show a wide variety of crystal morphology, precipitation, and coprecipitation of all three metals. Example images from CA are shown in Fig. 9 for primary precipitates and Fig. 10 for alternative precipitates. Energy dispersive X-ray spectroscopy (EDS) analysis was performed on all images to provide qualitative analysis of the regional chemical composition. The white regions in Figs. 9 and 10 are high in lead, which formed semi-planar hexagonal plates or localized amorphous scales. Cadmium-zinc coprecipitates were a common feature, as seen in the top left corner of Fig. 9(b) which shows a calcium crystal with an outer coating of a cadmium-zinc-rich layer and a calcium core, as indicated by the color differences in the cracks in the surface of the large (40 µm) crystal. Selective displacement for surface calcium ions is expected and has previously been shown for zinc and cadmium (Elzinga and Reeder 2002; Papadopoulos and Rowell 1988). In general, zinc and lead were evenly dispersed throughout the



(a)



(b)

Fig. 9. Low and high magnification of primary precipitates (images by Ryan R. Holmes)

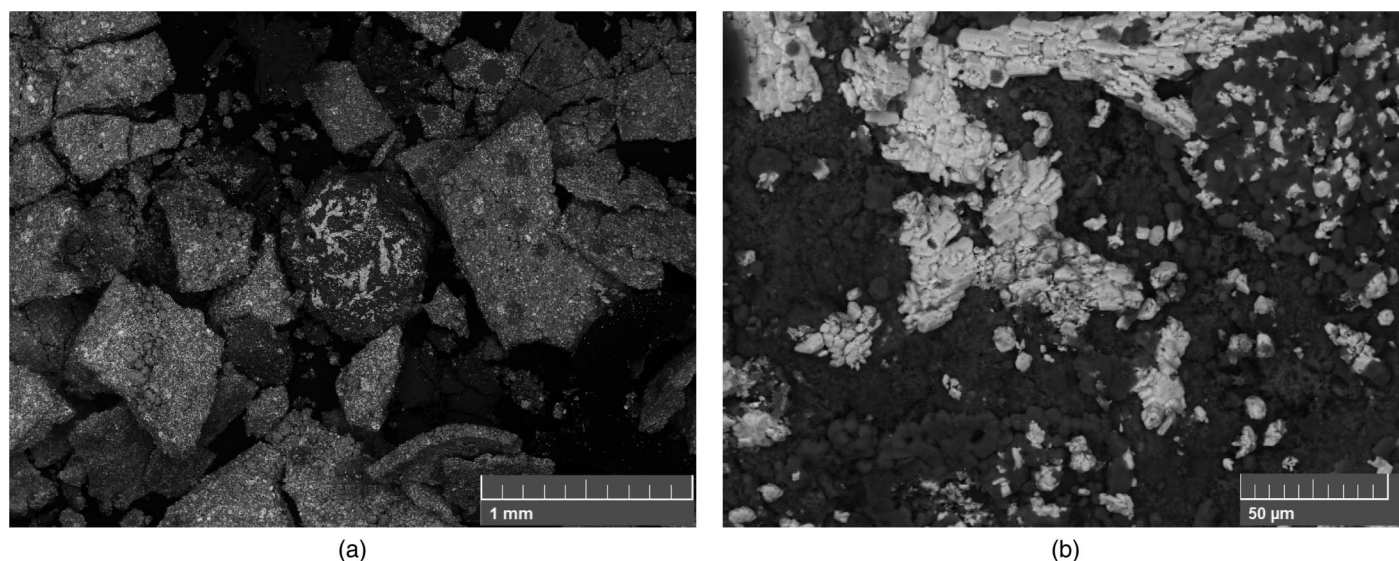


Fig. 10. Low and high magnification of alternate precipitates (images by Ryan R. Holmes)

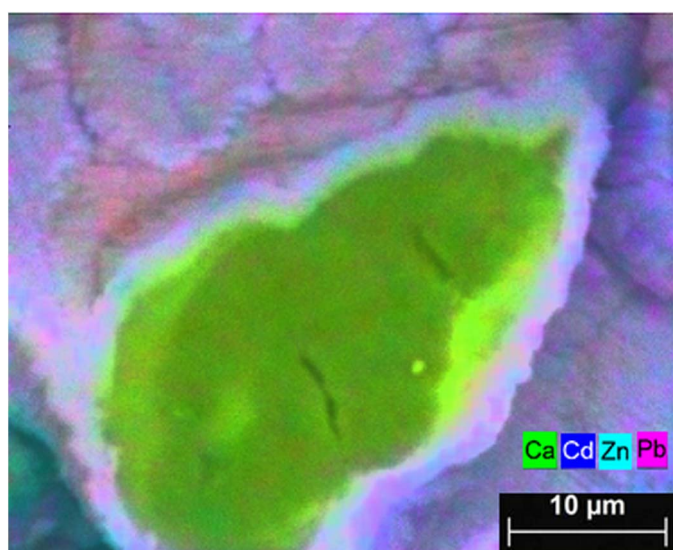


Fig. 11. Aggregate cross section showing heavy metal penetration (image by Ryan R. Holmes)

precipitates, with zinc being the most uniform because it readily nucleated in the lead or cadmium zones. Lead and cadmium were competitively precipitated with zinc and were self-nucleating, as shown by the clear zoning of each precipitate type. The composition of the cadmium rosettes was not fully observed because diffusion of the cadmium ions into the calcium core was below the EDS detectable limit of 0.03 wt%. A calcium core was observed in some fractured crystals, surrounded by a cadmium-zinc coating or layer 1–2 microns thick. In Fig. 10(b) the darker zones are primarily calcium with small amounts of zinc.

A fractured limestone coarse-aggregate cross section is shown in Fig. 11. The aggregate has a central core of calcium and an outer coating of cadmium-zinc-lead precipitates. The EDS analysis observed diffusion of lead and zinc into the calcium carbonate core, with lead being the primary diffuse layer, followed by zinc. Similar diffusion is noted in the literature, where lead was removed by coating carbonate soils in lead, cadmium, and copper diffused into cement kiln dust (Mercier et al. 2001; El Zayat et al. 2015). Cadmium

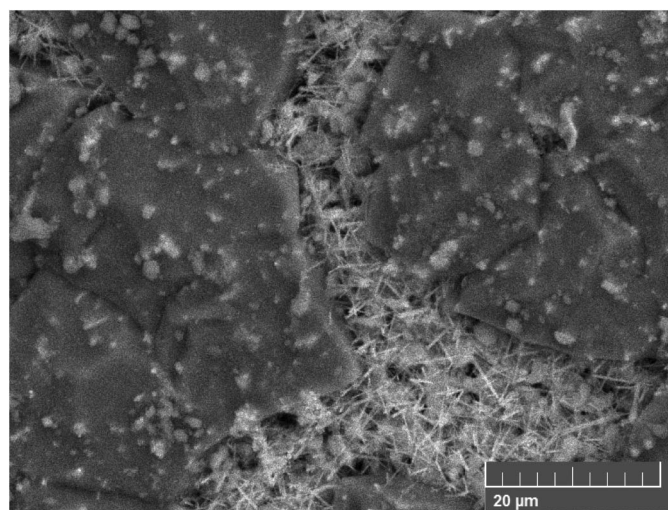


Fig. 12. Lead calcium crystals trapped in ettringite (image by Ryan R. Holmes)

occurred only on the surface and most likely precipitated readily with the available calcium and zinc surface sites. Observable lead diffusion into the aggregate core combined with the high removal rates during jar testing indicated substantially higher long-term capacity of removal of lead and zinc than isotherm calculations would initially suggest. Migration of metals through the cementitious paste into calcium carbonate-based aggregates also suggests that long-term removal may be higher than results from jar testing alone. Leaching of lead, cadmium, or zinc was measured and found to be minimal. Leaching will likely remain limited for the long term as long as the pH remains above 7.5 S/U, which is consistent with prior research into leachability of zinc and other trace metals from fly ash or recycled concrete aggregate (Chen et al. 2012; Morar et al. 2012).

When samples were cut using a water-cooled saw, only trace heavy metals were found on the concrete surface. This is largely attributed to the destruction of weak bonding of these highly concentrated surface precipitates to the limestone or cement paste during cutting. However, for one sample, lead-calcium precipitates

were observed entrapped by, or grown on, needle-like ettringite crystals in the pore space of the hydrated cement paste. As seen in Fig. 12, at least at young ages, ettringite or other intermediate hydration products when present may provide additional tortuosity and physical filtration within the permeable matrix or may add an additional source of nucleation sites (Janneck et al. 2012).

Application and Implication of Laboratory Results

Recent catastrophic environmental events from mine-tailing wastes and mining residuals in Colorado, U.S. and Minas Gerais, Brazil bring to the forefront the importance of managing toxins associated with existing and historic mining and active industrial stormwater runoff. Dam breaches conveyed water carrying toxins including lead, chromium, arsenic, zinc, cadmium, copper, and mercury (RCRA 7 metals), which are harmful to human health at the lowest doses and have relatively high mobility within groundwater (Bradl 2004; Mulligan et al. 2001; Xue et al. 2009). Lead, cadmium, and zinc are the most common contaminants for local groundwater (excluding lithological sources) from historic mining and active mining stormwater NPDES permits in Missouri (Missouri Department of Natural Resources 2012).

For demonstrative purposes, one prospective site for application of this technology would be Zone 4 of the Oronogo-Duenweg Mining Belt, an EPA Superfund site in Jasper County, Missouri. Chat and mining waste from the mining belts throughout the Midwest were commonly given away as fill material for home construction for the towns where support staff lived, and to the farmers in the surrounding area to increase soil pH. This was especially true in Southwest and Central Missouri. These materials leached heavy metals-laden stormwater for decades, infiltrating into the soil and forming a groundwater plume containing heavy metals that contaminated the area's drinking water. For the purposes of this paper, an analysis was performed to determine if pervious concrete could remove the equivalent mass of heavy metals in the regional aquifer conveyed by stormwater over decades of exposure and then compared the cost against the selected remedial intervention (activated carbon). Contaminants of cadmium, lead, and zinc average about 0.01, 0.016, and 1.6 mg/L, respectively, with maximums of 0.22, 0.29, and 21.8 mg/L, respectively (USEPA 1990). The overall volume of the contamination plume for this aquifer is estimated at 6.2 billion liters (1.63 billion gallons). Approximately 600 homes and 100–200 wells are affected, and current remediation will cost \$60 million to \$90 million. Although isotherms are essentially a best-fit method and generally should not be used for calculations beyond the scope of the experiment, in lieu of field testing they have been used for initial cost estimating. The total plume volume is assumed to be treated with a single mixture of pervious concrete or activated carbon (Kumar et al. 2009) presented in Column 1 of Table 4. The required remediation level was assumed to meet current EPA drinking water standards for lead (0.015 mg/L), cadmium (0.005 mg/L), and zinc (2,000 mg/L). The total costs to reduce contaminants in Zone 4 of Oronogo-Duenweg Mining Belt are shown in Table 5. Cost estimates are based on current U.S. estimates of \$110 per metric ton (\$100 per ton) of OPC and CA concrete, \$83 per metric ton (\$75 per ton) for concrete with 25% replacement by the HC or HS fly ash, and \$5.50 per kilogram (\$2.50 per pound) for activated carbon (ITRC 2011). Based on these assumptions and using removal efficiency determined from short-term jar testing, which is conservative for removal, pervious concretes made from HS or HC have a similar or significantly reduced cost for treatment compared with activated carbon. Using HS or HC fly ashes in this way also valorizes an otherwise waste material.

Table 5. Estimated Costs for Remediation

Mix design	Metal	Estimated cost
PC3	Cd	\$26,000,000,000.00
	Pb	\$1,200,000,000.00
	Zn	\$290,000,000.00
CA3	Cd	\$9,300,000,000.00
	Pb	\$790,000,000.00
	Zn	\$420,000,000.00
HS3	Cd	\$390,000,000.00
	Pb	\$89,000,000.00
	Zn	\$230,000,000.00
HC3	Cd	\$65,000,000.00
	Pb	\$86,000,000.00
	Zn	\$330,000,000.00
Carbon 1	Zn	\$270,000,000.00
Carbon 2	Pb	\$170,000,000.00

Heavy metals exist in urban stormwater and are present in almost every aspect of human existence. From washing of tires, painted structures, exhaust from vehicles, asphalt, combustion of fuel, dust from parking, and recreational land use such as by all-terrain vehicles, heavy metals are washed from surface water to subsurface water, which can eventually impact public health and the environment. In-ground permeable reactive filter systems have been proposed previously to treat contaminated urban stormwater (Reddy et al. 2014); however, no single filter material has been proven to remove all metals to the maximum extent needed to maintain public health safety and prevent groundwater contaminant (Reddy et al. 2014; Reddy 2013; Feng et al. 2012; Seelsaen et al. 2006). The literature suggests that in order to obtain optimal removal rates a variety of materials such as calcite, zeolite, sand, and iron should be combined to create a permeable inorganic filter material, but no mechanism or technology has yet been able to do so. The drawback of the technology presented in this study is that in order to maximize potential reaction sites, the durability of the concrete becomes substantially impacted. If enhanced pervious concrete is placed beneath another permeable layer, then any material can be incorporated within it, such as HS or HC waste fly ashes, without the durability concerns. Enhanced pervious concrete applications are then capable of removing cadmium, lead, and zinc at levels comparable to the best available technology.

Conclusions

Heavy metal contamination of urban and industrial stormwater, and therefore groundwater, is prevalent and persistent. The research presented herein describes the development of pervious concrete enhanced by waste materials for removal of heavy metals from aqueous systems. Results from this novel system indicate overall removal of cadmium, lead, and zinc to be comparable to or better than conventional systems (USEPA 1998). No other permeable reactive system provides such comprehensive removal which remediates by both pH and sorption and then buffers the effluent to alkalize most acidic conditions. Removal rates were extremely high: normal conditions would fall within the 0.01–0.1 mM level due to solubility limits of metals close to 1.0 mM. At low concentrations adsorption was the major removal mechanism; however, precipitation dominates at high concentration. Additionally, migration of metals into the carbonate aggregate further increases removal capacity. Lead had the highest removal, followed by zinc and cadmium, due to preferential coprecipitation and adsorption sites within the concrete matrix. Samples containing fly ash with naturally occurring HC content had the highest removal of

cadmium and zinc at the lowest concentration of heavy metals (0.01 mM). At the middle concentration (0.1 mM) significant differences between mixtures were observed. At the high concentration (1.0 mM) the HC fly ash mixture did not remove as much cadmium and zinc as the other mixtures. The precipitates were partially crystalline or crystal dependent, corresponding to low desorption of contaminants, which was also supported by the limited mobility observed through DI leaching. The reversibility is likely pH dependent; however, concrete has been shown to have strongly alkaline pore water pH even at older ages. As shown by the Freundlich isotherms, adsorption dose was equal to or lower than for activated carbon over the range of concentrations. Mixtures containing HC or HS fly ashes had additional sorption sites based on the curvilinear isotherm; additional research will be required to determine the additional removal mechanisms. The control mixture which contained only OPC provided the best removal for all metals.

No correlation between percent removal and conductivity was observed because the free calcium ions from the concrete completely overwhelmed the signal from the original heavy metal concentrations and any other displaced ions. Consequently, conductivity is not an appropriate test for evaluating removal performance of these systems. Cadmium and zinc preferentially coated calcium crystals, pointing in part to crystallographic compatibility or selectivity between cadmium, zinc, and calcium. Further investigation is required to evaluate if displacement of calcium ions or multilayered adsorption was occurring. Sulfur did not play a significant chemical role in the removal of heavy metals in the precipitates; however, the formation of needle-like ettringite crystals in the paste and micropores can increase tortuosity and potentially increase physical removal. In the proposed application, HC and HS fly ashes provided comparable or lower costs for remediation compared with activated carbon.

Future research should include an evaluation of kinetics and rate constants for bulk remediation of enhanced pervious concrete by breakthrough testing because the Freundlich isotherms do not clearly establish where saturation will occur and may not accurately represent bulk removal by precipitation. Other investigations should include the contact-time parameters, multiple load cycling, and multiple leach cycles after full saturation is reached. A comparison of leaching protocols would also be appropriate for final establishment of this technology as a future industrial product for remediation.

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Notation

The following symbols are used in this paper:

- C_e = metal concentration at equilibrium ($\mu\text{g/L}$);
- C_i = metal concentration at equilibrium ($\mu\text{g/L}$);
- C_L = metal concentration of leachate ($\mu\text{g/L}$);
- k_f = sorption capacity ($\mu\text{g/L}$);
- m = mass of concrete (g);
- n = heterogeneity factor;
- Q_e = amount of metal sorbed per unit mass ($\mu\text{g metals/g concrete}$);

V = volume of solution (L); and

$\%L$ = percentage of metals recovered by leaching.

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