LONGTERM METAL SORPTION IN PERVIOUS CONCRETE WITH ORDINARY PORTLAND CEMENT AND FLY ASH

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ABSTRACT

Pervious concrete is a potential stormwater best management practice. This study investigated the dissolved zinc and copper removal efficiency of pervious concrete made with ordinary portland cement and fly ash, and initiated evaluations into its metals' removal service life. Concentrated zinc and copper solutions were dripped onto the tops of pervious concrete cylinders in a series of accelerated aging events at a rate of 76 mm/hr. Percent mass retained removal efficiencies initially were ~60% and increased to ~80% for copper and 70% for zinc after approximately 15 equivalent years of accelerated metal loadings based on regions with 1020 mm annual rainfall. Cylinders were further tested with zinc and copper concentrations typical of highway runoff at approximately 7.5 and 12 equivalent years of accelerated metal loadings. Removal ranged from 77 to 87% for copper and 80 to 91 % for zinc for typical concentrations. Pervious concrete may be effective for stormwater quality control of dissolved zinc and copper, and therefore provide associated life cycle assessment benefits during its use stage. Further investigations are needed to evaluate metals' removal service lives beyond those already evaluated, but it is promising that this might extend to the pavement's life.

INTRODUCTION

Stormwater runoff from urbanized areas and roadways contains many contaminants *(1,2)*. Of particular concern for some receiving waters are elevated levels of dissolved metals such as zinc and copper which predominantly come from tires and brakes in vehicles respectively. Zinc has been shown to impact amphibians, and copper may impact the sensory systems of some species of fish such as salmon *(3,4)*. Stormwater runoff can be controlled and treated by many best management practices (BMPs) *(5)*. One developing BMP is pervious concrete, which is a type of pavement that allows water to pass through to water storage and detention or infiltration layers beneath. Pervious concrete systems have been shown to reduce many pollutants from stormwater runoff including zinc and copper. The pervious concrete pavement systems can filter particulates which may contain zinc and copper, and in addition dissolved metals may be substantially reduced *(6-8)*. These dissolved metals could be removed via sorption to material in the various layers of the pervious concrete system or the soils below, but recent research has shown that the pervious concrete layer itself has a large capacity for reduction of dissolved zinc and copper *(9)*. The mechanisms for removal of zinc and copper within the pervious concrete layer include complexation with and sorption to the hydroxide and carbonate species typical of hydrated ordinary portland cement (OPC), with subsequent diffusion into the matrix of pores within the concrete. Enhanced treatment for zinc and copper by pervious concrete may be important for applications of pavements near receiving waters to reduce the need for additional BMPs or treatment components prior to discharge, possibly reducing costs and decreasing the need for additional land for stormwater quality control. An example are ports and other intermodal marine facilities, where in addition to vehicle sources of copper and zinc there may be other facility sources such as zinc in galvanized fencing *(10)*. These facilities typically have limited space for additional treatment facilities, and pervious concrete systems or pervious concrete overlays in paved areas may be effective and economical solutions. In addition, in order to evaluate life cycle efficacy of the system, information is needed into the service life of pervious concrete for metals removal.

Pervious concrete is typically made with ordinary portland cement (OPC), narrowly graded aggregate, controlled portions of water, and various admixtures to improve workability and performance. It is also common to replace some of the OPC with supplementary cementitious materials (SCMs) such as fly ash (FA) in order to provide a more sustainable product *(11)*. The study by Haselbach et al. provided information on the efficacy of pervious concrete for dissolved zinc and copper removal when made with OPC without SCMs *(9).* The focus was on OPC since it contains significant amounts of calcium which are in hydroxide and carbonate forms that readily complex with the ionic zinc and copper species *(12)*. Pervious concrete containing fly ash may have slightly lower amounts of calcium in the hydrated paste since fly ash typically has fewer calcium species than OPC *(11)*. Even so, it is hypothesized that pervious concrete made with OPC and fly ash will still be very effective as a BMP for dissolved zinc and copper removal due to the large amounts of calcium hydroxide and carbonate species still remaining. In addition, it is hypothesized that the metals removal service life of pervious concrete with or without fly ash will extend many years, perhaps past the typical life of the pavement.

The objective of this research was to determine the impact of adding fly ash to pervious concrete on the efficacy and service life with respect to removing zinc and copper from stormwater. Pervious concrete samples made with cementitious materials containing 75% by mass OPC and 25% by mass fly ash (OPC/FA) were loaded with solutions containing extremely high levels of dissolved zinc and copper to simulate years of use (accelerated aging). In addition, a subset of the samples was tested with typical stormwater solutions (typical performance testing) after accelerated aging. These results were compared with the results of the OPC samples from Haselbach et al. *(9)*. Both studies were concurrent and followed the same methodologies.

METHODOLOGY

Highly concentrated metal solutions were applied to pervious concrete cylinders in the laboratory and both influent and effluent concentrations and volumes were measured to determine the mass loadings of the metals for this simulation of long-term use (accelerated aging). These applications of highly concentrated metal solutions are herein referred to as events. The events were at least 12 hours apart to allow for partial evaporation of some of the retained water in between similar to frequent precipitation cycles. To test removal efficiency at typical stormwater concentrations after accelerated aging, typical stormwater concentrations of zinc and copper were applied at two different times to one of the cylinders.

Preparation of Pervious Concrete Cylinders

The pervious concrete cylinders were selected from a large set of cylinders prepared in the Washington State University (WSU) Laboratories in 2008. The OPC/FA cylinders were made with narrowly graded #8 basalt aggregate, water at an approximately 0.30 water to cementitious-material mass ratio, and a mixture of ordinary portland cement with 25% by mass class F fly ash. When prepared, the fresh concrete in the cylindrical molds had been compacted from the top approximately 10% of their depth to simulate field surface compaction methods. The molds were then capped and the cylinders left for at least seven days to cure, after which the cylinders were removed from their molds.

The cylinders had been previously used for infiltration and pH testing using deionized and tap water *(13)*. Afterwards, they had been exposed in the laboratory to atmosphere conditions for several years and therefore were assumed to be partially carbonated particularly in the surface areas, typical of concrete in use *(14)*. All the cylinders were 102 mm (4 in.) in diameter and approximately 185 mm (7.3 in.) in depth.

Just prior to testing for metal sorption in 2012, the cylinders were re-evaluated for porosity using ASTM c1754 *(15)*. After metal sorption testing the cylinders were also evaluated for surface infiltration using a modified ASTM c1701, with one liter of water for each test due to the smaller surface area of the cylinders than the field single ring application *(16)*. Table 1 provides a listing of the six cylinders (labeled with a WD identification) used for the OPC/FA tests with their corresponding porosities and surface infiltration rates. Also provided are similar details for the comparative OPC cylinders (labeled with a WB identification) from Haselbach et al. *(9)*. Noted in Table 1 are the cylinders from each set which received typical concentration performance testing after 15 accelerated aging events, and the ones which received the same performance testing after 24 accelerated aging events. In order to perform the metal tests, each of the cylinders was wrapped with shrinkwrap along the sides to prevent water from passing through the sides and to make a column-like sample for testing. In all the tests, water was applied to the open top (compacted top) and allowed to drain through the open bottom.

Table 1: Pervious Concrete Samples Material Characteristics
[OPC data from Haselbach et al. *(9)*]

Specimen ID	Porosity (%)	Infiltration Rate (cm/hr)
WD03*	24.3	4,090
WD06	24.2	3,980
WD08	24.0	3,650
WD11	24.4	3,890
WD15^	23.8	3,820
WD16	24.0	3,900
Average WD (OPC/FA)	24.1 ± 0.2	3,890 ± 150
WB01	24.7	3,540
WB07	24.4	3,500
WB10*	24.8	3,870
WB11^	25.4	4,510
WB12	25.4	2,890
WB18	25.5	4,210
Average WB (OPC)	25.0 ± 0.5	3,750 ±570

* Received typical metal loading performance testing after 15 accelerated events.
^Received typical metal loading performance testing after 24 accelerated events.

Preparation of Solutions

All of the metal solutions were prepared by mixing a highly concentrated stock solution of dissolved zinc and copper with a synthetic rainwater solution. The synthetic rainwater was based on rain samples taken at the Hanford, WA site (Flury, unpublished data). It was made by adding 0.002472 mg of NaCl, 0.000336 mg of $NaHCO_3$, 0.003923 mg of KNO_3, 0.0003 mg of $KHCO_3$, and 0.0003 mg of $CaCO_3$ to one liter of deionized water. The synthetic rainwater was then left open to the atmosphere to equilibrate with the carbon dioxide in the air which resulted in a pH around 6.4. The metal stock solution contained 8 mg/L of copper and 40 mg/L of zinc from dissolving cupric chloride dihydrate and zinc chloride in deionized water.

The solutions for accelerated aging and for typical concentration performance testing were prepared by mixing metal stock with the synthetic rainwater solution. For the accelerated aging solution the levels ranged around 4,700 ppb and 800 ppb for dissolved zinc and copper respectively, while for the typical concentration simulated stormwater, the levels ranged between 100-200 ppb and 16-35 ppb for zinc and copper respectively *(1)*. (Note that it is difficult to prepare identical simulated stormwater solutions with such low zinc and copper concentrations due to laboratory errors compounding from very small volumes of stock solutions needing to be added for each test. Therefore actual concentrations were subsequently measured and also reported. Although variable, the results still provide information that supports the hypotheses.)

A composite sample of influent and a composite sample of effluent were analyzed for dissolved zinc and copper. For the accelerated aging events samples composited for each event for each type of cylinder of both the total influent and total effluent were analyzed. For the performance testing, samples were extracted from the total influent for each event and from the total effluent individually for each cylinder. Sample bottle preparation and sample handling followed standard methods *(17)*. The samples were analyzed using an Agilent Technologies 7700 Series Inductive Coupled Plasma – Mass Spectrometer (ICP-MS).

Accelerated Aging

Each accelerated aging event was performed by dripping 100 mL (6.1 in^3) of the accelerated aging solution onto the tops of each cylinder at a rate of approximately 10 mL (0.61 in^3) per minute. Effluent continued to be collected for at least 10 minutes after application, which allowed for dripping to slow significantly. The volume of effluent was always substantially less than the volume applied, usually around 30% less, as much of the solution remained in the cylinder and the water evaporated and/or was partially stored after events. Between events, the cylinders were allowed to dry for at least 12 hours in a warm (less than 50°C) oven. (Although the drying times varied, this is not expected to impact the interpretation of the results, as the measured influent and effluent concentration and volume data for each event provided sufficient information to estimate the metal uptake.)

The equivalent years of life for the 30 accelerated aging events will vary by the amounts of precipitation, pollutant loadings, catchment areas for additional runon, and other characteristics of the particular region and application. The calculations herein were based on applications such as parking lots or perhaps for an overlay on a trestle with only direct rainfall and no additional runon, and with a typical annual rainfall of 1020 mm (40 in.). The accelerated aging event influent metal concentrations were approximately forty times typical concentrations, so when considering only metal loading (not the water volumes), each concentrated event of 12.7 mm (½ in.) of water would represent approximately forty times the loading for metals or the equivalent of 508 mm (20 in.) of direct precipitation. Thus, each accelerated aging event represents approximately a half year of metal loading, based on the metal masses in the influent. This simplifies the conversion from number of events to number of years as a half year per event, or 7.5 years at the end of 15 events, 12 years at the end of 24 events and 15 years at the end of 30 events. These estimates of aging in years can be modified for other regions and applications by similarly using the typical metal concentrations in the stormwater and the volume of direct precipitation and runon expected in the system and relating these metal masses to the metal mass loadings in the experimental setup. (Regardless of the concentrations and volumes chosen for the accelerated aging events or their interpretation, the methodology still provides information into the relative performance of the two types of pervious concrete compared in the results section.)

Typical Performance Testing

The typical performance tests consisted of applying 100 mL (6.1 in^3) of the typical metal concentration stormwater solution to the top of each cylinder at a rate of approximately 10 mL (0.61 in^3) per minute. This might be representative of approximately 13 mm (½ in.) of runon for a peak portion of a storm at 76 mm/hr (3 in/hr). Storm intensity may vary with the contributing catchment area of the particular application, and the intensity, duration and frequency of storms in various regions of the country. Similar to the accelerated aging events, effluent was collected for at least 10 minutes after application, and the cylinders were allowed to partially dry between applications. Each cylinder had the typical performance test repeated three times in succession. Since the performance tests occurred after 15 and 24 accelerated aging events, they are labeled as 15-1, 15-2, and 15-3 for the first set, and 24-1, 24-2, and 24-3 for the later set.

RESULTS

The results from the testing on the OPC/FA cylinders are first presented. This is followed by a comparison of the OPC/FA results to OPC cylinders without fly ash in Haselbach et al. *(9)*. The OPC cylinders were similarly prepared and aged but without the fly ash, and tested concurrently with the OPC/FA cylinders in the same laboratory and by the same operators.

Pervious Concrete with 25% Fly Ash (OPC/FA) Results

The OPC/FA cylinders had significant amounts of metals retained during the 30 accelerated aging events as depicted in Figure 1. The percent mass retained was calculated using a mass balance with the influent and effluent mass calculated with concentration and volume. Note that some of the retention may have been due to physical capture, evaporation and precipitation of the solution within some of the tortuous interconnected channels in the pervious concrete, in addition to the sorption mechanism. During these tests, the removal efficiencies increased as the metal loading increased, particularly for copper. Since there were no significant differences in volumes retained over the course of the accelerated aging portion of the research, these changes are assumed to not be due to physical processes such as capture in the connected flow channels of the pervious concrete. Instead, this improvement is assumed to be due to a series of chemical removal mechanisms such as surface sorption and/or complexation within the connected flow channels of the pervious concrete, and then diffusion into the porous mortar with subsequent interior sorption and/or complexation, providing for initially covered sites in the channels to become available again.

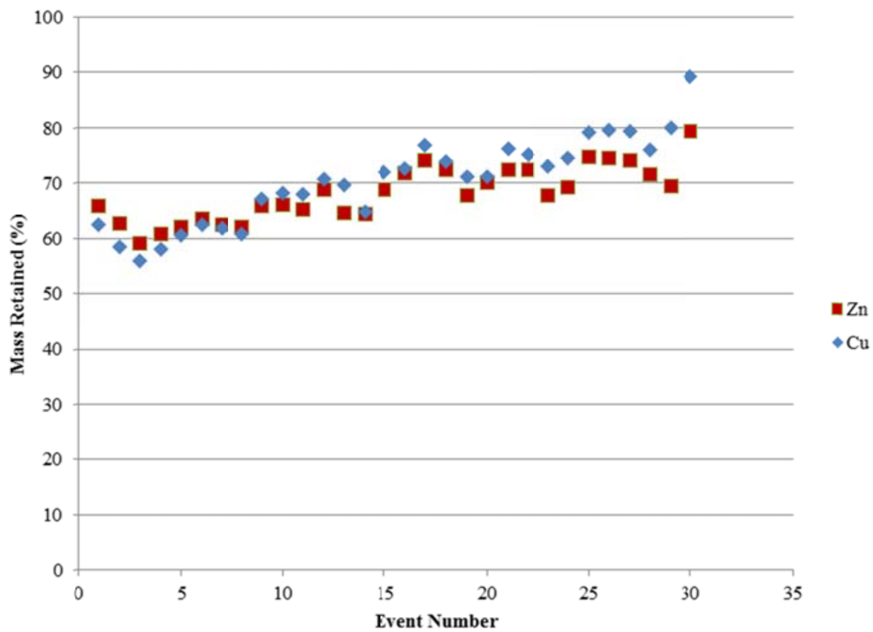

Figure 1: Average mass percent retained in OPC/FA cylinders during accelerated aging.

After 15 accelerated aging events one OPC/FA cylinder (WD03) underwent typical metal concentration performance testing. The influent and effluent concentrations for the three consecutive performance tests are listed in Table 2. Table 2 also has the results of the typical metal concentration performance testing for the OPC/FA cylinder (WD15) performed after 24 accelerated aging events, and comparable data from the OPC research *(9).*

Table 2: Results from Typical Metal Loading Performance Test
[OPC data from Haselbach et al. *(9)*]

After Accelerated Event - Run	Zinc Influent (ppb)	Zinc OPC Effluent (ppb)	Zinc OPC/FA Effluent (ppb)	Copper Influent (ppb)	Copper OPC Effluent (ppb)	Copper OPC/FA Effluent (ppb)
15-1	134	18	19	22	4	4
15-2	217	21	23	35	5	5
15-3	99	10	20	17	3	3
Average		16.3 ± 5.7	20.7 ± 2.1		4.0 ± 1.0	4.0 ± 1.0
24-1	118	11	11	19	3	3
24-2	107	21	17	18	4	4
24-3	101	13	16	16	3	4
Average		15.0 ± 5.3	14.7 ± 3.2		3.3 ± 0.6	3.7 ± 0.6

Percent concentration decrease is another form of evaluating removal efficiencies in BMPs and is based on the influent and effluent concentrations only; it does not include the additional masses removed due to physical capture of some of the influent. The percent concentration decrease versus influent concentration for these six performance tests for copper and zinc are depicted in Figures 2 and 3 respectively. The percent decrease in concentration was substantial, from 77 to 86% for the copper and from 80 to 91% for the zinc. A slight trend of increased removal at the higher influent concentration can be seen for the copper, which is expected as the influent concentrations for copper are extremely low. Very low concentrations tend to have lower percent removal. However, with the limited data and also the aging involved this is not conclusive.

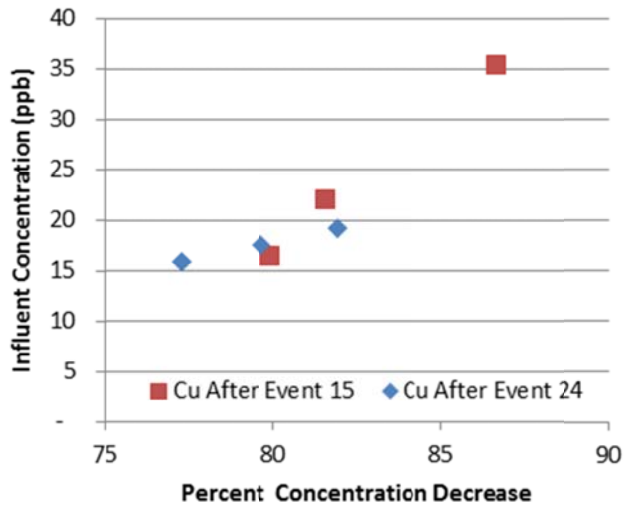

Figure 2: Percent concentration decrease of copper for typical loading performance tests in the OPC/FA cylinders after accelerated loading.

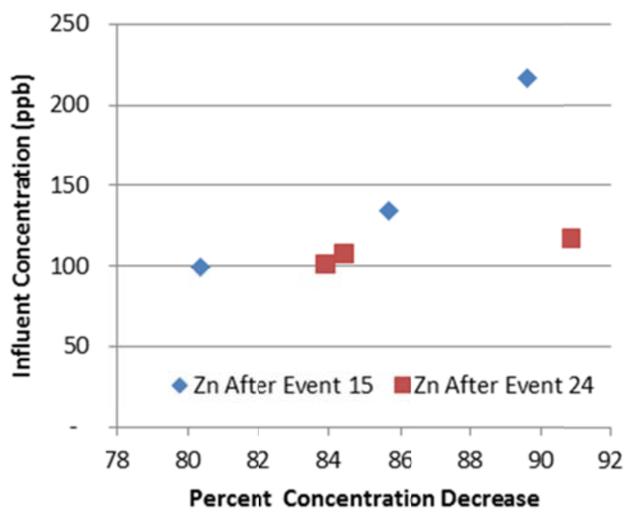

Figure 3: Percent concentration decrease of zinc for typical loading performance tests in the OPC/FA cylinders after accelerated loading.

Comparison to Pervious Concrete with Ordinary Portland Cement (OPC)

Percent porosity and infiltration rates from the OPC cylinders used in Haselbach et al. *(9)* are also listed in Table 1, and, as previously mentioned, the influent and effluent concentrations for the two OPC cylinders which underwent typical metal concentration performance testing are included in Table 2 along with the similarly aged and tested OPC/FA cylinder results. The effluent concentrations for both types of cylinders are very similar.

Figures 4 and 5 depict the influent and effluent concentrations for zinc and copper respectively for both the OPC and the OPC/FA cylinders during accelerated aging *(9)*. The tests on both the OPC and the OPC/FA cylinders were performed at the same time using the same influent so the results can be paired. The OPC cylinders have consistent performance over time for the 30 events for zinc, with a noticeable improvement in removal efficiency for copper.

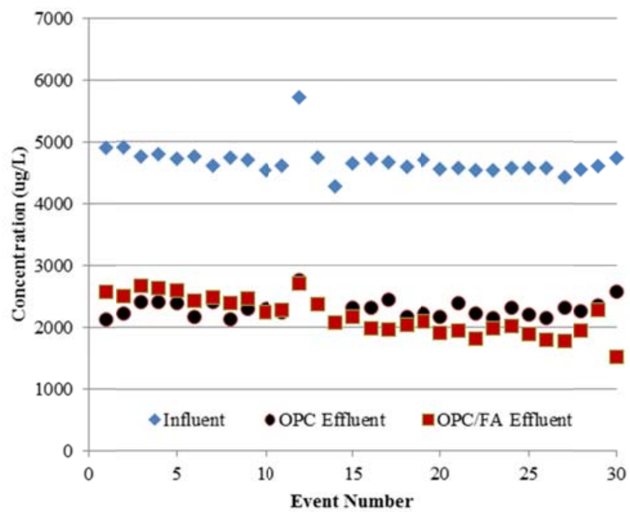

Figure 4: Zinc influent and effluent concentrations during accelerated aging events for OPC/FA and OPC samples [OPC data from Haselbach et al. *(9)*].

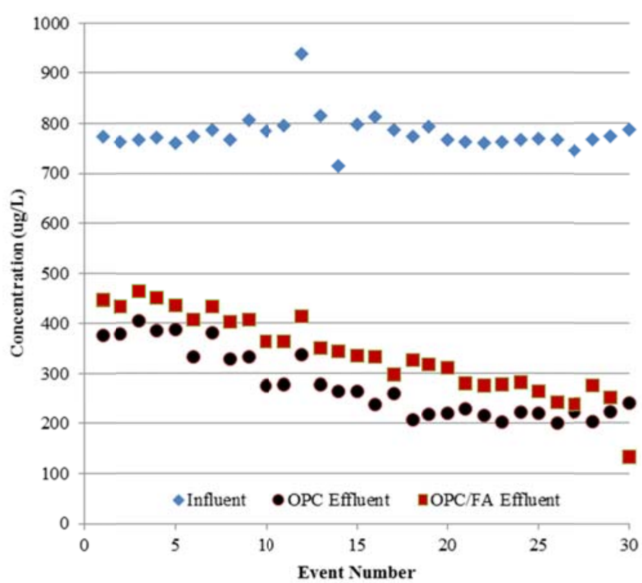

Figure 5: Copper influent and effluent concentrations during accelerated aging events for OPC/FA and OPC samples [OPC data from Haselbach et al. *(9)*]

The OPC/FA cylinders at first had slightly lower removal efficiency for both copper and zinc than the OPC cylinders. This was expected as there would be fewer hydroxide and carbonate species attached to calcium ions to complex with in the flow channels. However, over time the removal efficiencies for both zinc and copper for the OPC/FA cylinders improved, with the OPC/FA efficiencies exceeding the OPC after approximately 15 events for zinc, and with the trends suggesting that the OPC/FA efficiencies for copper may exceed the OPC efficiencies at or beyond event 30, but further study would need to confirm this. These trends are not unexpected, since, with initially increased removal efficiencies, the OPC cylinders would eventually have more metals retained than the OPC/FA cylinders which might reduce the number of available adsorption or surface complexation sites in these channels. Both the OPC/FA cylinders and the OPC cylinders were effective in dissolved zinc and copper removal.

DISCUSSION

A noticeable phenomenon is the improved efficiency of copper removal evidenced in both the OPC and OPC/FA cylinders during accelerated aging. Complexation formation and diffusion with several anions (calcium, copper and zinc) and the two anions (hydroxides and carbonates) is difficult to model simply and includes both the equilibrium stability constants and the kinetics of the various mechanisms. Initially it is assumed that the copper and zinc will preferably complex with the two anions on the surfaces in the tortuous channels in the pervious concrete as their stability constants tend to be higher than those for calcium *(12)*. However, in this one case of copper, there might be a kinetic reason for the improvement. The influent concentration of zinc is approximately five times that of copper and over time zinc will replace many of the sites previously complexed with calcium. The kinetics of the reactions, which are important in the relatively short residence times for the experiments, might be significant for copper. The rate constants for water exchange for copper, calcium and zinc are 1×10^9, 6×10^8, and 7×10^7 s^{-1}, respectively *(12)*. As many of the sites previously occupied by calcium are now occupied by zinc, the copper might more rapidly exchanged with the zinc than before with the calcium. In addition, copper complexes preferentially with hydroxides as compared to zinc and may have a greater tendency to diffuse into the porous concrete mortar where the pH is higher than on the surfaces *(12, 13)*.

The reasons for the improvement of the removal efficiencies over time for the OPC/FA cylinders relative to the OPC cylinders seem reasonable as the OPC cylinders will have retained more metals in the initial events and thus might have more surface sorption sites occupied and increased competition, but the exact mechanisms are also difficult to simply isolate. More detailed equilibrium and kinetic experiments will need to be designed with isolated anion exchange pairs instead of the three main anions to have a more complete understanding of these phenomena. In addition, consideration of chemical equilibria, and kinetics for the other minerals in pervious concrete should be evaluated, as should the altered chemistry of the mortar in the two different pervious concrete mixes due to formation of different ratios of the main calcium species such as the more leachable calcium hydroxides and the calcium-silicate-hydrates. The latter tends to be more prevalent in the mixes with fly ash *(18)*.

There are other pollutants in stormwater runoff such as dissolved organic compounds (DOC). Metals are also known to complex with DOC. The complex interactions of dissolved copper and zinc and multiple ligands such as carbonates, hydroxides and DOC are difficult to model and not well known. However, a study has shown that for a set DOC concentration, when the total copper concentration (as sorbed to the DOC and as dissolved) decreases, as would be experienced with copper removal by the pervious concrete, the equilibrium dissolved copper concentration with the DOC would similarly decrease *(19)*. This implies that introduction of DOC into the system would alter the removal efficiencies for copper in a negative way. Since both copper and zinc are divalent and have similar complexation constants in these systems with hydroxides, carbonates and various organic ligands, a similar result might be expected for zinc *(12)*.

The benefits for pervious concrete with respect to zinc and copper removal from stormwater runoff provide a novel aspect for the use stage for environmental life cycle assessments (LCA) of this pavement type. In many LCA studies related to product selection, the releases of zinc and copper to the environment prior to the use stage are typically included in the impact category of ecological toxicity *(20)*. Although the full extent of pervious concrete on this aspect of LCA is not conclusive from the results, and is also dependent on the location of a pervious concrete placement with respect to release to sensitive waters, this research indicates that there is the potential for not only reducing the typically negative impacts of these metal releases from product manufacture, but to also provide a net positive impact instead.

CONCLUSIONS

Pervious concrete made with ordinary portland cement and 25% by mass fly ash is effective as a treatment BMP for dissolved zinc and copper in stormwater. Based on the scenarios modeled, the extended effective lifespan is likely well beyond fifteen years. The experiments used column set-ups with depths of approximately 185 mm (7.3 in.) representative of a typical parking area or low volume street use. Overlay type applications such as may be found at ports, may provide for longer residence times due to increased horizontal flow as compared to vertical flow which might even increase the removal efficiencies. The results from these experiments can also be applied to precipitation and runon models for different regions and different applications such as highway shoulders if the estimated aging in years is modified for those levels of precipitation, runon and estimated metal loadings.

Additional research is warranted to extend the accelerated aging well beyond the 30 event tests performed in order to understand the longer-term removal efficiencies of the pervious concrete. Detailed experimentation into the various chemical component complexation equilibria and kinetics with other stormwater pollutants and other pervious concrete mixes will also provide useful information to extend the results to other applications and regions.

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