

THE EVALUATION OF PERMEABLE CEMENTITIOUS MEDIA
FOR NUTRIENT REMOVAL

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ABSTRACT

Excessive amounts of nutrients in surface and ground waters can interfere with the quality of aquatic and human life. Permeable pavement systems have been studied for contaminant removal, but there are limitations to the current state of knowledge. Laboratory studies were utilized to fundamentally characterize permeable cementitious media for the removal of nitrate-nitrogen and orthophosphate-phosphorus. Batch reactor tests were used to determine nitrate and orthophosphate removal and retention for five permeable reactive concrete mixtures. Additionally, fixed-bed breakthrough experiments were used to determine the nitrate removal for five permeable lightweight cellular concrete mixtures. Finally, one breakthrough experiment was used to determine the nitrate removal of a lightweight cementitious media.

It was determined that nitrate and orthophosphate removal isotherms of permeable reactive concrete were linear within the range of concentrations tested. The greatest nitrate removal in batch reactor and column tests were with ordinary portland cement (OPC), 50% replacement with ground-granulated blast-furnace slag, and 3% replacement with titanium

dioxide (TiO_2). OPC cellular concrete mixtures demonstrated beneficial removal at a lower w/c ratio. The nitrate removal process was characterized as slow for the cellular concrete and lightweight media mixtures during column tests. Multiple rates of nitrate removal observed during column testing may indicate multiple mechanisms of removal. Leach testing indicated that nitrate removal may not be permanent, although over 85% was retained by the TiO_2 and OPC mixtures. Orthophosphate removal and retention was effective for all PRC specimen with greater removal for the mixtures containing 3% replacement with TiO_2 and 25% replacement with fly ash.

In addition to nutrient removal, correlations between nitrate removed and sulfate leached were investigated. It was determined that soluble sulfate slowly leaches from the hydrated concrete and foaming agent in all mixtures. Specimen that were flushed with deionized water experienced lower removal rates than their counterparts. No direct correlation between mass of sulfate leached and mass of nitrate removed was observed in batch reactor testing or cellular concrete tests, although supplementary materials and the foaming agent could affect the relationship.

APPROVAL PAGE

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CHAPTER 1

INTRODUCTION

Permeable pavement systems have been recognized for decreasing pollutant loadings in surface waters, but there is a lack in fundamental knowledge of the removal capacity of individual pavement components. Limited studies have investigated the effects of cementitious materials on removal and retention of stormwater pollutants, especially dissolved, inorganic nutrients. As nutrient pollution to surface and ground water in the United States ceases to decrease, a need is established to reduce nutrient loadings to water systems. The current study is thereby designed to investigate the nature of dissolved, inorganic nutrient removal by cementitious media in controlled laboratory experiments. Three cementitious media were tested to identify maximum removal potential, with a focus on nitrate-nitrogen. The results of batch isotherm and continuous fixed-bed breakthrough testing presented herein are discussed in the following manner:

- Chapter 2: A current state of knowledge is reviewed for nutrient removal by permeable pavement systems, permeable pavements and cementitious materials.
- Chapter 3 To establish fundamental nutrient removal rates of permeable reactive concrete, and compare the influence of replacement with supplementary material, five permeable reactive concrete mixture proportions were tested utilizing batch reactor testing scenarios. The mixture proportions were designed to have a consistent w/c, reactive surface area, total reactive material, and void content amongst all mixture proportions.

- Chapter 4: Nitrate-nitrogen batch isotherm results are discussed after flushing permeable concrete specimen with deionized water. This chapter is intended to investigate the effects of flushing and aging permeable concrete on nitrate removal.
- Chapter 5: To investigate the nature of nitrate removal over time, five light-weight permeable cellular concrete mixtures were tested under fixed-bed continuous breakthrough conditions. Permeable light-weight cellular concrete was used to increase the amount of reactive surface area and available reactive material in an effort to increase total removal potential.
- Chapter 6: Continuous fixed-bed breakthrough results are discussed for a light-weight permeable concrete, as an alternative to the cellular concrete due to suspected interference with the surfactant used in cellular concrete. The mixture proportion were designed to maximize the amount of reactive material.
- Chapter 7: Overarching conclusions between the batch isotherm and fixed-bed continuous breakthrough experiments are discussed.

CHAPTER 2

LITERATURE REVIEW

The literature review in the current thesis is outlined to discuss how nutrients become an issue in the environment, how nutrients are removed from water systems, previous literature that has investigated permeable pavement systems and nutrient removal, and additional laboratory studies that have focused on cementitious materials or permeable pavement systems for nutrient removal. Pervious pavements have been studied for contaminant removal, but there are limitations to the data collected in many cases. Field studies, and some laboratory studies, on permeable pavement systems generally introduce additional variables such as multiple aggregates types and inconsistent inflow concentrations which does not allow for the characterization of the permeable pavement in question. Therefore, permeable pavement systems have been compared to one another, but the permeable pavement has not. Some laboratory studies have compared the nutrient removal rates of unhydrated cementitious and filler materials, which does not represent removal in hydrated structures. A minimal amount of studies have focused on hydrated cementitious materials or permeable concrete for nutrient removal, especially nitrate.

Nutrients and Treatment Technologies

Nutrient contamination, primarily caused by human activity, has resulted in impaired surface and ground waters across the globe and are known to have cascading effects in the environment (Galloway, 1998). Numerous studies have discussed how high concentrations of phosphorus and nitrogen promote the growth of algae in aquatic systems including lakes, coastal areas, large rivers, and wetlands, affecting the health of humans and aquatic species

(CENR, 2000; USEPA, 1993a). Major contributors to nutrient pollution include agricultural industry, including the applications fertilizers and manure, urban runoff, wastewater treatment plants, and atmospheric deposition (Bricker et al., 2008; Line et al., 2002; Puckett, 1994). Nutrient contamination has been problematic a crossed the United States including the Florida Bay, the Chesapeake Bay and the Gulf of Mexico (Zhang et al., 2015; Schade-Poole and Gregory, 2016; Wendel, 2015). Phosphorus is known as the limiting nutrient while, although there has been some disagreements over the years, nitrogen is generally considered the limiting nutrient for eutrophication in coastal marine ecosystems (Howarth and Marino, 2006; USEPA, 1993). The solubility and mobility of nitrate (NO_3) increases the likelihood of groundwater contamination (Bernard et al., 1998; Puckett, 1994).

Several chemical and microbiological mechanisms exist to remove nitrogen species from water and transform them to gas (Safferman et al., 2004). Microbial treatment systems utilize bacteria that convert ammonia (NH_3) to inert nitrogen gas through ammonification, nitrification, and denitrification in processes such as filtration-infiltration, rotating biological contactors, trickling filters, and activated sludge (Kang et al., 2008; Safferman et al., 2004). NH_3 is converted to NO_3 by aerobically reacting the NH_3 with oxygen in a process called nitrification, then NO_3 is converted to nitrogen gas by reacting the NO_3 with organic carbon under anoxic conditions in a process called microbial denitrification (Kang et al., 2008). Secondary biological treatment is generally required to reduce nitrogen and phosphorus in which advanced stages of removal would require extensions of the secondary treatment process (Kang et al., 2008). Other physical-chemical water treatment processes include breakpoint chlorination, ion exchange, and air stripping (Kang et al., 2008). Microbial treatment is preferred because it results in elemental nitrogen leaving the water system passively through

the denitrification process, opposed to actively maintaining physical-chemical processes (Safferman et al., 2004).

Common water treatment removal mechanisms for phosphorus include chemical precipitation, microbial uptake under anaerobic conditions (luxury uptake), and ion exchange (Kang et al., 2008; Safferman et al., 2004). Precipitation of phosphorus is achieved by adding lime or metal salts. The dissolved forms of phosphorus, orthophosphate (PO_4) consumes alkalinity, then an equilibrium precipitation is formed (Kang et al., 2008). Sorption is the predominant removal process occurring in precipitation (Kang et al., 2008). Recent research indicates that the highest phosphorus removal efficiency occurs at a pH range between 5.5 and 7.0 S.U (Kang et al., 2008). Phosphorus removal is an active treatment process, meaning residual products (sludge) from the biological processes or chemical reaction is collected and disposed of (Safferman et al., 2004). Precipitants can be filtered with a granular media, cloth media or membrane (Kang et al., 2008).

Treatment technologies of nutrients in structural stormwater best management practices are similar to that of water and wastewater treatment. Removal of nutrients is traditionally thought to occur through biological uptake, biological transformation processes, or chemical or physical sorption and filtration (NCHRP, 2006). Nutrients are degraded through biological processes utilizing living organisms (plants, algae and microbes microbial mediated transformations) in stormwater treatment. The organisms decrease organic pollutants through degradation and oxidation of inorganic pollutants. Removal of phosphorus is the most significant uptake mechanism in stormwater treatment systems (NCHRP, 2006). On the other hand, the reduction of nitrogen species through the nitrogen cycle is probably the most significant in stormwater treatment systems (NCHRP, 2006). The removal of nitrogen through

the nitrogen cycle includes the transformation of nitrogen species as discussed with the water treatment facilities. There is, however, a symbiotic relationship that forms with microbes and plants during the reduction of nitrogen. Ammonification is the first step in stormwater treatment which may occur aerobically (with oxygen) or anaerobically (without oxygen). Next is the two-step process of nitrification in which ammonium is oxidized to nitrite (NO_2) by *Nitrosomonas* bacteria, then NO_3 by *Nitrobacter*. A sequential step in the nutrient reduction process is uptake or storage which may be present in bio retention or wet land systems. NO_3 reduction in bioretention infrastructure can be accomplished through denitrification in anoxic zones and carbon-based electron donors (Kim et al., 2003). In many cases, vegetative BMPs have demonstrated how nitrogen, especially NO_3 removal can be highly variable across removal rates and in many cases, an increase in NO_3 can be observed (Collins et al., 2010a; Hurley et al., 2017; Kochv et al., 2014). NO_3 is more likely to be leached because the second step of nitrification is much quicker than the former (NCHRP, 2006). Phosphorus, on the other hand, can be regenerated into water systems through the death or dormancy of an organism or plant (NCHRP 2006).

Reduction of phosphorus species through coagulation and flocculation is also present in stormwater treatment (NCHRP 2006). Another major form of nutrient reduction for either stormwater, drinking or waste water treatment is physical sorption. Removal can be facilitated through filtering media or adsorption materials such as activated carbon. Adsorption of pollutants to a particular media is based upon the characteristics of the sorption media and constituents present. Green media such as sawdust, clays, sand, and tire crumbs has been investigated for sorption of nutrients (Jones et al., 2015; Xuan et al., 2010). Additional sorption

media for NO₃ may include sepiolite, activated carbon, metal oxides and agricultural wastes (Bhatnagar and Sillanpää 2011; Grace et al., 2016; Loganathan et al., 2013).

Permeable Pavement Systems

Structural permeable pavement systems are designed with several components, most commonly including a permeable surface, several sections of granular sub-base, geotextile members, and a soil sub-base (Scholz and Grabowiecki, 2007). A commonly designed permeable pavement system is shown in Figure 1. Permeable surfaces can range from permeable concrete, permeable asphalt, permeable interlocking concrete pavers (PICP), or alternative surfaces (Scholz and Grabowiecki, 2007). Permeable pavement systems are well known for the hydrologic benefits of reducing run-off volume and peak flow rates (Abbott and Comino-Mateos, 2003). Current research has also demonstrated increased water quality by the reduction of nutrients, metals, hydrocarbons, fecal coliforms and other contaminants (ACI, 2011; Scholz and Grabowiecki, 2007; Imran et al., 2013). Permeable pavements systems can sustain microbial activity which can enhance biodegradation of stormwater contaminants (Coupe et al., 2003). Permeable pavement systems also present a beneficial environment for phosphorus removal by increasing effluent pH, providing favorable calcium ions for phosphorus attenuation, and filtering particulate pollutants.

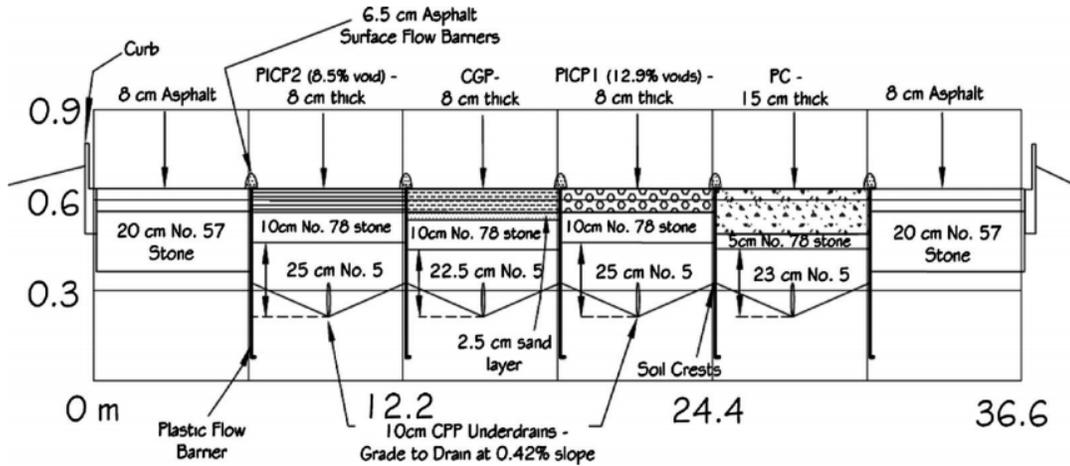


Figure 1. Typical Permeable Pavement System Design (Collins et al., 2010b)

Generally, field studies are designed to compare the stormwater pollutant reduction by permeable pavement systems and/or conventional impermeable surfaces. Studies on permeable pavement systems and nutrient reduction commonly include the comparison of conventional asphalt to permeable interlocking concrete pavers, porous asphalt, or pervious concrete (Andrewa et al., 2012; Bean et al., 2007; Beecham et al., 2012; Brown and Borst, 2015; Collins et al., 2010b; Drake et al., 2014; Gilbert and Clausen, 2006; Haung et al., 2016; James and Shahin, 1998; Winston et al., 2016). Additional laboratory studies investigate the nutrient removal by a single permeable pavement system design (Day et al., 1981; Kamali et al., 2017; Scholz and Grabowiecki 2009; Tota-Maharaj and Scholz 2010). Porous asphalt alone has also been studied (Jiang et al., 2015; Pagotto et al., 2000; Roseen et al., 2012; Stotz and Krauth 1994). The studies on permeable pavement systems discussed herein have provided a background on how a system can influence nutrients loadings in stormwater, but the variables introduced do not permit quantification of individual component performance.

Bean et al. (2007), Brown and Borst (2015), Collins et al. (2010b) and Drake et al. (2014) compared the effluent quality of PICP, permeable concrete, and conventional asphalt. Bean et al. (2007) observed stormwater quality effluent from four independent parking lots, two of which were PICP systems. Each pavement system was monitored at separate times during a 5 year period. Pavement age and testing duration varied among each system. The pavement systems were unlined, allowing water to infiltrate into the soil subsurface, so no pollutants left the site for several rainfall events. Bean et al. (2007) observed decreases in the total nitrogen (TN) and NH_4 loadings and increases NO_2 and NO_3 loadings by the permeable pavement systems. Bean et al. (2007) postulated that aerobic conditions were present in the granular storage section of the pavement system which contributed to nitrification. The pavement systems reduced particle bound phosphorus while dissolved PO_4 was not significantly reduced indicating filtration as a major removal mechanism.

In 2007, Collins et al. (2010b) studied the reduction of nitrogen species by pervious concrete, two PICP, and concrete grid pavers when compared to asphalt in a side-by-side field study in North Carolina. The study by Collins et al. (2010b) allowed for a more direct comparison than Bean et al. (2007) because the pavement systems were adjacent to one another; each pavement system, however, had varying pavement and sub-base thicknesses which prohibits comparison of pavement types. Each pavement system was constructed on poorly drained soils with similar crushed stone bases and perforated pipe underdrains. Collins et al. (2010b) noted the pH buffering capacity of the permeable pavement systems. Collins et al. (2010b) observed significantly lower NH_4 concentrations and greater NO_2 and NO_3 concentrations for permeable concrete and PICP systems. Collins et al. (2010b) noted how soil below the pavement system could contribute to higher N loadings and suggested that sand

filters could enhance the TN removal. The North Carolina climate did not vary enough to affect stormwater treatment by permeable pavement systems.

Effluent water quality for permeable concrete and two PICP systems were compared to asphalt by Drake et al. (2014). Each pavement system had similar designs and a filter to prevent interactions with the soil below the system. Drake et al. (2014) observed significant decreases in TN, NH_4 NH_3 and NO_2 concentrations and loadings for all permeable pavement systems while noting an increase in NO_3 . The PICP and permeable concrete systems differed in NO_2 , NO_3 , and organic nitrogen (ON) effluent concentrations. Drake et al. (2014) attributed the reductions in NH_4 , NH_3 , and NO_2 to the nitrification process in the aerobic conditions present in the pavement systems. Drake et al. (2014) attributed phosphorus removal through filtration of organic phosphorous and geochemical sorption and precipitation for dissolved phosphorus and reduced loading up to 75%. An adjustable storage could increase favorable anoxic conditions for denitrification, increasing NO_3 removal (Drake et al., 2014). With the limited amount of research, it was unclear if the nutrients bound in the system were permanent.

Brown and Borst (2015) compared the effluent nutrient concentrations of permeable concrete, PICP, and porous asphalt systems in a side-by-side field study. Results indicated higher dissolved PO_4 removal from the porous asphalt which correlated to an unexpectedly high effluent from the porous asphalt. The high pH of the porous asphalt was suggested to negatively influence the nitrification process of NO_2 to NO_3 as out of range for optimal transformation. NO_3 was the predominant nitrogen species in PICP and pervious concrete effluent, suggesting nitrification processes occurred. However, the TN concentrations were not significantly different than the rainfall concentrations.

Winston et al. (2016) reported significant reductions in organic nitrogen and phosphorus with little to no treatment of dissolved nutrients concentrations for PICP. Porous asphalt was studied by Jiang et al. (2015) and no significant removal of TN was observed while there was removal of TP. Day et al. (1981) found that grid pavers had no significant effect on nitrogen reductions and found removal of TP in a lab study. Loimula et al (2013) tested the water quality parameters of a porous asphalt highway over two years. The results suggested that changes in flow through permeable pavement systems may change as the pavement ages well as the influence of microorganisms on total nitrogen removal.

Beecham et al. (2012) investigated the stormwater quality of PICP in a field study and a replicated laboratory. Beecham et al. (2012) reported similar total P and N removal between the field study and laboratory study. Removal of TP and TN was due to nutrients bound to sediment and filtration by pavers as agreed by Winston et al. (2016). Kamali et al. (2017) continuously flushed a PICP system with stormwater runoff to investigate the nutrient reductions and the influence of drainage path in a laboratory study. Influent consisted of stormwater runoff collected in the field and was continuously diluted throughout the 270 min experiment. Effluent was collected at different stages in the system to evaluate the effect of system components and flow length. Kamali et al. (2017) observed decreases in NH_4 and increased NO_3 due to nitrification. PO_4 removal increased with travel distance or time dependency. Nutrient reductions were greater at the start of the experiment. Decreases in nutrient removal over time were attributed to a decrease in dissolved oxygen for microbial activity. The effectiveness of PCIP to remove nutrients was limited due to the short bed depth and young age of the pavement system by limiting microbial populations (Kamali et al., 2017).

In a field study for permeable concrete, permeable asphalt and PICP, Huang et al. (2016) used simulated rainfall events to investigate seasonal effects on stormwater quality. Huang et al. (2016) determined that summer conditions affect TN removal, but not TP removal. Huang et al. (2016) concluded that TN removal increased due to a reliance on microbial activity. Scholz and Grabowiecki (2009) also found that nutrient degradation increased with increasing temperatures. Tota-Maharaj and Scholz (2010) found no difference in NH₃ and TP removal when heating a permeable pavement system in laboratory conditions.

Previous research has observed and described variable nutrient removal in permeable pavement systems. Microorganisms and the storage capacity of the pavement systems were expected to have a significant influence on nutrient reductions. Numerous variables introduced by permeable pavement system designs may influence removal. Field studies also introduce variables such as climate, rainfall events, and influent quality further complicating comparisons between studies. Additionally, pavement pore size, tortuosity, and pore distribution ultimately affect the removal by filtration (Sansalone et al., 2008). Both permeable pavement systems and field studies do not allow for a fundamental characterization of contaminant removal by the individual permeable pavement components.

Permeable Concrete

Several studies have investigated the removal of nutrients in permeable concrete alone or hydrated cementitious paste (Luck and Workman 2007; Kim et al., 2017; Molle et al., 2002; Ong et al., 2016; Park et al., 2003; Park et al., 2008; Wang et al., 2014). Laboratory experiments may include batch reactor testing, continuous fixed-bed breakthrough testing, or other flushing apparatuses. Similar to permeable pavement systems, hardened permeable concrete can have several factors that may affect nutrient removal. Increased water to unhydrated cement ratio

(w/c) has resulted in higher porosity of cement paste (Zeng et al., 2014). Pore volumes, sizes, and connectivity can affect the permeability of a mixture proportion (Neithalath et al., 2010). Aggregate size and paste content can also affect the pore volumes properties (Sumanasooriya and Neithalath, 2011). An alternative to permeable concrete may be cellular concrete. Cellular concrete is known to have flowability and self-compatibility which allows for it to be pumped over long distances (ACI, 2006; Amran et al., 2015; Wee et al., 2006). Low-density cellular concrete can be classified as having a dry density less than 800 kg/m^3 (ACI, 2006). Foamed cellular concrete applications include soil stability, fill for abandoned structures, and roof decking to decrease structural dead loads (ACI, 2006). Similar to permeable concrete, foamed concrete may contain entrapped air, capillary pores, and gel pores with varying pore sizes and distribution amongst different mixture proportions (Wee et al., 2006).

Park and Tia (2004) evaluated how microbial organisms reduce nutrients on permeable concrete surfaces and how aggregate size may affect the efficiency of removal. The concrete mixture proportion used in Park and Tia (2004) included silica fume and fly ash without insight to why the mixture proportion was chosen or how it could benefit removal. Specimens with dimensions of 400 mm x 400 mm x 100 mm were immersed in river water then dissolved oxygen, TP and TN were measured over time. The pH rose to 11.2 and slowly decreased over the 90-day experiment with lower pH for the fly ash and silica fume effluents. Nutrient removal decreased over the 90-day experiment due to changes in microbial behavior and available dissolved oxygen. Park and Tia (2004) emphasized how microorganisms may affect nutrient removal, rather than the materials and quantities used. The influence of microbial activity on nutrient removal do not allow for comparisons between the performance of the mixture proportions of Park and Tia (2004) or the performance determined in other studies. Permeable

concrete was also investigated for removal and retention of nutrients contained in cow manure compost (Luck and Workman 2007). Pervious concrete specimens were effective at removing particulate N and P reducing TN and TP level. NO_3 , NO_2 , and NH_4 concentrations were greater in the treated effluent than expected (Luck and Workman 2007). Luck and Workman (2007) focused mainly on filtration by the permeable pavement although other means of removal may have been present.

Phosphorus and fecal coliform removal were observed for pervious permeable concrete with either 100% ordinary portland cement (OPC) or 10% or 35% fly ash replacement in a column study by Soto-Pérez and Hwang (2016). Permeable concrete specimens were cured for 28 days and were then placed in wastewater effluent for 2 hours. The wastewater effluent was drained, and each specimen was tested an additional 9 times. Specimens raised the effluent pH to 10.5 for the initial trials, then effluent pH slowly decreased in the later trials. Soto-Pérez and Hwang (2016) observed reductions in phosphorus postulating precipitation of P in the forms of hydroxyapatite and amorphous calcium phosphate and a strong correlation between pH and removal. The addition of fly ash reduced the P removal and higher initial P concentrations resulted in higher removal percentages. However, a reduction in phosphorus removal and pH observed with the addition of fly ash in the mixture proportion was not proportional to the amount of fly ash used. The quantity of cementitious materials in each mixture proportion or other mixture proportion variables such as w/c may have caused reduced phosphorus removal.

Kim et al. (2017) investigated the particulate and dissolved phosphorus and nitrogen removal of permeable concrete and crushed hydrated portland cement and calcium sulfoaluminate (CSA) of varying w/c. An apparatus was rotated 50 times to allow a constant 3000 mL of nutrient water to flow freely through a rectangular specimen with dimensions of

10 cm x 10 cm x 20 cm and a w/c between 0.3 and 0.4. The results indicated no significant difference in nutrient removal regarding w/c. The reduction in TN was over 40% after the first 10 cycles but decreased as the test continued for the total of 50 cycles. The CSA specimen removed more TN than the OPC. The net increase in dissolved nitrogen and decrease net suspended nitrogen is suggestive of nitrification seen in other studies (Luck and Workman, 2007; Kamali et al., 2017). Both the CSA and OPC specimens effectively removed dissolved and suspended phosphorus with no significant differences in removal between either mixture proportions or w/c. Suspended nitrogen and phosphorus were reduced through physical filtration. Dissolved phosphorus could be adsorbed by the formation of hydroxyapatite in both types of cement. Crushed hydrated CSA and OPC were also tested for dissolved NO₃ and PO₄ removal utilizing 60 min adsorption tested (Kim et al., 2017). Two grams of CSA or OPC were placed in 250 mL of 50 mg/L NO₃ or PO₄. Specimen were stirred for 5 min, then let sit for an additional 55 min. CSA was noted to have a slightly higher removal of orthophosphate, although the two materials came to a possible equilibrium of the same concentration at the end of the 60 min test. No significant NO₃ removal was observed in the 60 min test. X-Ray diffraction (XRD) testing indicated the formation of hydroxyapatite indicating a chemical reaction between the Ca⁺² and dissolved phosphorus.

Wang et al. (2014) reported the adsorption potential of four crushed mortar mixtures containing either OPC or FA in small 24 hr batch reactor experiments. Mixture proportions had varying w/c ranging from 0.28 for the fly ash mixture and 0.45 for the OPC mixture. Aggregate types varied for each mixture proportion as well as additives including polysiloxane-modified montmorillonite for the OPC mixture and nano-clay or gypsum for the fly ash mixtures. It was noted that the FA mixtures had reduced phosphorus adsorption, but

had less phosphorus desorption. Wang et al. (2014) noted that the P removal was affected by Ca^{+2} fractions in the binders but did not evaluate the effects of the add\mixtures, different aggregates, or w/c when comparing the performance of the different mixture proportions

Park et al. (2008) compared the fluoride, sulfate (SO_4), PO_4 , and NO_3 removal capacity of crushed, hydrated cement paste and lime. Concrete cubes were cured for 28 days, then crushed. Cement paste particles less than 0.15 mm were used for batch experiments while particle sizes between 1 and 2 mm were used for a continuous fixed-bed column test. Phosphate removal of crushed cement paste and lime was suggested to reach equilibrium after 12 hours in 48 hr batch reactor tests. In 24 hr batch tests, PO_4 removal increased for increasing doses of crushed cement paste. The effluent of the breakthrough experiment had a pH of 12.4 for 100 pore volumes of breakthrough solution and the pH was decreased to about 2 by the end of 200 pore volumes. SO_4 and NO_3 concentrations were greatly reduced, although it was suggested that the SO_4 leached from the specimens. Park et al. (2008) postulated a relationship in which the NO_3 went through an anionic exchange with the monosulfate formation in the concrete. NO_3 removal was calculated to be 10.8 mg/g of cement paste with an initial concentration of about 300 mg NO_3/L of breakthrough solution. The computation for sulfate leached is questionable because the initial influent concentration was 516 mg SO_4 /L of breakthrough solution, so it may have been a reduction in SO_4 removal efficiency by the specimens. The removal of sulfate began to decrease until the effluent concentrations were comparable to the inlet concentration of sulfate.

Molle et al. (2002) found significant PO_4 removal capacity by recycled, crushed concrete made from quicklime when compared to calcite in batch isotherms and breakthrough curve testing. Effluent pH values were between 11 and 12. Crystal growth of calcium

phosphate species is the final removal mechanism in calcareous materials. Molle et al. (2002) found that phosphate removal by recycled crushed concrete was almost instantaneous. Ong et al. (2016) experimented with four pervious concrete mix designs removal of organic naphthalene using a column set up in laboratory conditions. Ong et al. (2016) noted variability in the workability and permeability amongst the different concrete mixture proportions, which would not allow for an objective comparison between how the chemical properties of the mix designs affect contaminate removal.

More recently, Li et al. (2017) studied six permeable pavement materials in 4 cm x 20 cm column tests at a flow of 30 ml/min. Materials were crushed and sieved between 2 to 5 mm. Porous concrete and asphalt decreased pH from neutral, which may have been a factor of constituents in the influent water. NH_4 was assumed to be decreased by an ion exchange mechanism. The porous concrete did not reduce NH_4 as effectively as ceramic brick, cement brick, porous asphalt or shale brick possibly due to less monovalent cations. The pervious concrete performed similarly to cement brick, porous asphalt, and sand-based brick regarding NO_3 removal. Shale brick had the greatest removal presumably due to the higher iron content. Removal was attributed to redox adsorption. PO_4 removal was similar for the porous concrete, cement brick, sand-based brick and shale brick materials. There was a maximum removal accompanied by a rapid decrease in removal, then a slower decrease in removal rate.

Limited studies have been conducted on cellular concrete (aerated autoclaved (ACC) or foamed) and stormwater contaminant reduction. Wee et al. (2006) compared the air void characteristics for a 0.3 w/c with slag with a freshly mixed density of 600 – 1900 kg/m^3 . Average air void size increased and spacing factor (thickness of cement walls) decreased with increasing air content. The viscosity of the initial cement paste can also influence pore

structures of foamed concrete (Esmaily and Nuranian, 2012). Esmaily and Nuranian (2012) focused on compressive strength, but these variables could be important for increasing removal rates, etc. Crushed ACC was tested for phosphorus removal in continuous-flow fixed-bed column experiments (Berg et al., 2005). Aerated autoclaved light-weight concrete (aerocrete, ACC) was studied for the removal of arsenic, but ACC is fabricated differently than foamed concrete (Martemianov et al., 2017; Narayanan and Ramamurthy, 2000). Shershneva et al. (2017) briefly investigated the oil absorption capacity of foam concrete, although results were not discussed. de Andrade et al. (2015) investigated the removal of organic dye from an aqueous solution using ACC mixed with TiO_2 .

Cementitious and Supplementary Materials

Permeable concrete typically consists of coarse aggregate, portland cement, water, and little to no fines and 15-35% voids. Portions of the portland cement can be replaced with supplementary cementitious materials (SCMs) (ACI 2011). SCMs could potentially increase the removal rates of PRC. Some studies have focused on the removal of water contaminants by hydrated or unhydrated cementitious products.

Agyei et al. (2002) compared the phosphorus removal of unhydrated fly ash, slag and OPC in isotherm and column testing. Phosphorus removal was related to calcium oxide percentage with max removal occurring from OPC, slag, and then fly ash. Phosphorus removal came to an equilibrium at 6 hours for fly ash opposed to 3 hours for slag and OPC. Agyei et al. (2002) proposed that calcium phosphate precipitation species may depend on initial pH due to increased availability of more acidic forms of dissolved PO_4 . In a fixed-bed column breakthrough study, Agyei et al. (2002) found that unhydrated OPC removal of phosphate decreased with the addition of slag or fly ash similar to what was found with Soto-Pérez and

Hwang (2016). Agyei et al. (2002) suggested that chemisorption was predominant over physical removal because the crushed particle size did not affect removal which agrees with Johansson and Gustafsson (2000). Agyei et al. (2002) also suggested intraparticle diffusion was proposed to be the controlling mechanism of removal because mixing rate affected removal rates. Johansson and Gustafsson (2000) found that slag particle size had an effect on P removal at smaller concentrations while larger fractions become more effective at higher concentrations.

Fly ash powder is well known for having phosphorus adsorbing capacity and is frequently tested for phosphorus removal for soil or water remediation (Cheung and Venkitachalam, 2000; Cheung et al., 1994; Forbes et al., 2004; Kirk et al., 2003; Lu et al., 2009; Li et al., 2006; Lu et al., 2009; Ugurlu and Salman, 1998; Zhang et al., 2008). Lu et al. (2009) noted a rapid increase in pH accompanied by rapid removal of phosphorus. Lu et al. (2009) demonstrated how the majority of phosphorus removal (68-96%) occurred in the first 5 min of batch reactor test with a strong dependency on Ca^{+2} dissolution, then a slower reaction occurred after. Precipitation was the quick and short removal mechanism accounting for nearly 70% of removal. Precipitation products were primarily calcium phosphates in the form of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and minor amounts of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and calcium hydrogen phosphate (CaHPO_4). Slower and longer removal was due to adsorption onto hydroxylated oxides which accounted for the remaining 30% of PO_4 removal. Initial PO_4 concentration was found to affect the initial pH and when the batch reactor may reach equilibrium. Lu et al. (2009) demonstrated how important factors like time, pH, and treatment can affect adsorption. Lu et al. (2006) found that low levels of acidification can positively influence PO_4 sorption, while higher levels of acid treatment

decreased removal. The decrease in removal was explained by Lu et al. (2009), acknowledging that the acidification would strip Ca^{+2} ions, decreasing the precipitation process thus relying on the adsorption process. Heat treating fly-ash above 400°C prior to testing was also found to positively influence PO_4 removal (Li et al., 2006). Li et al. (2006) found that phosphate was slowly removed up to 24 hrs with the possibility of further removal beyond the 24 hrs.

Class C, lignite and Class F, bituminous bottom ash tested were tested in a field study for the treatment of wastewater (Kirk et al., 2003). The Class C bottom ash had greater removal for total suspended solids, biochemical oxygen demand, TP, TKN, and NH_3 than the Class F bottom ash in the 2-year study. Laboratory studies also indicated higher desorption for the bottom ash compared to fly ash and bituminous compared to lignite. There was a correlation between available calcium and pH and soluble phosphorus in laboratory batch studies for bottom ash. Higher Ca^{+2} dissolution concentrations favored lower phosphorus concentrations. Removal was attributed to surface precipitation on the ash. A Langmuir fit isotherm was determined for phosphorus removal by fly ash (Kirk et al., 2003). Wastewater batch isotherms tested by Ragheb (2013) showed fast removal at approximately 30 minutes. Ragheb (2013) suggested the most efficient removal at an initial pH of 5 for slag and 7 for fly ash, although the results did not appear significantly different for the slag. Percent of PO_4 removed increased with increased initial concentrations for FA and Slag (Ragheb 2013).

Limestone and ground-granulated blast-furnace slag were studied for phosphorus removal for wetland remediation (Postila et al., 2016). Batch testing resulted in a pH of 12.2 for slag and removal up to 99%. The limestone effluent had lower pH (7.9) and removal of 70-93%. Column testing of slag resulted in greater PO_4 adsorption capacity by smaller particle sizes (3-10 mm) opposed to larger (10-20 mm) similar to what was found by Johansson and

Gustafsson (2000). The effluent pH of steel slag started around 12 and ended above 9 after 80 days. The steel slag did not perform as well in the field studies due to the short contact time (10-20 min) which did not allow the pH to become greater than neutral (Postila et al., 2016). Powdered slag was found to be ineffective at NO₃ removal when compared to activated carbon and sepiolite (about 2 mg/g after 200 min in a batch jar study) (Öztürk and Bektaş, 2004). The authors speculated that Ca⁺² and Mg⁺² leached from the slag and formed stable compounds in the solution. The NO₃ removal capacity of activated carbon powder was greatly decreased at an initial pH of above 6 with a maximum percentage removal at a pH of 2. Limestone was not as effective at removing P as other materials such as a lightweight and calcined expanded clay and iron oxide aggregates in batch testing, but was, however, effective at retaining P in leach column testing (Canga et al., 2016). Limestone was also found ineffective at P removal by (Johansson and Gustafsson, 2000). Canga et al., (2016) did demonstrate, however, how residence times can greatly impact adsorption isotherms. Limestone removed less than 5 mg P/ g limestone at 0.5 hrs and over 30 mg P/ g limestone over 48 hrs.

Drinking water and wastewater treatment processes can produce waste at a rate of 4% by volume of the overall water treated (Safferman et al., 2004; Sanin et al., 2010). To avoid confusion with the many types of water treatment residuals, the acronym DWTR (drinking water treatment residual) will be used to describe the lime-based product used in the current study (this thesis). The DWTR used in the current study was a derivative of lime softening industrial drinking water treatment with low organic content opposed to other WRT types. Because of the high calcite calcium content, flocculated structure, and high accessible moisture content, lime-derived DWTR has been used as an internal curing agent in cement mortar (Nowasell and Kevern, 2015). The literature reviewing water treatment residuals (WTR),

mostly alum and ferric based, tends to focus on the capacity for phosphorus removal, rather than species of nitrogen (Krishna et al., 2017). Few studies have compared alum, ferric, and lime based WTR regarding nutrient removal. Elliot et al. (2002) experimented with WTR as an amendment to sandy soils, finding decreased P leachability by alum WTR opposed lime and ferric counterparts. Adhikari et al. (2016) concluded higher P removal for alum-based DWTR when compared to the ferric and lime derivatives. Ippolito et al., (2003) proposed longer residual time could form less soluble phosphate crystals with the calcium in lime similar what was found by Kirk et al., (2003) with fly ash. Alum-based DWTR has reduced TP, TKN and produced NO_2 and NO_3 which suggests ammonification or nitrification (O'Neill and Davis 2012).

The addition of cementitious materials may also affect removal for several reasons. Considering the hydrated cementitious structures in either permeable concrete or cellular lightweight concrete, adding supplementary materials as little as 10% replacement of OPC by limestone fines can promote heterogeneous nucleation of OPC hydrates which accelerate the early age hydration (Berodier and Scrivener, 2014; Kadri, et al. 2010). The addition of limestone can increase the density of C-S-H nuclei on limestone surfaces (Berodier and Scrivener 2014). Additionally, supplementary materials can affect other properties of cement paste such as porosity (absorption and sorptivity) of cement paste (Elgalhud et al., 2016), which could ultimately affect removal. Above 25% limestone replacement, the pore structures related properties such as porosity, absorption and sportively should increase (Elgalhud et al., 2016). Increasing the limestone fines content above 20% causes a dilution effect which also increases porosity (Elgalhud et al., 2016).

Some replacement products may be chemically inert and will not participate in any hydraulic reaction. Titanium dioxide, having nano-scale properties, modifies the hydration rate primarily due to dilution, modification of particle size distribution and heterogeneous nucleation. The addition of fine non-reactive filler, such as TiO₂ particles, to cement modifies the hydration rate primarily due to modification of particle size distribution, providing heterogeneous nucleation sites, accelerating hydration reaction in early age (80 hr), and accelerating degree of hydration (Lee 2012).

TiO₂ is typically used as a self-cleaning agent for pavements (Asadi et al., 2012). Asadi et al. (2012) and Shen et al. (2012) demonstrated how atmospheric nitric oxide (NO) gas could be reduced by photocatalytic TiO₂ applied to pervious concrete. NO removal decreased with increased air flow rate. An optimal void content of 27% was determined (Asadi, et al. 2012). Shen et al., (2012) studied how several application methods of TiO₂ can be effective at removing nitrox gases. Lee (2012) studied the effects of replacing 5%, 10%, and 15% of OPC with TiO₂ on specimen deterioration in NO₃ salt water for 65 days. A dosing rate of 15% of P25-cement was not examined due to difficulties mixing at the highest dosage rate examined. Lee (2012) found formations of calcium nitrate (Ca(OH)NO₃(H₂O)) after the 65-day tests which suggested chemical reactions between the NO₃ and concrete specimen. The P25 TiO₂ specimen resulted in higher degradation due to greater pore area and pore volumes for pores less than 10 nm, suggesting the nanoparticles changed the microstructure of the cement paste. Individually, TiO₂ powder was observed to remove NO₃ from an aqueous solution through photocatalytic reduction by Doudrick et al. (2017). Three TiO₂ powders were tested at 1 g TiO₂ /L of solution irradiated by a UV lamp to facilitate the photocatalytic activity. NO₃ reduction was observed by the powders in an unlit setting after 1 hour of contact (Doudrick et al., 2012). NO₃ leaching,

however, can be a by-product of photocatalytic degradation of nitric gases (Dylla, 2013). Dylla (2013) found that NO_3 was excreted from TiO_2 covered concrete, but the TiO_2 had some capacity to retain the NO_3 .

Sulfate

Calcium sulfate, generally in the form of gypsum, is added to portland cement to control the hydration rate, especially with the addition of supplementary materials (FHWA 2007). Ettringite forms in the first few hours of hydration from the calcium sulfate sources (generally gypsum). Remaining tricalcium aluminate (C_3A) will react with the ettringite to create calcium monosulfoaluminate. Ettringite can be reformed in expansive reaction. There may be a slowly soluble form of sulfate by hard burned anhydrite. Increased total clinker sulfate may lead to a greater potential for soluble sulfates. Sulfur increases in clinker may be attributed to fuel sources (PCA, 2001). The selective dissolution tests indicate that clinkers manufactured in accordance with conventional industrial practices do not contain slowly soluble sulfates that could cause cements to induce deleterious expansions in concretes (PCA, 2001). Sulfate solubility has been shown to increase with increasing temperature (Perkins and Palmer, 1999).

Testing Considerations

Anion ion chromatography was used in the current study to determine effluent concentrations for NO_2 , NO_3 , PO_4 , and SO_4 . Ion chromatography provides the convenience of passively analyzing small aliquots effluent samples. Ion chromatography has been used since 1975 and improvements have been continuously made since (Small et al., 1975; Tartari et al., 1995). A variety of inorganic anions and cations, low-molecular-weight organic acids and bases, and transition metals can be determined through ion chromatography systems (López-

Ruiz 2000; Jackson, 2006). Applications for ion chromatography analysis include water and wastewater analysis, environmental waters, soils, and solid waste (Jackson 2006).

An ion chromatography system can contain hardware including a guard column, ion exchange column, and conductivity detector. Typical reagents include an eluent and regenerant. Eluent is used to transport an aliquot of solution through an ion separation column of opposite charge which slows and separates the ions (SeQuant, 2007). The eluent also provides buffering capacity to stabilize the pH. Separated ions are passed through a suppressor where the conductivity of the eluent is suppressed, and sensitivity is increased by the regenerant. The reagents used are determined by the sample concentration and ions of interest (selectivity, sensitivity, and type anion/ion). The electrolytic conductivity of the ion is then measured by the detector with respect to time. The resulting changes in conductivity are produced into a chromatography as shown in Figure 2. A concentration is generally determined by a linear calibration of the area under the curve (uS/sec). The capacity of the system is limited to the columns strength. Precision has been shown to be 2-5% RSD between 3-600 μM over periods of months to years (Tartari et al., 1995).

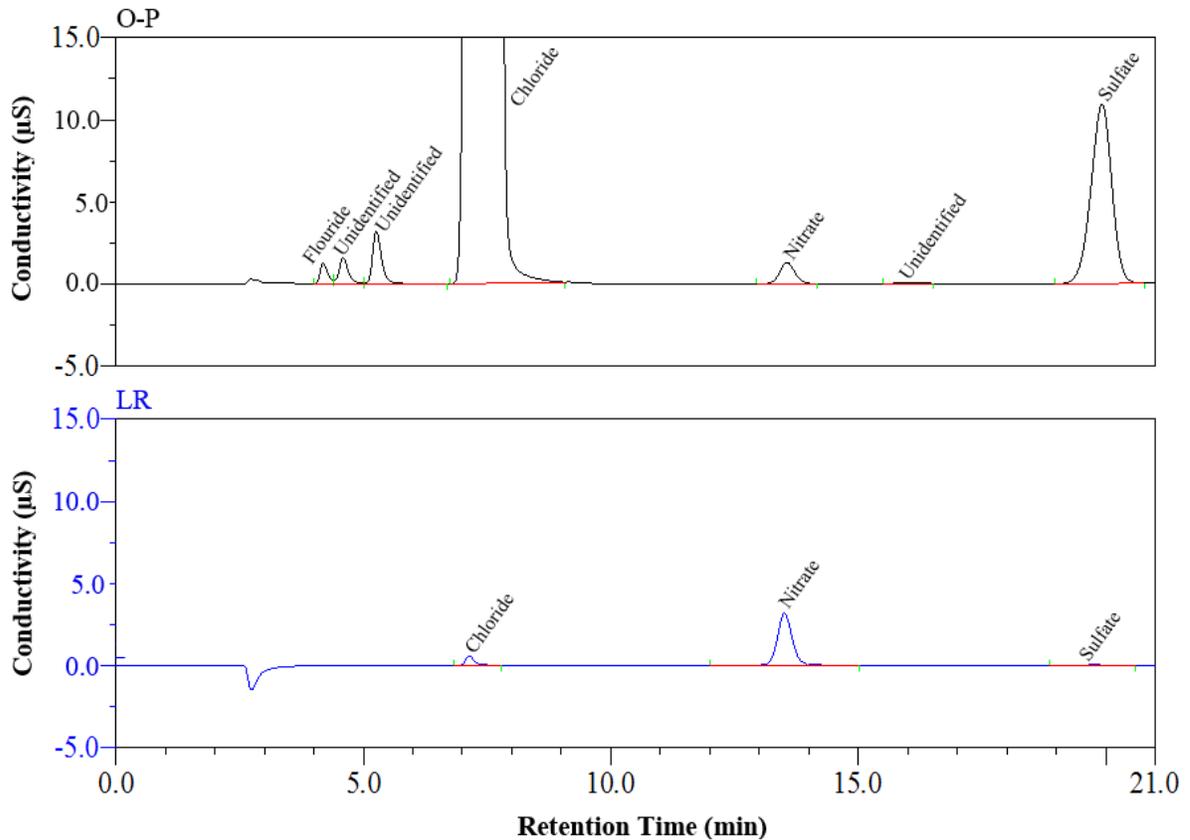


Figure 2. Chromatogram of Laboratory Reference and Sample Batch Reactor Sample (O-P) after Testing with IC

Typical samples include a calibration blank, calibration standards, validation standards, and laboratory blanks (laboratory references) (USEPA, 1993b). Linear calibration range is determined with a minimum of 3 standards which must be within $\pm 10\%$ of the initial concentrations (USEPA, 1993b). Linear calibration must be established every six months and verified at the start of each day and after every 20 samples tested. A linear calibration determined in the current study for nitrate is shown in Figure 3. Calibrations curves can be non-linear in which a sufficient number of standards would need to be tested to verify the nature and precision of the calibration curve (Tartari et al., 1995). A method detection limit is

established to determine the minimum concentration that can be accurately measured by the system.

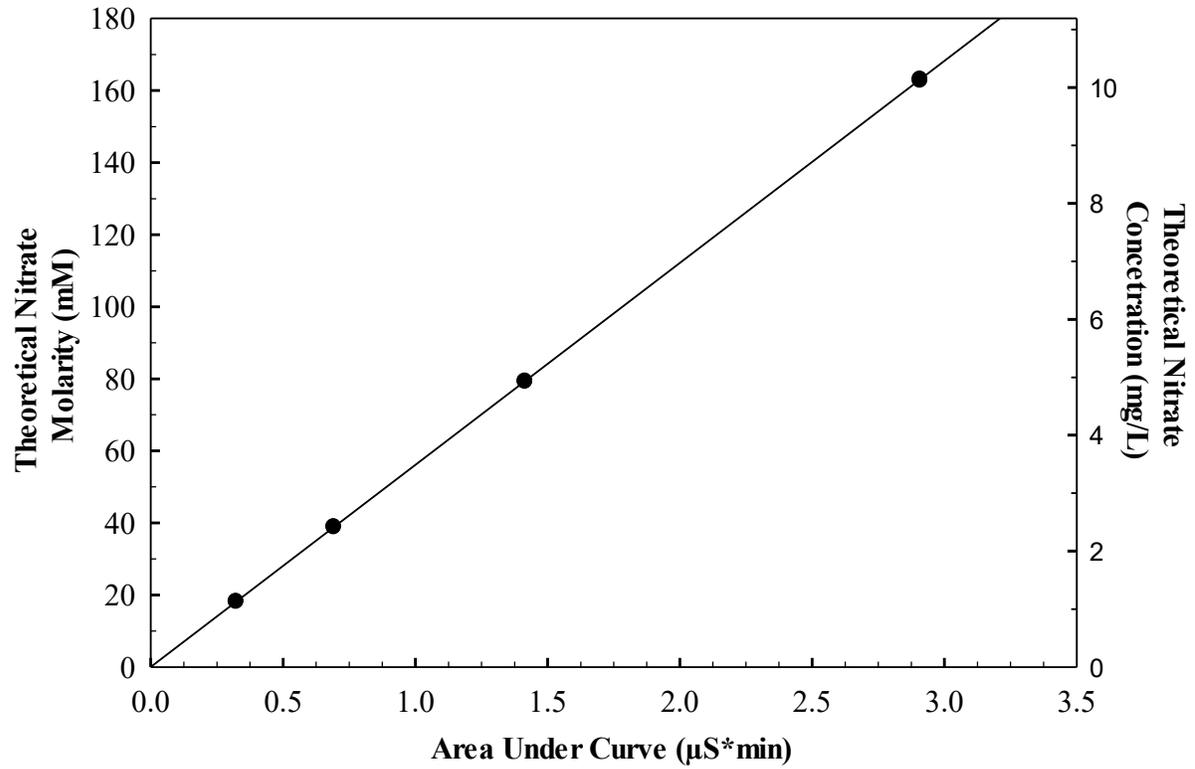


Figure 3. Linear Calibration Curve for Nitrate ($R^2 = 1$)

CHAPTER 3

PERMEABLE REACTIVE CONCRETE

Permeable reactive concrete (PRC) specimens were tested for nitrogen-nitrate ($\text{NO}_3\text{-N}$) and orthophosphate-phosphorus ($\text{PO}_4\text{-P}$) removal and retention in batch reactor experiments. Sulfate concentrations, of which leached from the PRC specimen, were measured after each test as well. To eliminate potential errors, preparation and curing of the specimen occurred in sequential steps to ensure each mixture and specimen were handled identically. Additional testing included compressive strength and void content. This chapter is outlined to discuss the methods and results.

Concrete Preparation and Mixing

Five PRC mixture proportions were prepared for testing the removal rates of orthophosphate and nitrate-nitrogen as shown in Table 1. Permeable concrete specimens were designed to have similar characteristics for objective comparisons of the influence on replacement materials on nutrient removal. Cement was replaced by either 25% ASTM C618 Class C fly ash from La Cygne, KS, USA (F25-P), 25% DWTR from WaterOne Kansas City, MO, USA (D25-P), 3% activated carbon (A3-P) or 3% titanium dioxide P25 from Degussa, Germany T3-P (ASTM 2017a). Chemical properties of the cement, fly ash, and DWTR are shown in Table 2. Ohtani et al. (2010) evaluated Degussa P25 for chemical composition and determined mostly anatase crystalline structure followed by rutile and little amorphous phases. An 18 M Ω Type I deionized (DI) water in accordance to ASTM D1193 was used as the mixing water to avoid contamination (ASTM, 2011). An 8mm limestone from Randolph, MO was used as a coarse aggregate which was dried before mixing. The porosity of the freshly mixed

concrete was fixed at 25% for each mixture proportion. Mixture proportions used in the current research are part of a series of treatment technologies, permeable reactive concrete (PRC), similar to that of Holmes et al. (2017) and Ramsey et al. (2017). PRC cannot be classified as pervious concrete as it does not meet the technical criteria (ACI 522.1-13). PRC mixtures were designed to maximize available surface area, cement porosity, and reactive material, consequently reducing the cement paste thickness needed for durability (ACI, 2011); therefore, the primary purpose of PRC is water treatment technology, not structural.

Table 1. Permeable Reactive Concrete Mixture Proportions

Mixture	Cement (kg/m³)	Cementitious (dry) (kg/m³)	Coarse Aggregate (kg/m³)	Mixing Water (kg/m³)
O-P	265	0	1500	110
F25-P	200	65	1490	110
D25-P	260	10	1500	110
A3-P	200	65	1485	110
T3-P	260	10	1500	110

Table 2. Chemical Composition of Cementitious Materials

Compound	Portland Cement (%)	Class C Fly Ash (%)	DWTR (%)
SiO ₂	20.49	40.71	5.84
A ₂ O ₃	4.26	18.99	1.55
Fe ₂ O ₃	3.14	6.05	0.78
CaO	63.48	20.1	43.93
MgO	2.11	4.82	4.24
SO ₃	2.9	0.83	0.31
Na ₂ O	0.18	1.46	-
K ₂ O	0.47	0.65	0.2
CO ₂	1.48	0.0	-
CaCO ₃	3.41	0.0	-
P ₂ O ₅	-	-	0.1
LOI*	2.2	0.08	42.59

*LOI (loss on ignition)

Freshly mixed PRC was prepared and cured in accordance to ASTM C192 (ASTM, 2016). All SCMs were thoroughly mixed with the portland cement in a dry condition, except for the DWTR which was mixed at an in-situ moisture content of 59%. The freshly mixed PRC was placed into 100 mm x 200 mm plastic molds in 3 tamped layers. Compaction effort was applied to place the specified mass (± 0.1 grams) into the plastic mold, such that 25% voids would be achieved. Specimens were then stored in the sealed molds for 24 hrs. Specimens were then stripped from the molds and allowed to cure 6 days in a cure room at 100% humidity and 23°C. Specimens were then allowed to dry for 14 days in a 50% relative humidity, 23°C environmental chamber. A cured specimen for each mixture proportion is shown in Figure 4.

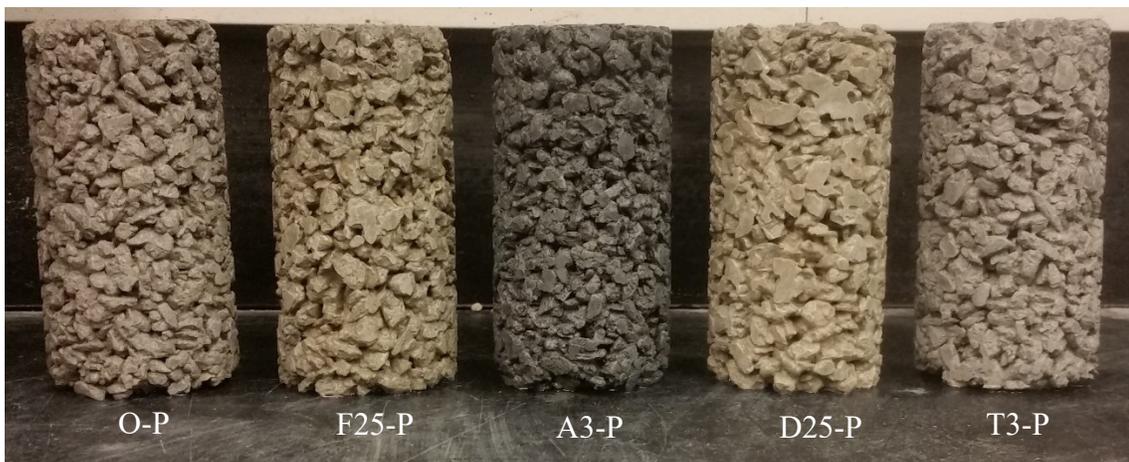


Figure 4. Cured PRC Specimens

Concrete Mechanical Properties

Hardened pervious concrete specimens were tested for total void content and density following ASTM C1754 (ASTM, 2012a). Water permeable voids were determined by sawing 100 mm x 200 mm specimens with a diamond blade wet saw. Specimens were coated in black sharpie to highlight the aggregate and cement paste, then a mixture of TiO₂ and petroleum jelly was pressed into the voids. The sawed surface was scraped clean to reveal the black sharpie and

images were taken, then analyzed in binary colors as shown in Figure 5. Compressive strength was determined in accordance with ASTM C29 on 200 mm x 400 mm specimen (ASTM 2017b). Specimens were sulfur capped following ASTM C617 (ASTM, 2015a).



Figure 5. PRC Specimen Formatted to Binary Colors

Jar Testing and Column Leach

Removal rates and retention of nitrate-nitrogen and orthophosphate-phosphorus were determined for the 5 PRC mixture proportions using bench scale batch reactor testing. Specimens were suspended by non-reactive nylon string as shown in Figure 6. Batch reactors were continuously stirred for 72 hrs at 400 rpm. Specimens were individually placed in a continuously stirring jar test containing 750 ml either nitrate-nitrogen or orthophosphate-phosphorus solution. Nitrate-nitrogen was used in the form of dissolved potassium nitrate (MP Biomedicals, LLC, CAT NO. 191428, LOT NO. 9328K) at concentrations of 2.2 mg, 1.1, or 0.2 mg $\text{NO}_3\text{-N/L}$ (35, 18, or 3 mM $\text{NO}_3\text{-N}$). Orthophosphate was used in the form of potassium phosphate (Fisher Scientific, BP 362-800, LOT 141262A) 3.3, 1.6, or 0.3 mg $\text{PO}_4\text{-P/L}$ (34.7, 16.8, 3.2 mM $\text{PO}_4\text{-P}$). ASTM Grade I DI water was used. The nutrient concentrations ranged at least one order of magnitude for isotherm models and reflected state regulations for reservoirs of the state of Missouri (State of Missouri, 2014).

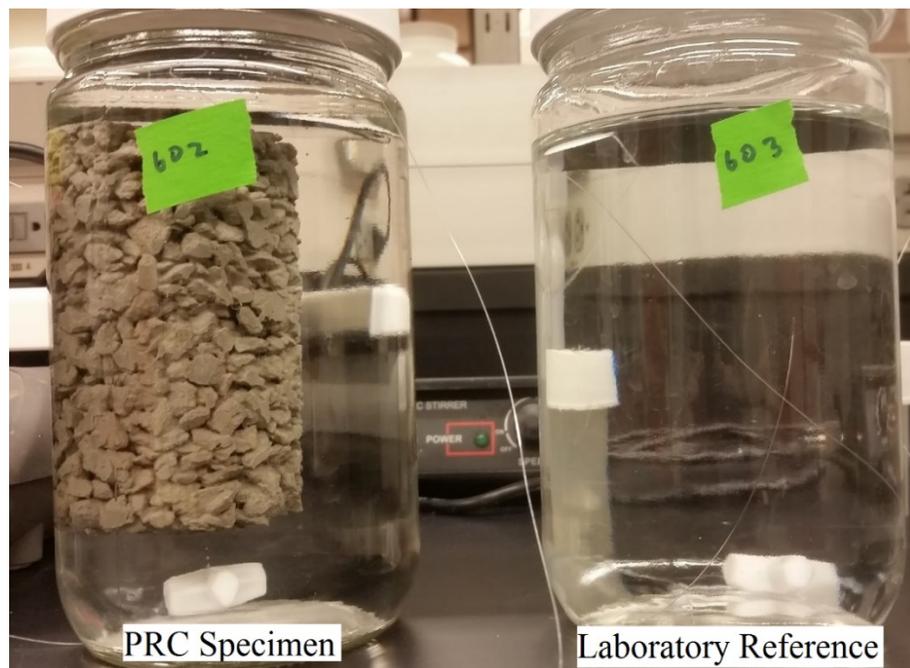


Figure 6. Batch Reactor Testing for PRC

Once each 72 hr jar test was complete, the PRC specimens were allowed to drip dry over the jar. Initial jar testing specimens were placed in the environmental chamber for 28 days, then retested in 750 mL of DI water for 72hr leach testing similarly completed as the initial batch reactor test. For each mixture, a fresh specimen was tested in triplicates for each of the 6 nutrient solutions (3 NO₃-N and 3 PO₄-P). Three specimens for each mixture proportion were jar tested in 750 mL of DI to establish background concentrations of NO₂-N, NO₃-N, and PO₄-P. One laboratory reference (LR) was jar tested for each of the corresponding stock solutions (NO₃-N, PO₄-P or DI water) was concentrations and set of batch reactor tests.

After each batch reactor test, pH, temperature, and total conductivity were measured. The pH was adjusted for each effluent sample using 1.0 N HCl solution to a pH below 8 to be consistent with the ion chromatography reagents and to reduce peak interference. Effluent samples were stored in accordance with phosphate and nitrate standards until IC analysis was available (Clesceri et al., 1989). Anions were measured in triplicate samples for all batch testing effluents using an Ion Chromatography System (ICS-90) with an Automated Sampler (AS40). IC hardware included a 4 mm x 250 mm AS23 anion column (P/N 064149), AG23 guard column (P/N 064147), AMMS 300 suppressor (P/N 064558), D5 stabilizer, and a 50 µL injection loop. IC reagents included 4.5 mM Sodium Carbonate/0.8 mM Sodium Bicarbonate Eluent and 2.0N Sulfuric Acid regenerant was used at a flow rate of 1.0 mL/min. Replicated effluent samples were checked for a 5% relative standard deviation (RSD) and additional quality control was followed per EPA Method 300.0 (USEPA, 1993b). Specimens and equipment were handled with no-reactive gloves and laboratory equipment were thoroughly cleaned with ASTM Type I DI water. Glassware was cleaned with a 9N HCl solution to remove any residuals.

Mass removal rates of NO₃-N and PO₄-P were determined for each jar test by comparing the post jar test results to the corresponding LR solution. Background concentrations were subtracted from the reference samples. Mass leached were determined for NO₃-N and PO₄-P by comparing the mass initially removed to the mass leached. Triplicate results for each mixture proportion at each concentration were subject to an RSD of 15%. pH was determined by averaging hydronium concentrations between similar jar testing series.

Concrete Mechanical Properties

Table 3 shows the average density, water permeable voids, bulk voids, and paste porosity for each PRC mixture proportion. The water permeable voids are statistically similar ($P > 0.05$), per design. The bulk voids are similar for all mixture proportions, except D25-P ($P < 0.05$). The decreased bulk void content of D25-P is due the in-situ moisture content of 59% of the DWTR prior to the mixing of PRC. The greater paste porosity of D25-P specimen are a result the evaporation of excess water which was not necessary for the formation of hydration products. The average density were all statistically similar ($P > 0.05$) for all mixture proportions, per design. Similar water permeable voids and density were controlling design parameters due to the potential effects on adsorption rate. Compressive strength at 7-, 28-, and 90-days was determined to be 7.9 ± 0.5 MPa, 9.3 ± 0.9 MPa, and 10.0 ± 0.7 MPa for O-P.

Table 3. Average Density and Bulk Void Content for Pervious Concrete Mix Designs

Mixture Proportion	Water Permeable Voids	Bulk Voids (Scanner)	Paste Porosity	Average Density (kg/m³)
O-P	33.2%	28.1%	5.1%	1810.0
F25-P	32.9%	26.6%	6.3%	1810.0
A3-P	33.3%	28.4%	4.9%	1804.8
D25-P	32.7%	23.5%	9.2%	1800.0
T3-P	33.5%	27.8%	5.7%	1804.4

pH and Conductivity

The effluent pH and conductivity for jar testing and leach testing are shown in Figure 7 and Figure 8. Each mixture had statistically similar effluent pH ($P > 0.005$). A minor decrease in pH was observed after leach testing ($P = 0.001$), likely due to the loss of Ca and Mg ions in the initial jar test. F25-P had a lower leaching test pH and conductivity than the other mixture proportions ($P < 0.05$). The laboratory reference had a pH below 6 due to the initial pH of the deionized water. Effluent conductivity varied among the mixture proportions. T3-P had the greatest effluent conductivity followed by similar results for O-P, D25-P, and C-P. Leach testing resulted in significantly lower conductivity ($P < 0.001$). A decrease in conductivity is not expected to decrease removal, however, since the pH was not significantly decreased.

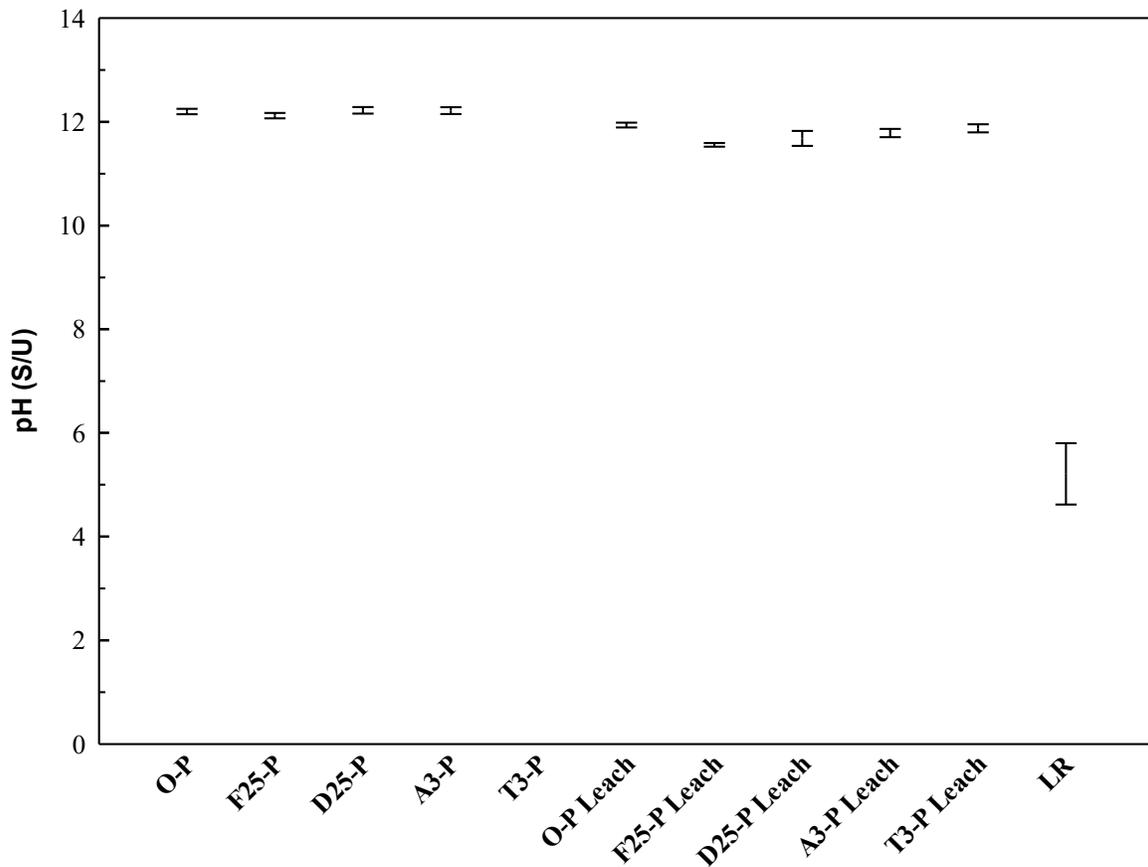


Figure 7. Effluent pH after Batch Reactor Testing (One Standard Deviation)

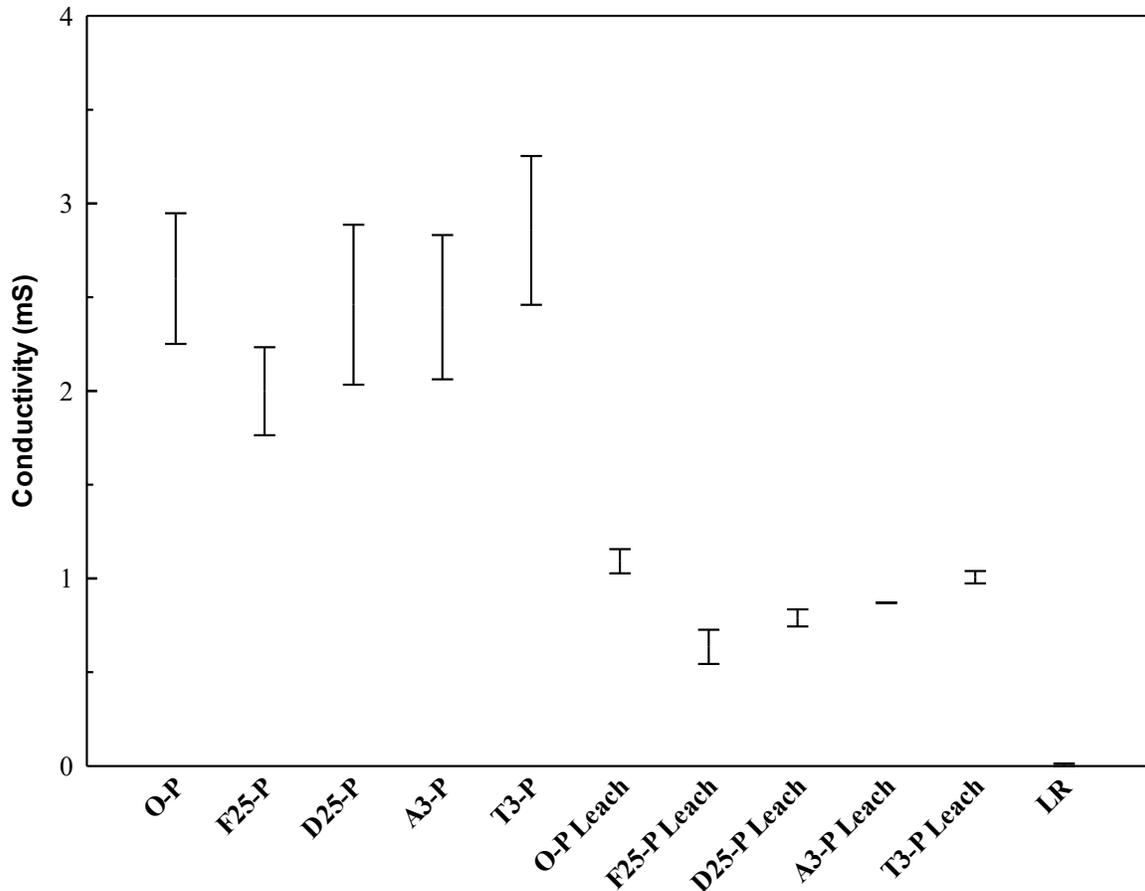


Figure 8. Total Effluent Conductivity after Batch Reactor Testing (One Standard Deviation)

Nitrate-nitrogen Removal

Figure 9 shows the percent and mass removal rates for the PRC specimen. D.25-P resulted in negative for $\text{NO}_3\text{-N}$ removal rates, so the results were not included in the figure. An average of $77 \pm 6.5 \mu\text{g NO}_3\text{-N} / \text{g}$ of DWTR (1.1 mg of $\text{NO}_3\text{-N}$) leached from the specimens in DI, resulting in as great as 1.2 mg of $\text{NO}_3\text{-N}$ increases in additional tests. O-P and T3-P had greater mass removal rates than the F25-P and A3-P mixtures with F25-P being the lowest ($P > 0.05$). The O-P mixture removed as much as 0.95 mg of $\text{NO}_3\text{-N}$ with an average mass removal of 53%. Although powered activated carbon has been used to remove $\text{NO}_3\text{-N}$

(Bhatnagar and Sillanpää, 2011; Grace et al., 2016; Loganathan et al., 2013), replacing OPC with activated carbon resulted in lower removal rates. There may have been a chemical reaction with the activated carbon and the hydrations products that hindered the OPC removal mechanisms.

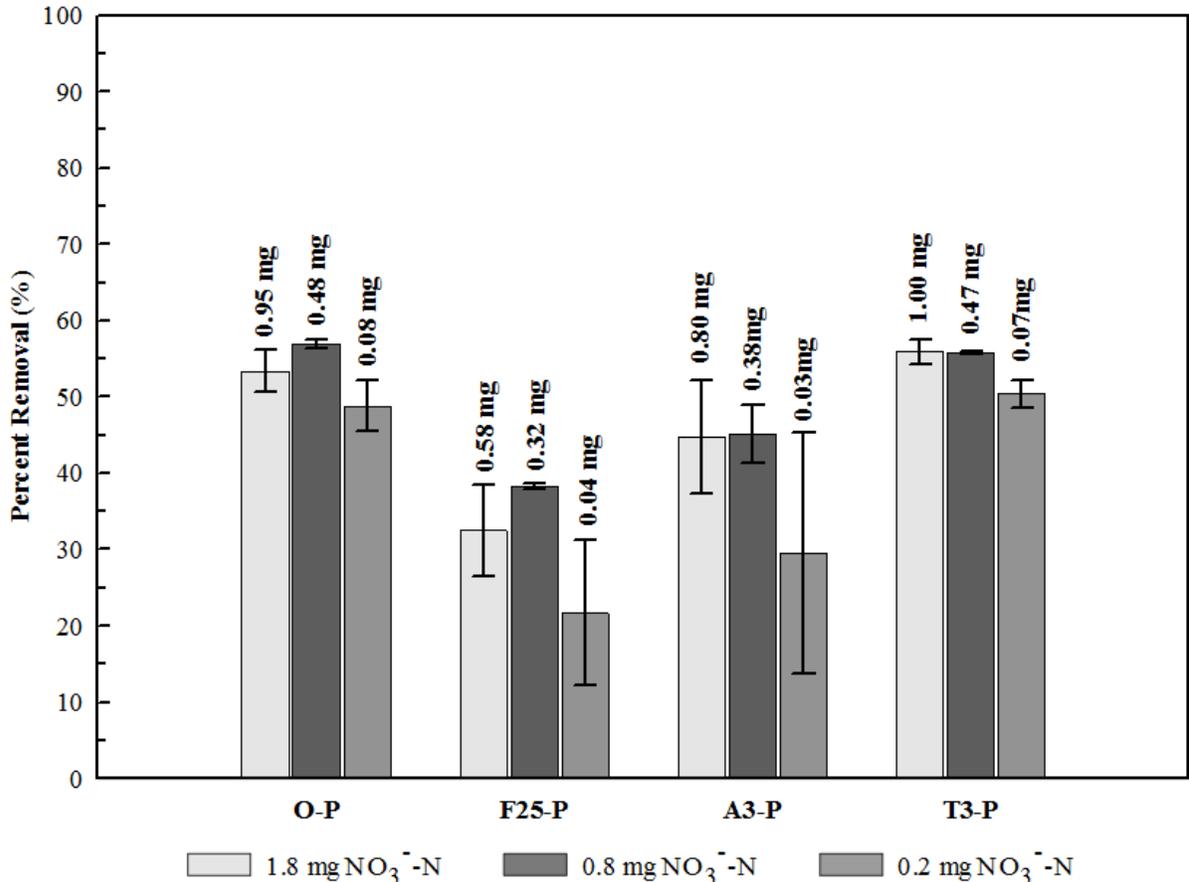


Figure 9. Nitrate-nitrogen Percent Removal for Jar Testing (One Standard Deviation)

There was not a definitive correlation between initial concentration and mass removal percentages for any of the mixtures which was similar to what was found for cadmium, lead and zinc (Holmes et al, 2017). Further investigation was completed with adsorptions isotherms as shown in Figure 10. The adsorption isotherms further demonstrate how the O-F and T3-F had preferential removal when compared to F25-F and A3-F. Adsorption isotherms were

normalized to freshly mixed cementitious mass for each specimen. Reactions most likely occurred in the cementitious structure of the PRC. Freundlich, Langmuir, and linear isotherms were fit to the data as shown in Table 4. Isotherm regressions indicate linear adsorption isotherms within the range of data tested. Although the R^2 value slightly increased from linear to Freundlich for F25-P and A3-P, there was not a significant difference from the linear fit. Since no additional testing was performed after leach testing, it is unknown how well the specimens may continue to remove $\text{NO}_3\text{-N}$.

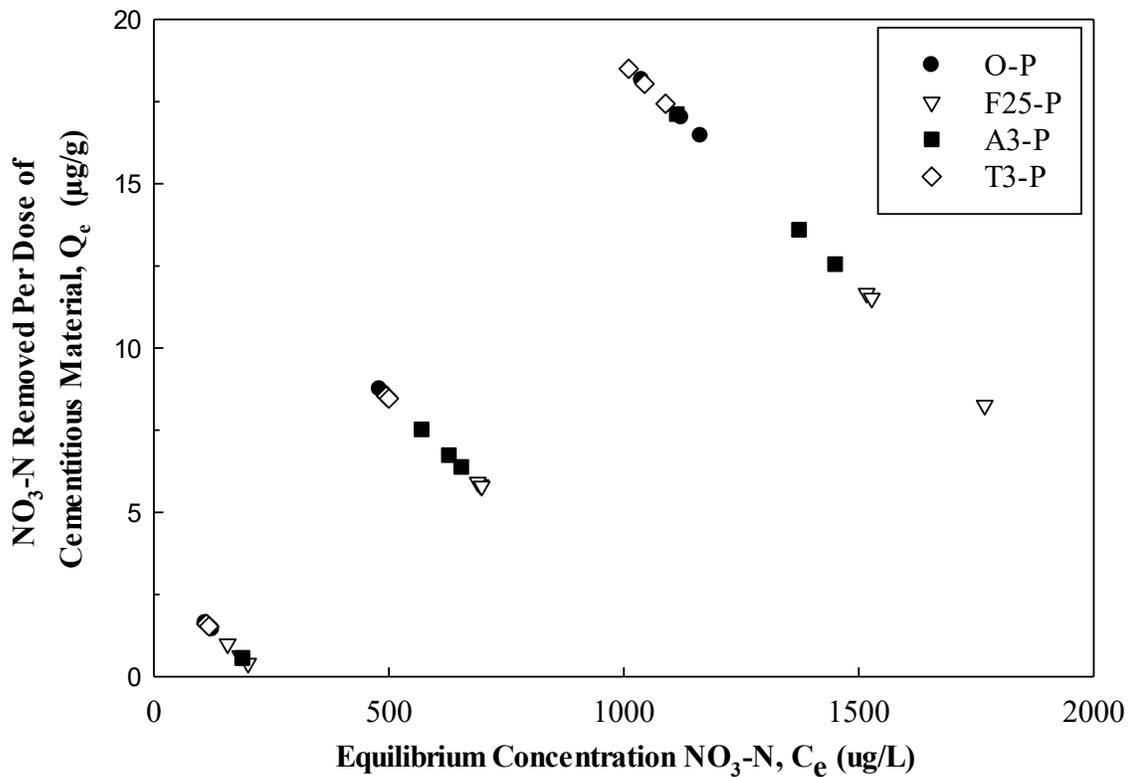


Figure 10. Adsorption Isotherm for Nitrate-Nitrogen onto PRC

Table 4. Nitrate-Nitrogen Isotherm Coefficients

Mixture	Linear		Freundlich			Langmuir		
	k	R^2	k	n	R^2	k	q_m	R^2
O-P	0.016	0.973	0.030	0.91	0.977	2.4E-04	82	0.981
F25-P	0.007	0.853	0.025	0.82	0.873	3.6E-04	28	0.892
A3-P	0.011	0.825	0.018	0.93	0.828	1.9E-04	68	0.837
T3-P	0.017	0.990	0.016	1.01	0.991	4.0E-06	4312	0.990

Nitrate-nitrogen Leached

The percent and mass of NO₃-N retained during leach testing is shown in Figure 11 and a net nitrate-nitrogen removal was determined as shown in Figure 12. In general, the percentage and mass of NO₃-N retained was greater for greater initial concentrations, except for some comparisons to the 0.8 mg NO₃-N and A3-P mixture. There was no statistical difference ($P < 0.05$) in percent retained for A3-P among the different initial concentrations, probably due to the standard deviation at 0.2 mg NO₃-N. The F25-P mixture leached the greatest mass of NO₃-N ($P > 0.05$). For each individual initial concentration, the A3-P mixture retained a statistically similar ($P > 0.05$) percent of NO₃-N as the O-P and T3-P mixtures, despite removing less NO₃-N initially. Additionally, a statistically similar mass of NO₃-N leached from A3-P, O-P and T3-P specimen as shown in linear desorption isotherm (Figure 13). The similarities between mass leached and percent retained by A3-P, O-P, and T3-P, despite dissimilar initial removal rates, may indicate how a baseline of leachable NO₃-N from PRC regardless of the materials used or how multiple mechanisms of removal are present in which one is not as permanent as others. Figure 13 further demonstrates how there is a linear trend between mass of NO₃-N leached and initial mass removed within the range of initial concentrations tested and how F25-P leached a greater mass of NO₃-N, despite removing less initially.

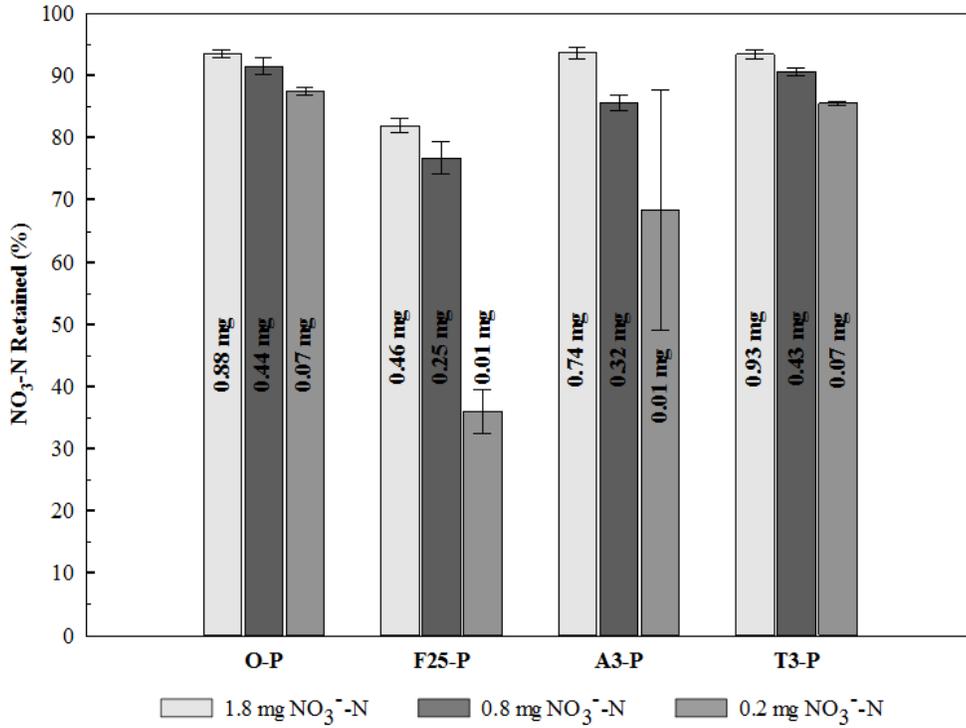


Figure 11. Percent of Initially Removed Nitrate-Nitrogen Retained During Leach Testing of Permeable Reactive Concrete Specimen (One Standard Deviation)

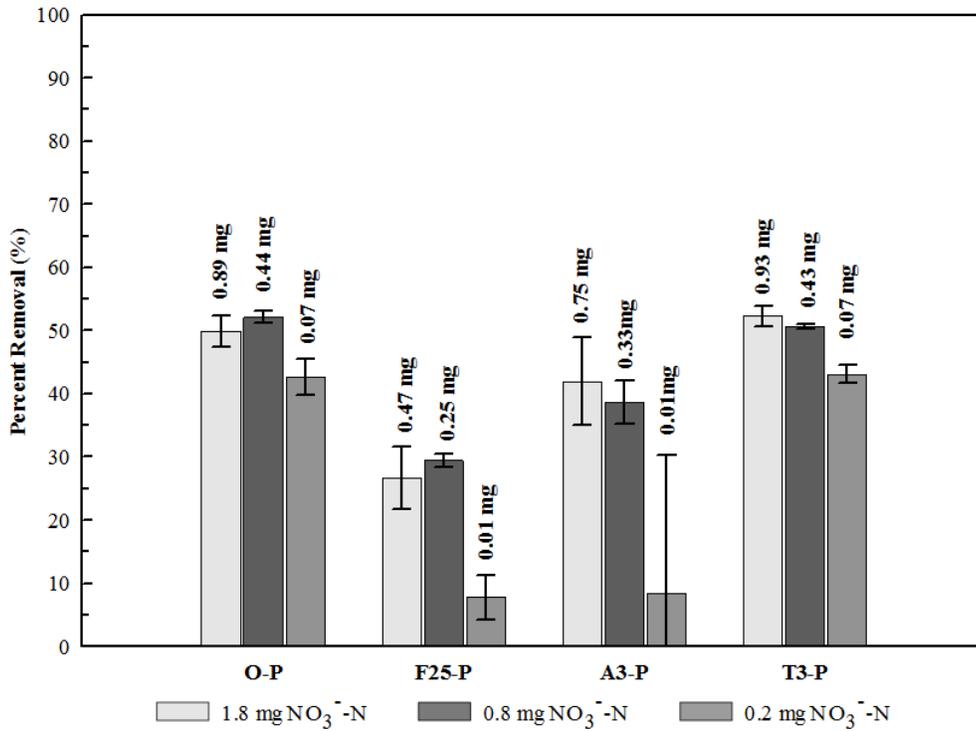


Figure 12. Net Nitrate-nitrogen Percent Removal Post Leach Testing (One Standard Deviation)

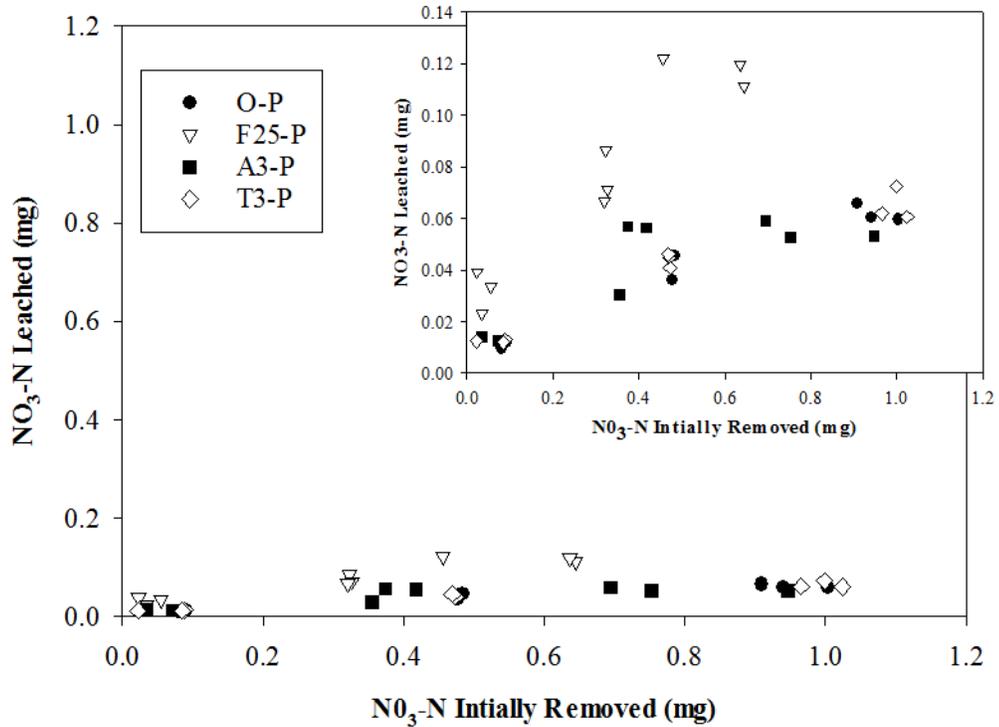


Figure 13. Desorption Rate for Nitrate-Nitrate from Permeable Reactive Concrete

The literature does not discuss NO₃-N leaching from WTR, whether derived from drinking or waste water, often, especially from where it may originate. Excess NO₃-N may leached or been oxidized from organic material in the LOI fraction of the DWTR used in the current reserach. Organic material and nitrogen species have been found in alum-based drinking water treatment waste (Ippolito et al., 2003). Gallimore et al. (1999) and Ippolito et al. (2003) found NO₃-N as the majority of nitrogen species in alum-based drinking water treatment waste. Background NO₃-N concentrations were observed in six alum-based drinking water treatment sludges by Hidalgo et al. (2017). Nitrogen species were also found in an alum sludge reuse investigation (Maiden et al., 2015). On the other hand, repeated studies have shown little to no phosphorus or nitrogen in lime, alum, and ferric sludges from Florida water treatment plants (Townsend et al., 2001). The composition of a WTR is related to source of

water and treatment operating conditions, hence differences in leaching constituents are plausible (Babatunde and Zhao, 2006). NO₂-N concentrations were below 0.02 mg for the specimens tested in DI water and all other jar testing. Since NO₂-N background concentrations were similar to that of the jar testing, no NO₃-N was reduced in the batch reactor system. In addition to NO₂-N monitoring, no biological activity was noted in the jar test, reducing the likelihood that dissimilatory nitrate reduction to NH₃, denitrification or anaerobic NH₃ oxidation could occur (Denk et al 2017). While other nitrogen reducing species exist, it would be highly unlikely for NH₄-N to exist in the absence of growing bacterial colonies. Several samples were analyzed for NH₃ using colorimetry standard methodology EPA Method 350.1 where a non-detectable amount was found (USEPA, 1993c).

Orthophosphate-phosphorus Removal

Flocculants were observed in jar testing effluent for the PO₄-P series. Free calcium hydroxydes were suspected to react with the dissolved phosphorus and form calcium phosphate precipitants as found in other studies (Lu et al., 2009). Flocculants began to dissolve once the samples were titrated with 1N HCl to a pH below 8. The F25-P mixture, however, created no visible flocculants during the batch reactor test until after the effluent samples were titrated. Figure 14 shows the mass and percent removal rates for each mixture proportion. The T3-P and F25-P had the greatest PO₄-P removal rates ($P < 0.05$). There was no statistical difference ($P > 0.05$) for 0.2 mg PO₄-P among each mixture proportion. For all designs, PO₄-P removal rates decreased with increasing concentration. Figure 15 shows a linear adsorption isotherm for each mix design normalized to cementitious mass. Linear, Freundlich, and Langmuir isotherm parameters are shown in Table 5. Isotherm models were not significantly different for each of the mixtures proportions with all R² values greater than 0.98. No observable PO₄-

P leached from the specimen after the greatest treatment; therefore, the lower concentrations were not tested. The lack of PO₄ leaching was consistent with recycled concrete tested by Molle et al (2002).

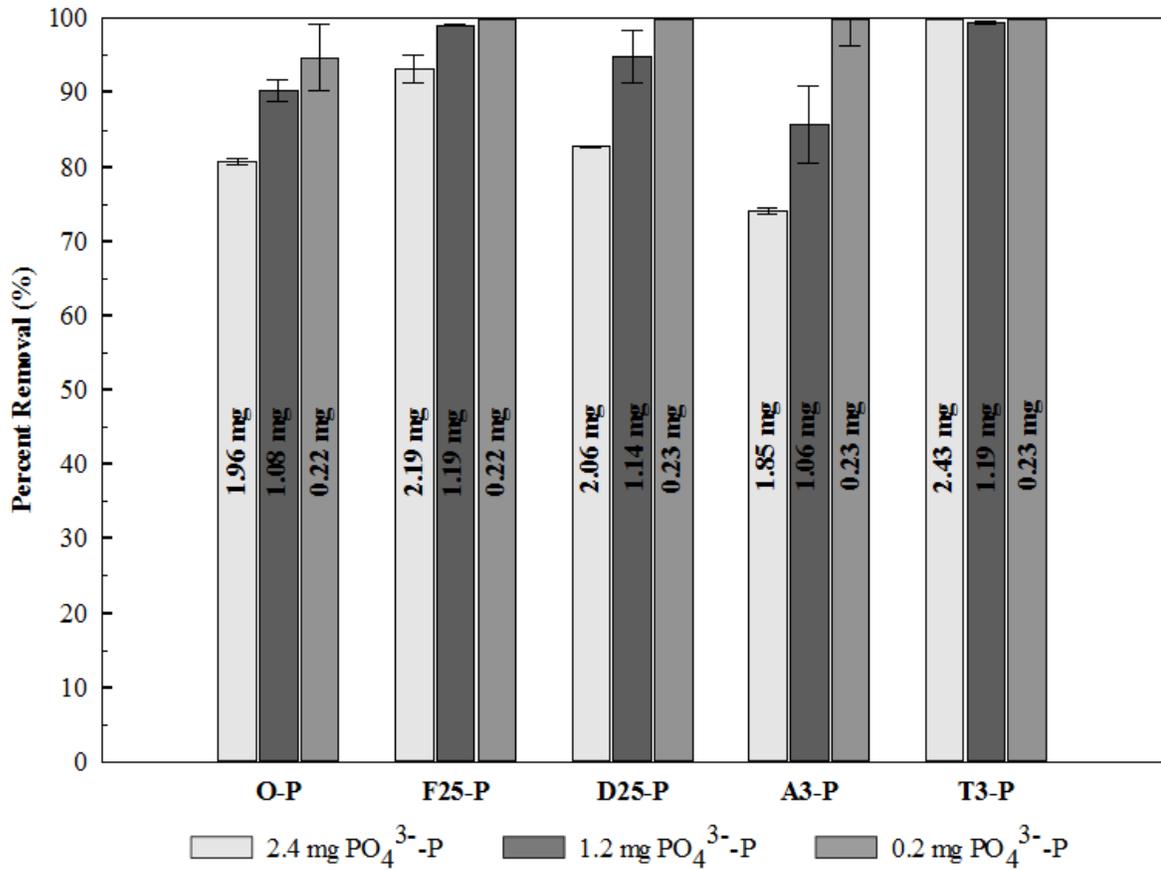


Figure 14. Orthophosphate-phosphorus Percent Removal for Batch Reactor Tests (One Standard Deviation)

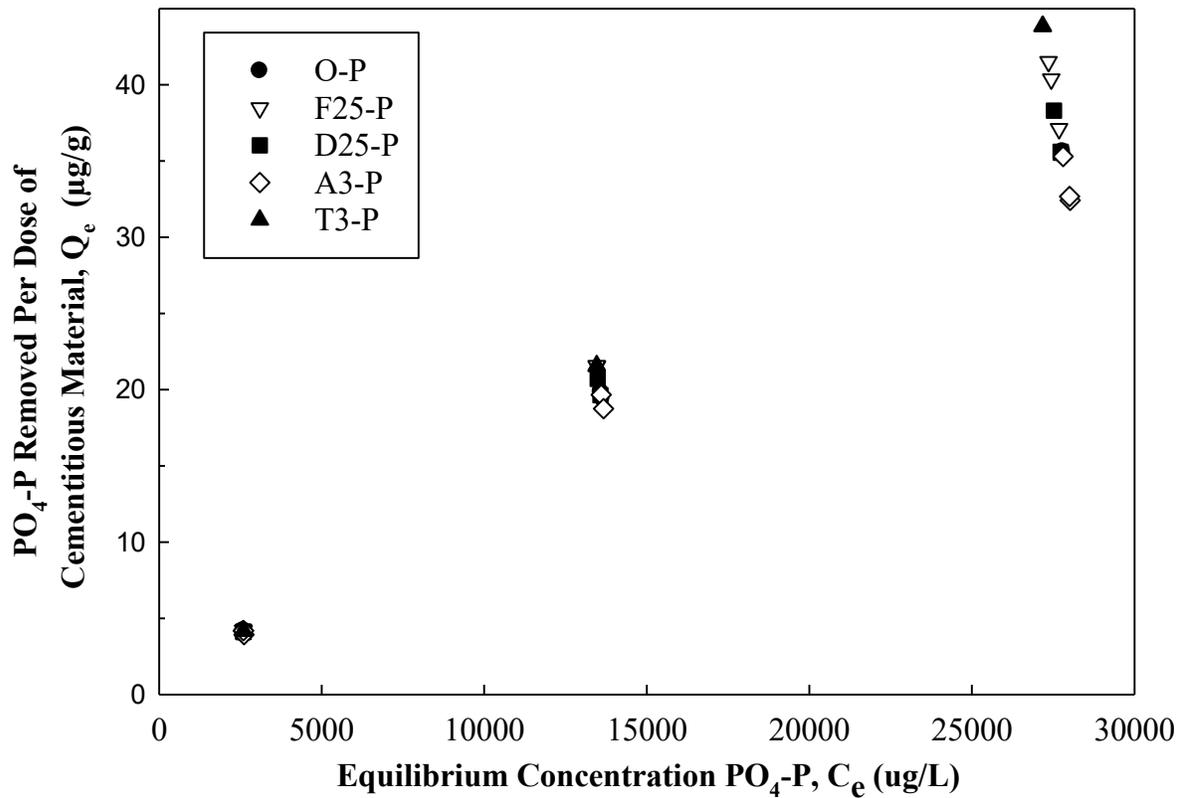


Figure 15. Adsorption Isotherm for Orthophosphate-phosphorus onto Permeable Reactive Concrete Specimen

Table 5. Orthophosphate-Phosphorus Isotherm Coefficients

Mix	Linear		Freundlich			Langmuir		
	k	R ²	k	n	R ²	K	q _m	R ²
O-P	0.0013	0.992	0.0046	0.874	0.999	1.0E-05	161	1.000
F25-P	0.0015	0.989	0.0041	0.899	0.992	8.1E-06	218	0.993
D25-P	0.0013	0.989	0.0048	0.875	0.995	1.0E-05	167	0.996
A3-P	0.0012	0.982	0.0067	0.832	0.994	1.4E-05	116	0.995
T3-P	0.0016	1.000	0.0015	1.006	1.000	-4.4E-07	-3597	1.000

Soto-Pérez and Hwang (2016) reported that phosphate removal increased with increasing concentrations in a column experiment with fly ash and OPC permeable concrete. The permeable concrete with fly ash resulted in lower PO₄-P removal, although the decrease

was not consistent with the amount of fly ash added as the 10% fly ash replacement resulted in lower removal than the 35% replacement. Reduction in PO₄-P removal with the addition of fly ash and slag was also observed by Agyei et al., (2002). Soto-Pérez and Hwang (2016) experiment had shorter contact time (~2 hours) and greater PO₄-P concentrations (26.5 ± 11.6 mg PO₄-P /L) than the current study. Little contact time with the permeable concrete resulted in a lower effluent pH (10.21 ± 0.20 for control and 9.95 ± 0.12 for 35% fly ash replacement) than currently observed. Equilibrium for phosphate removal by fly ash has been reported up to or over 24 hours (Li et al., 2006). On the other hand, Park et al., (2008) found equilibrium was reached after 12 hours. The concrete was also cured for 28 days (opposed to 7 days) in Soto-Perez and Hwang (2016) which may have affected the removal of the fly ash mix design due to a reduction in available calcium hydroxide. Ugurlu and Salman (1998) reported removal of PO₄-P by powdered fly ash decreased as the initial concentration increased in 24 hour batch testing. Hence, phosphorus removal rates with respect to initial concentration must be dependent on contact time or pH by enhancing the formation of less soluble calcium phosphate structures as discussed by Sikdar (2007). Since dissolved PO₄-P was measured with no filtration, adsorption or precipitation onto the PRC surfaces is likely the primary mechanism of removal. Although Lu et al., (2009) suggested that nearly 70% of PO₄-P removal was caused by precipitation in unhydrated fly ash.

Soluble Sulfate

As a result of limited jar testing equipment, batch reactor experiments for each concentration were tested on separate days and were consequently different ages when tested. Although the PRC specimens had the same cure duration and were kept in a suspended state in the environmental chamber, total specimen age varied between 19-47 total days. An average

mass of sulfate leached for each mixture proportion during the 72 hr jar tests are shown in Figure 16. The least amount of SO₄ leached from the T3-P and O-P specimens. The greatest amount of SO₄ leached from F25-P, A3-P, and D25-P, respectively. The addition of supplementary materials increased the SO₄ leached in the current study. A positive Pearson correlation ($P < 0.05$) was determined between sulfate leached and total duration in the EC for O-P, D25-P, and F25-P mixtures. Increases in soluble SO₄ may indicate phases changes in the in the EC.

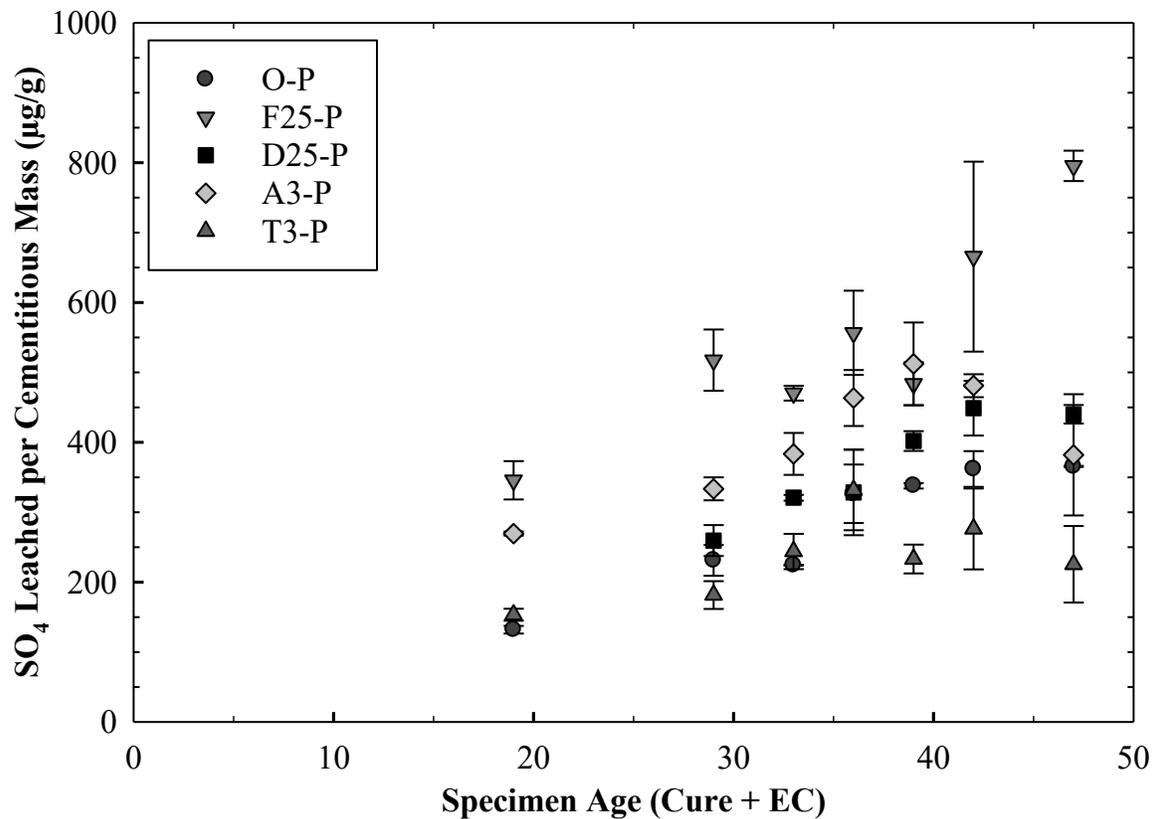


Figure 16. Sulfate Leached from PRC Specimen During Batch Reactor Testing with Respect to Total Specimen Age (One Standard Deviation)

Conclusions

Five PRC mixture proportions were tested for nitrate-nitrogen removal, orthophosphate-phosphorus removal and sulfate leachability utilizing batch reactor testing. PRC was determined to have the capacity to remove and retain dissolved, inorganic nutrients, during the 72 hr batch reactor tests. No correlation between nitrate removed and sulfate leached was determined but a correlation between specimen age and soluble sulfate was. A linear isotherm was determined for the range of nitrate-nitrogen and orthophosphate-phosphorus concentrations tested. The additions of supplementary materials decreased the nitrate removal capacity, except for titanium dioxide. Fly ash significantly decreased the nitrate and retention capacity of PRC. The DWTR residual leached nitrate, resulting in negative removal rates. Activated carbon may have negatively influenced removal by reacting with OPC hydrates. The mass of nitrate leached was consistent with the control, titanium oxide and activated carbon mixtures. Mass of nitrate leached increased initial mass removed. The addition fly ash further decreased the PRC performance by greatly increasing the mass of nitrate leached. The addition of fly ash and titanium dioxide increased the orthophosphate removal of PRC, although the addition of fly ash has been known to decrease removal in other studies. Differences in phosphate removal may be due to contact time or differences in final effluent pH. Orthophosphate mass removal increased with increased initial concentration while percent removal decreased with increasing concentrations. Further improvements could be made on the current study by testing a greater range of initial nutrient concentrations to further characterize adsorption isotherms. With the linear isotherms determined in the current range of concentrations tested, the effect of specimen dose on removal could be the next step.

CHAPTER 4

SPECIMEN AGE AND FLUSHING

Upon reviewing the variable amount of sulfate leached from the PRC in initial batch reactor testing, additional experiments were designed to investigate the amount of SO_4 leached NO_3 removed. Park et al. (2008) postulated a relationship between NO_3 removal and SO_4 leached from permeable concrete. Additionally, no research has investigated the effect of aging permeable concrete and nutrient removal. Therefore, the control PRC specimen were tested for $\text{NO}_3\text{-N}$ removal after varying cure times and ‘flushing’.

Methods

O-P specimens were mixed and cured in accordance ASTM C192 and as discussed in the previous chapter (ASTM, 2016). Two specimens were cured for 7 days, one for 14 days and one for 28 days before drying for an additional 14 days in an environmental chamber. Individually, specimens were then placed in Spectra/Por 6-8 kD dialysis tubing (P/N 142110) and suspended in 3000 mL of continuously stirred of ASTM Grade I DI water as shown in Figure 17. The dialysis tube provided a beneficial environment to strip SO_4 from the PRC specimen by permitting SO_4 to exit the tubing but prohibiting SO_4 from entering the tubing because of the molecular selectivity of the molecular shape and ionic charge. The DI water was replaced every day for 36 days, except for the solution that was retained in the dialysis tube. The SO_4 that leached from the PRC specimens was measured for each flush following the same method as described for the jar testing effluent. After the 36 days, specimens were allowed to dry in an environmental chamber for at least 14 days until further testing. After the

specimens were dried, all specimens were jar tested in 2.3 mg NO₃N /L (35 mM NO₃-N) in the same procedure as described in the previous batch reactor testing.



Figure 17. Anion Leaching for O-P Specimen Aged Either 7, 14, or 28 Days.

Soluble Sulfate

The anion leaching tests resulted effluent pH and conductivity that was not significantly different ($P > 0.05$) amongst the 7, 14, and 28-day curing durations. The initial pH was around 11 and slowly decreased to 10.6 over the 36-day flush. pH trends in the current study are consistent with trends by permeable pavement systems or permeable concrete in other studies (Molle et al., 2002; Park and Tia, 2003; Park et al., 2008). The conductivity of the effluent started between 140-250 μS with older specimens resulting in lower conductivity. Final effluent conductivity values were between 65-75 μS at the end of the 36 days. A decrease in conductivity is an indicator of the dissolved constituents (SO_4 , Ca^{+2} , etc.) leaching from the PRC.

The mass of sulfate leached from the PRC specimens cured for 7-day (two), 14-day (one) and 28-day (one) shown in Figure 18. Two rates of SO_4 leaching were observed during the duration of the experiment. The first rate was within 250 pore flushes (2-5 days). The second rate continued for the remainder of the experiment. The rates of sulfate leaching observed were representative of Fickian diffusion. Over the 36 days, more sulfate leached from the specimens aged for 7 days than the specimens aged at 14 and 28 days. A greater mass of SO_4 leached from the O-P specimen tested in the previous batch reactor tests, presumably due to longer drying times in the EC. The results may indicate that the rate of SO_4 leaching is not a factor of pore flushes, but of time. The results observed in this study do not imply that a larger total mass of SO_4 would be leached by younger specimen over a longer period of time. Due to a comparable mass of initial SO_4 available in each specimen, the total mass of SO_4 leached could come to an equilibrium at a longer duration. After the amount of SO_4 leached from each specimen, for each cure duration, came to an equilibrium, the total mass leached could be similar for each cure duration.

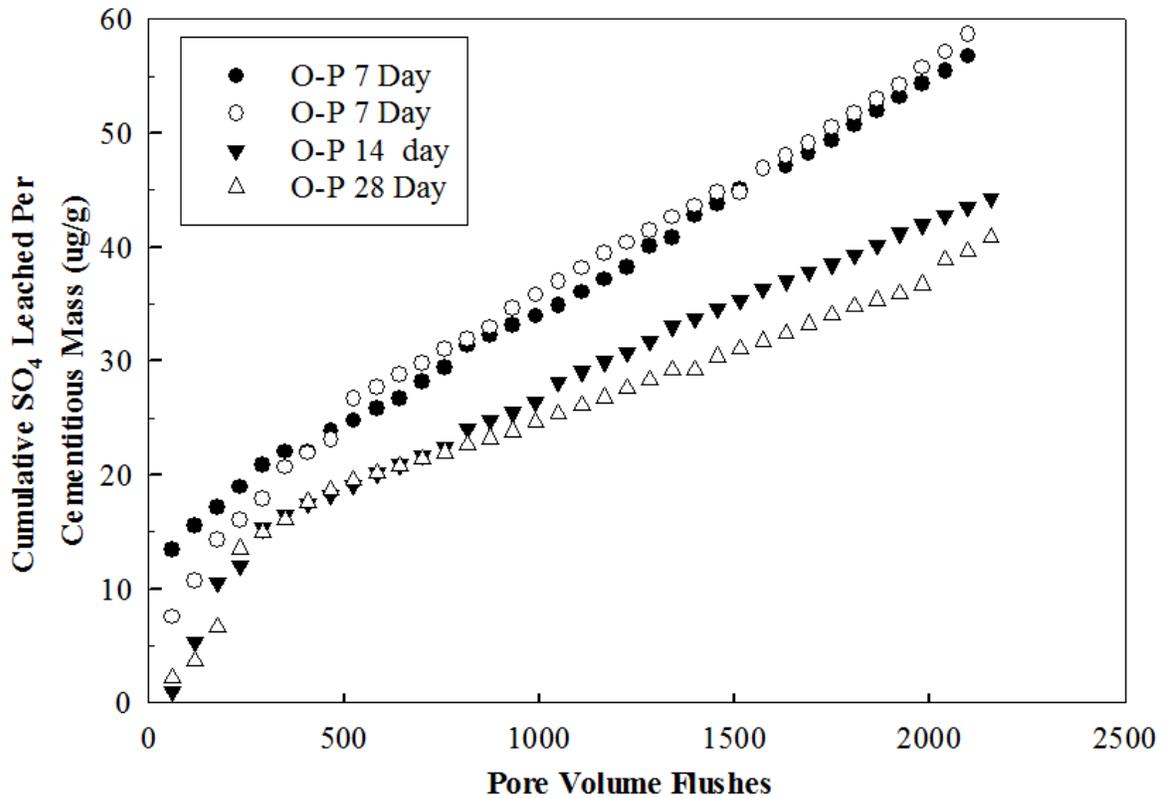


Figure 18. Sulfate Leached from PRC (O-P) Specimens after Flushing with DI Water

Jar Testing Results

Table 6 shows the water quality measurements after the batch reactor testing was complete on the flushed specimen in 2.3 mg NO₃N /L (35 mM NO₃-N). The cure durations presented in Table 6 represent initial cure durations and do not consider any additional curing during the 36 day flushing experiment. Effluent pH and conductivity were similar for all initial cure durations. NO₃-N removal decreased after the 36 day flush when compared to the O-P specimens in the previous batch reactor testing (fresh specimen at 7-day cure). Removal also decreased with increased specimen curing. Caution should be used when considering the data as the younger specimen would have had a greater total age (cure + EC) and the lack of replicates used for each cure duration. Additional sulfate was leached during the batch reactor test with the lower specimen ages leaching a greater amount of sulfate.

Table 6. Flushed OPC (O-P) Jar Testing Results

Cure Time (days)	pH (S/U)	Conductivity (mS)	NO₃-N Removal	NO₃-N Removed per Specimen Dose (mg/g)	SO₄ Leached per Specimen Dose (ug/g)
7	11.53	0.706	42%	8.1	145.8
14	11.54	0.604	38%	7.2	82.4
28	11.50	0.575	28%	5.4	22.9

Conclusions

It was determined that sulfate slowly leaches from the PRC control specimen at two rates; one within the first 250 pore volumes (2-5 days) and another slower rate for the duration of the test. Dialysis tubing and increased pore volumes did not necessary increase the rate of sulfate leached. Older specimens leached less sulfate than the younger specimens. Lower NO₃ removal was observed for flushed specimen when compared to the previous jar testing cure of 7-days, although the specimens were also curing while being flushed. Specimen with greater cure duration removed less NO₃ than younger specimen. Additional testing could be done with longer specimen cure durations and decreased flushing times to prevent the aging of the specimen (perhaps flushing for 100 pore volumes (2 days)). Further adsorption isotherms should be determined for aged/flushed specimen as presented in the previous chapter.

CHAPTER 5

LIGHT-WEIGHT PERMEABLE CELLULAR CONCRETE

The cementitious materials were expected to provide the bulk of nutrient removal in the previous jar testing. To increase the amount of cementitious material, light-weight permeable cellular concrete was used in continuous fixed-bed breakthrough experiments. Light-weight permeable cellular concrete consists of a foaming agent and cementitious pastes only. Eliminating aggregate allows an increase in the reactive cementitious material. Due to the high solubility and mobility of nitrate-nitrogen, and expected performance of phosphate removal, the fixed-bed breakthrough experiments only considered nitrate-nitrogen alone.

Concrete Preparation and Mixing

Five light-weight permeable cellular concrete mixture proportions were tested for nitrate-nitrogen removal in continuous fixed-bed breakthrough experiments. Mixture proportions are shown in Table 7. Mixture proportions for the cellular concrete, “-F”, had varying w/c of either 0.5 or 0.3. The mixtures were either a control OPC at a w/c of 0.5 (O.5-F), OPC at a w/c of 0.3 (O.3-F) or replacements of the OPC at either 50% Skyway Cement 100 Slag replacement (S.5-F), 50% replacement of limestone fines from Sunflower MO, USA (L.3-F), or 100% replacement with Fastrac 300 (C.3-F). Limestone fines, as described by Shah (2012), were used at a gradation below sieve size 0.149 mm. The cellular concrete was prepared similarly to the procedure for wet pre-foamed concrete described in (Amran, Farzadnia and Ali 2015). Wet foam was prepared by diluting Aerix Industries™ Aquaerix™ (Lot # 13243) pervious synthetic liquid foam concentrate 50:1 with ASTM Grade I DI water. The wet density as produced by the foam generator was $36.0 \pm 4.0 \text{ kg/m}^3$. Cementitious

materials were thoroughly mixed together with ASTM Grade I DI water with a high-shear mixture in a five-gallon bucket for a 5 min mix, 2 min rest, 1 min mix. Fresh cement paste was tested with the mini-slump cone test. MasterGlenium 7500 high range water reducer (Batch # 2037345717) was added to the cement paste until a mini-slump was similar to the control mixture (O.5-F) to achieve similar workability and viscosity. Mini-slumps for all cement pastes were within 20% of the control mixture, except for the Fastrac 300 which promotes rapid early age hydration. Cement paste was then mixed into a large mixer and foam was added until the desired density of $400 \pm 8.0 \text{ kg/m}^3$, except for the Fastrac 300 mixture (C.3-F) which had a density of 295.4 kg/m^3 . Freshly mixed cellular concrete density and mini-slump can be found in Table A-1 **Error! Reference source not found.** of the appendix.

Table 7. Permeable Light-weight Cellular Concrete Mixture Proportions

Mix	PC (kg/m^3)	SMC (kg/m^3)	Water (kg/m^3)	HRWR (% of cementitious mass)	Foam (kg/m^3)
O.5-F	270	0	130	0.7	30
S.5-F	130	130	130	0.7	30
O.3-F	310	0	90	1.2	30
L.3-F	150	150	90	1.2	30
C.3-F	0	300	80	1.2	30

Freshly mixed cellular concrete was poured into either 30.5 cm x 30.5 cm x 15.2 cm boxes (O.5-F, S0.5-F and O.3-F) or 10.0 cm diameter PVC pipes (L.3-F and C.3-F). The specimens were cured in their respective molds, uncovered, for 7 days, except for the control which cured for 39 days. A 5 cm diameter by 10 cm tall PVC pipe was pushed through the cellular concrete in the box and the specimen in the 10 diameter PVC were cut to approximately 20 cm as shown in Figure 19. All PVC pipe was in accordance to ASTM D2466 (ASTM, 2017c). Specimens were then cured in the environmental chamber for a minimum of 7 days.

Due to time constraints, total specimen age varied from 14-26 days, except for the control which was 82 days old. Detailed information on each specimen can be found in A1 of the appendix.

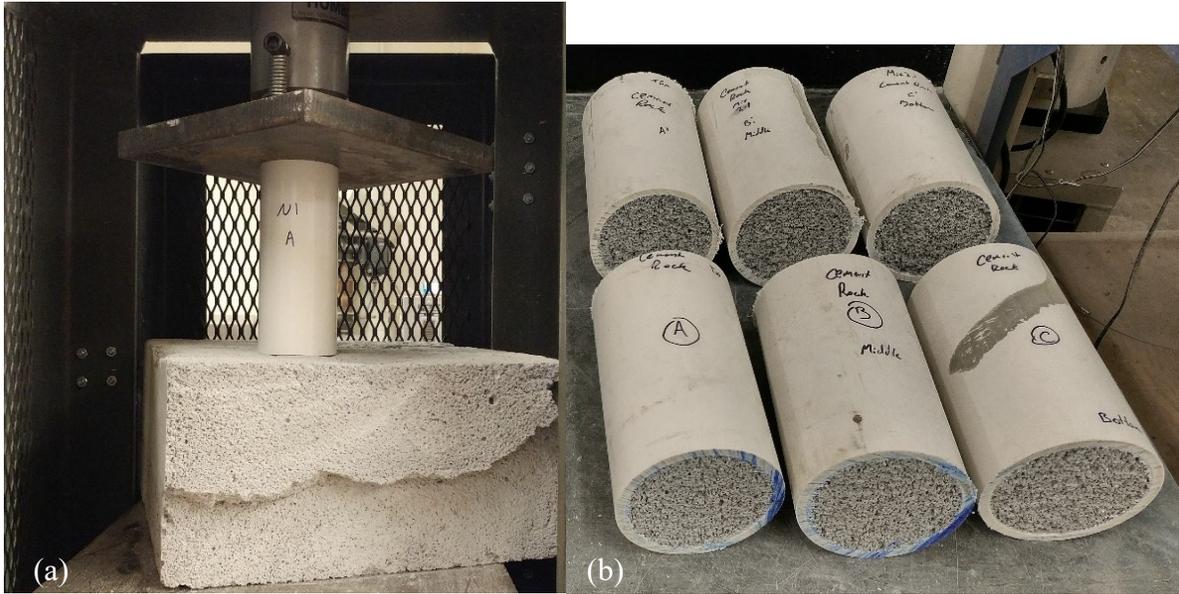


Figure 19. Cellular Concrete Specimen (a) Mechanically pressing cured cellular concrete into PVC pipe and (b) Cured cellular concrete in PVC pipe

Cellular concrete specimens were tested for $\text{NO}_3\text{-N}$ removal using continuous fixed-bed testing as shown in as shown in Figure 20. Specimen columns were sealed with Sch. 40 PVC caps in accordance to ASTM D2416 and Oatey clear PVC cement in accordance to ASTM D2466 (ASTM 2015b; ASTM 2017). Specimens in PVC pipe were subject to a continuous flow of $2.2 \text{ mg NO}_3\text{-N /L}$ solution at a rate of $3.5 \pm 0.5 \text{ mL/min}$. Marriot flasks, designed from non-reactive Nalgene containers, were used to maintain constant head during the experiment. The static head of the Marriott flask inlet to the column outlet was approximately 30 cm. The breakthrough solution entered the bottom of the column to reduce the chance of air entrapment in the column. A ball valve was used for initial priming and release of any air entrapment. A needle valve was used to adjust the flow. Influent entered

through Fisher Brand 0.6 cm inner diameter flexible, vinyl plastic. Effluent samples were collected at initial intervals of 3, 6, 12, 30, 60, 240, 480, and 720 minutes, then reoccurring sampling occurred every 12 hours until the experiments were terminated. If any leaks were found during the experiment, Dow Corning high vacuum grease in compliance with NSF/ANSI 61 or PVC cement glue was used to stop the leak. Effluent water quality was analyzed following the same procedure as the batch reactor samples tested earlier. Initial concentrations were measured by taking a LR when the Nalgene container was refilled (approximately every 2.5 days).

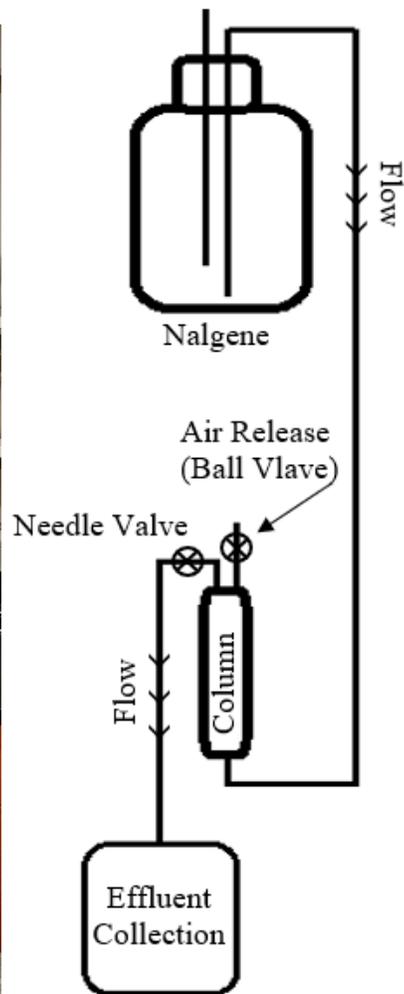
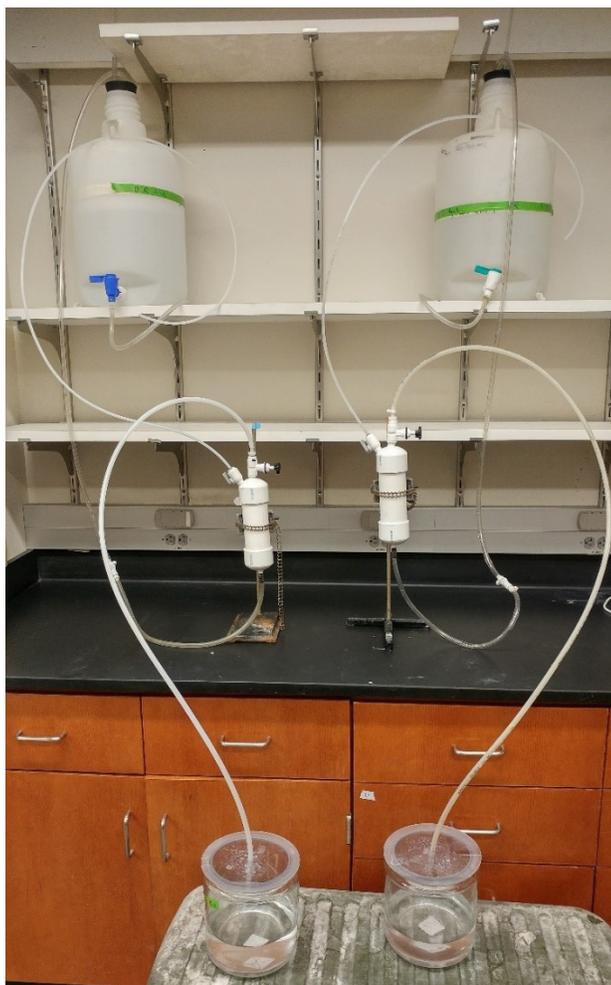


Figure 20. Continuous Fixed-bed Breakthrough Experiment

pH and Conductivity

The effluent pH and conductivity for the O.3-F mixtures is shown in Figure 21 and Figure 22, respectively. Effluent pH and conductivity generally ended around 12.6 and 2-6 mS. Table 8 shows the final pH and conductivity at 90% breakthrough. It should be noted that 90% breakthrough would occur at different total effluent volumes, which could result in varying final pH and conductivity. For example, the O.5-F mixture had the highest pH and conductivity but was tested for the least amount of time, while the L.3-F and C.3-F had the lowest pH and conductivity and were tested for the greatest amount of time. There were no significant differences between different mixtures and trends in pH or conductivity. Initial pH started near 12.5, then increased to 12.9 in approximately 1 hr. Effluent conductivity began around 6 μ S, then increased to a maximum above 8 μ S after 1 hr. Both pH and conductivity decreased from the maximum for the remainder of the experiments. A delay in maximum pH and conductivity indicates when full saturation of the capillary pores was reached.

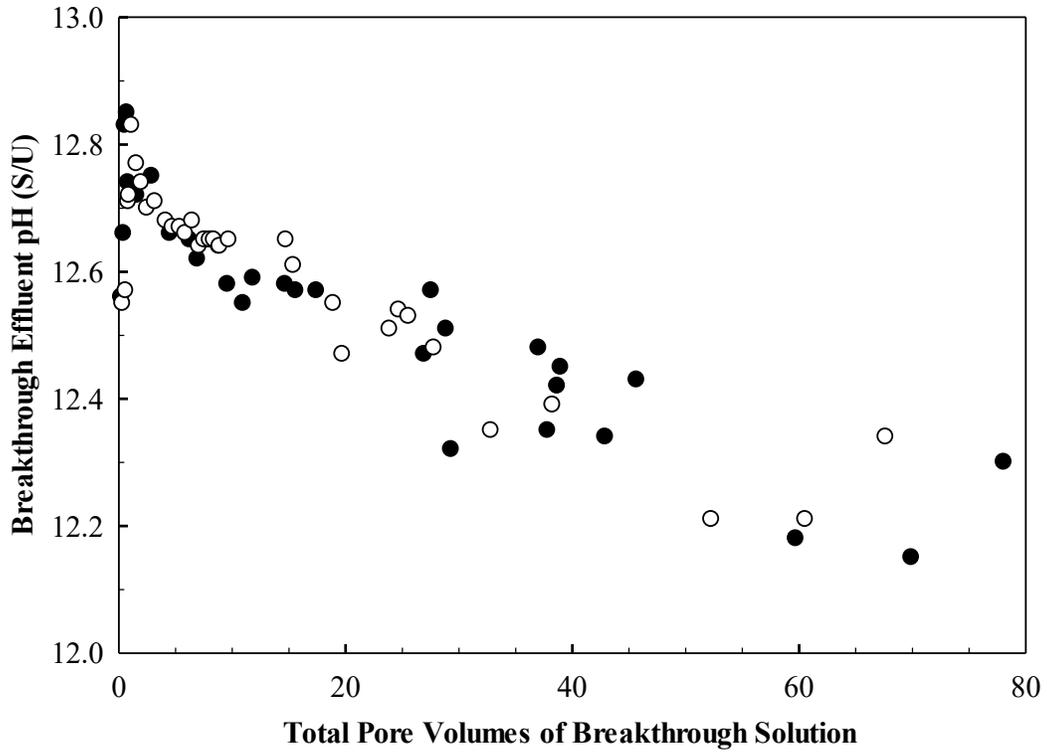


Figure 21. Effluent pH for Cellular Concrete (0.3-F)

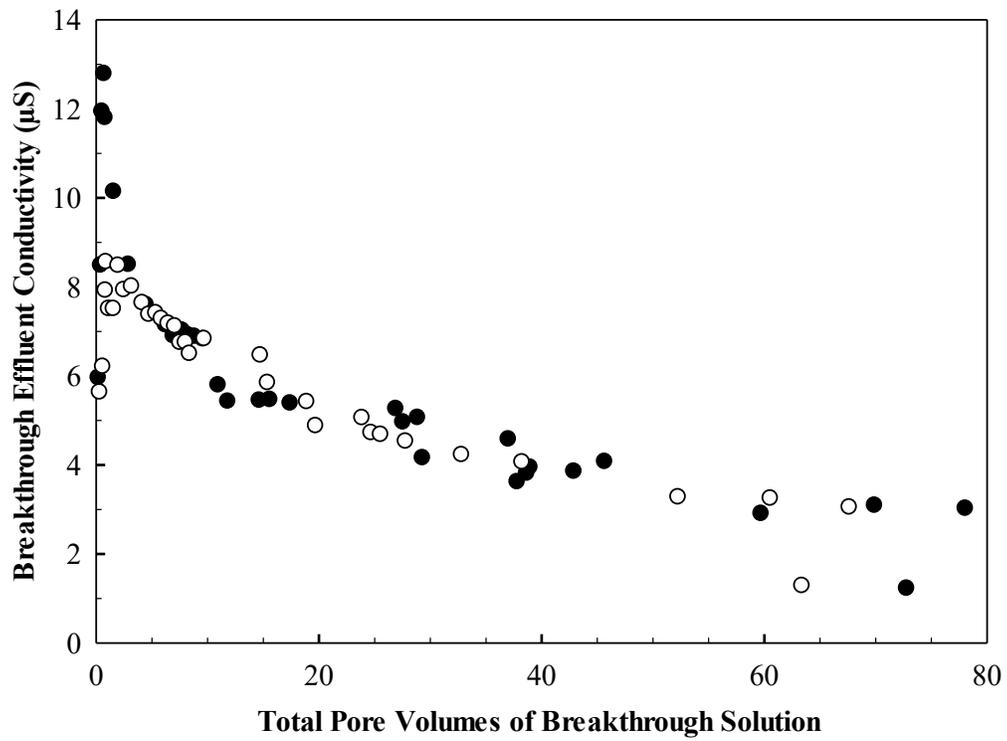


Figure 22. Effluent Conductivity for Cellular Concrete (0.3-F)

Nitrate-nitrogen Removal

Figure 23 shows the breakthrough curve for the O.3-F mixture normalized to the influent concentration of 2.3 of $\text{NO}_3\text{-N}$ mg/L. All breakthrough curves for the cellular mixtures followed similar trends with three slopes for increases or decreases in removal. Removal increased to a maximum removal after 1-3 pore volumes (0.5-5 hrs) from the start of the experiment. The delay in maximum removal is attributed to full saturation of the pores within the concrete structure. Maximum removal was then accompanied by two decreases in removal rates. First, a more rapid decrease in removal was observed between 3-15 pore volumes (5-15 hrs). Second, a slower decrease removal was observed between 15-80 pore volumes (15-30 hrs). Increased capacity for $\text{NO}_3\text{-N}$ removal was attributed to reductions of the two slopes. Since the breakthrough experiment did not reach 100% removal at any point for any of the mixtures and the post removal rates did not decrease rapidly, it can be said that the removal mechanism in cellular concrete is a slow process. The two slopes after maximum removal may indicate separate mechanisms of removal or a decrease in efficiency of a major mechanism of removal.

A superimposed breakthrough curve for each mixture would result in too many overlapping overlapping data points as the trend did not follow the typical breakthrough curves found in other literature (Agyei et al. 2002). Therefore,

Figure 24 shows the cumulative $\text{NO}_3\text{-N}$ removed normalized to cementitious mass calculated from the mixture proportions. Table 8 also shows the total mass of $\text{NO}_3\text{-N}$ removed by the cementitious dose of each specimen and the volume in m^3 of cellular concrete needed to reduce 1 kg of $\text{NO}_3\text{-N}$ at 90% breakthrough.

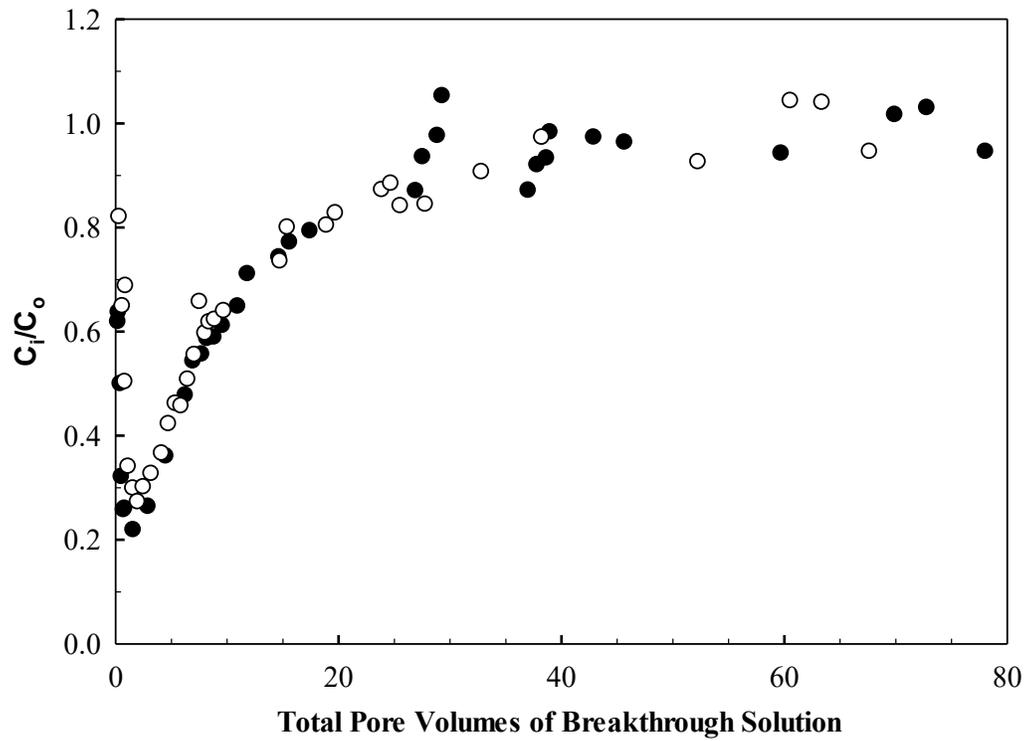


Figure 23. Breakthrough Curve for Cellular Concrete (O.3-F) Normalized to Influent Concentration of 2.3 mg NO₃-N /L

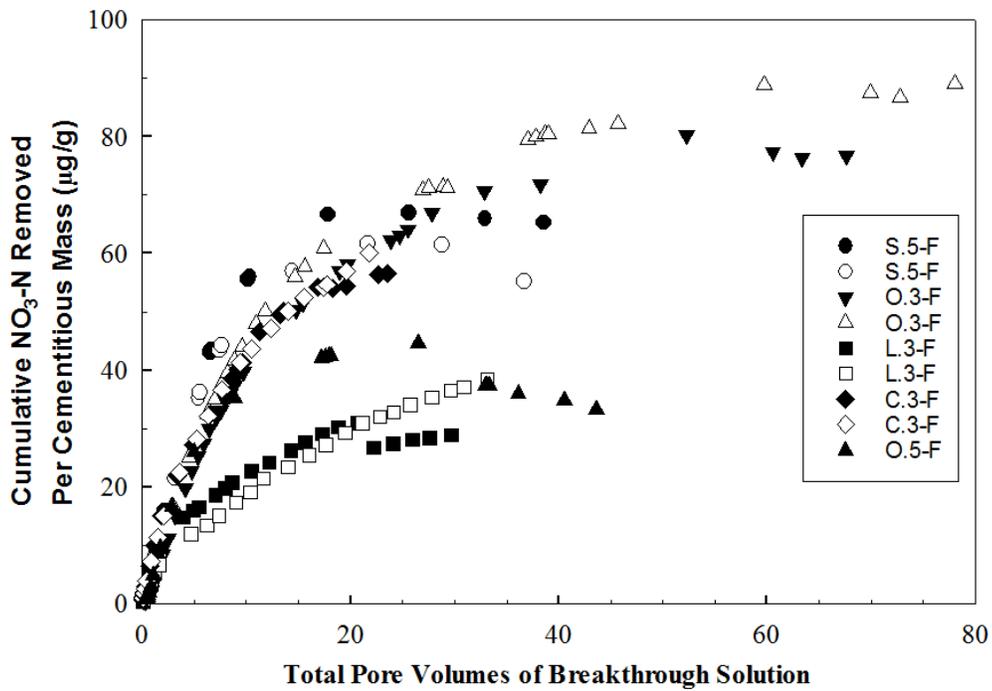


Figure 24. Cumulative Nitrate-Nitrogen Removed Normalized to Cementitious Mass of Cellular Concrete

Table 8. Continuous Fixed-Bed Column Parameters at 90% Breakthrough

Mixture	pH	Cond (mS)	NO ₃ -N Mass Removed / Cementitious Mass (µg/g)	Volume of Concrete to Treat 1 kg of NO ₃ -N (m ³)	Sulfate Leached / Cementitious Mass (µg/g)
O.5-F	12.7	6.9	35.1	125	1064
S.5-F	12.6	5.4	56.9	80	193
	12.6	5.2	66.7	72	224
O.3-F	12.5	5.3	70.9	55	1166
	12.5	4.5	66.9	58	1084
L.3-F	12.5	2.3	25.5	201	516
	12.5	2.2	26.3	197	418
C.3-F	12.4	3.7	52.4	147	1143
	12.5	3.9	50.0	151	985

NO₃-N removal determined through the breakthrough experiments in the current study must be taken with caution due to the change in dosed volume and cross-sectional diameter found in mixtures L.3-F and C.3-F. Increased cross-sectional diameter at a constant flow rate would decrease the velocity and increase the residence time in the fixed-bed. Furthermore, increasing the bed length would increase the residence time. Table A2 in the appendix shows the column parameters for each mixture proportion. The Fastrac 300 and limestone should have had an advantage due to the increased bed depth and larger cross-sectional area which would decrease the velocity through the material. A decrease in As (iii) removal was observed by Singh & Pant (2006) when increasing the flow rate which was explained by the low contact time which could result in low diffusion of solute into the pores of the sorbent. Whether or not the changes in bed dimensions influence removal, a dimensionless time variable should be used on the x-axis of the breakthrough curves or cumulative removal figures to correctly compare the different set-ups. Dimensionless time variables can be a factor of cross-sectional area, bed length velocity, diffusivity and tortuosity (Ruthven, 1984; Singh and Pant, 2006).

It should be noted that the O.3-F mixture removed a greater amount of $\text{NO}_3\text{-N}$ per cementitious dose and volume than O.5-F, indicating that the w/c ratio of the cement paste influenced removal. Increased removal for lower w/c ratios may indicate a dependence on unhydrated cement similar the decrease in $\text{NO}_3\text{-N}$ removal for the older specimen in batched jar testing. The replacement of OPC with slag increased $\text{NO}_3\text{-N}$ removal for the 0.5 w/c series, and, in theory, would increase the removal at a lower w/c. Although the L.3-F and C.3-F experiments should have had the advantage of longer residual times and increased mass, the addition of limestone fines and 100% replacement of Fastrac 300 decreased the $\text{NO}_3\text{-N}$ removal substantially. Although the C.3-F mixture had similar removal to slag per cementitious mass, a greater volume of the C.3-F mixture is needed to treat 1 kg of $\text{NO}_3\text{-N}$ due to the lower density.

Sulfate Leached

The cumulative mass of sulfate leached from the cellular concrete specimen during breakthrough testing is shown in Figure 25. The replacement of OPC with supplementary materials decreased the sulfate leached due to dilution or chemical reactions between the excess SO_4 and supplementary materials in the hydration process. A greater w/c resulted a greater mass of sulfate leached at similar times for OPC specimen, although the 0.3 w/c specimens leached more sulfate after the 0.5 w/c experiment was terminated. There is clearly a much greater mass of leached sulfate than nitrate removed for the cellular specimen. The amount of SO_4 leached did not correlated to increased $\text{NO}_3\text{-N}$ removal. This is merely speculative because there may be many reactions occurring reducing $\text{NO}_3\text{-N}$ that are not sulfate-based.

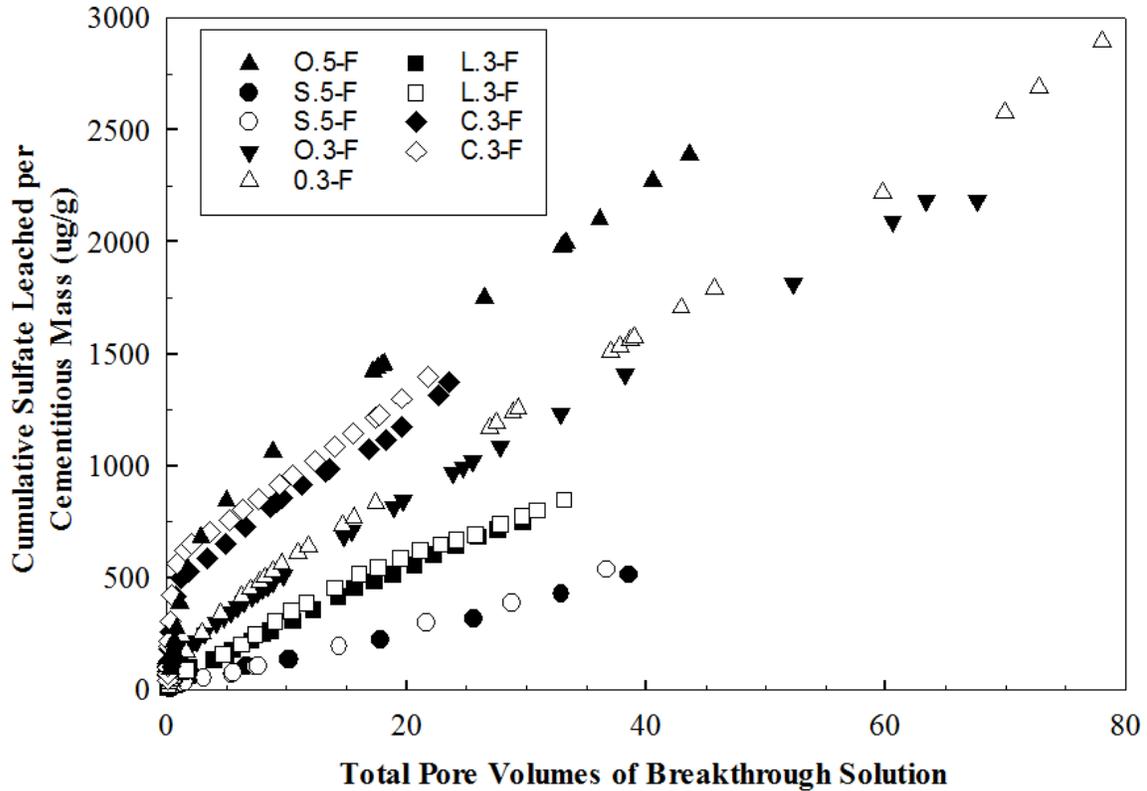


Figure 25. Cumulative Sulfate Leached by Cellular Concrete Specimen Normalized to Cementitious Mass

Conclusions

Five cellular concrete mixture proportions were tested under fixed-bed breakthrough conditions to determine the effects of supplementary materials on nitrate-nitrogen removal. Cellular concrete was used because the structure provided beneficial characteristics including increased reactive surface area and increased reactive material. During the breakthrough testing, similar trends were observed in effluent pH and conductivity for each mixture proportion. The delayed occurrence of maximum pH and conductivity may have indicated full saturation of the specimen. The maximum pH and conductivity values were accompanied by a slow decrease in pH and rapid decrease in conductivity for the remainder of the experiment.

The nitrate removal rates and mass of sulfate leached was also measured during the breakthrough experiment. The mass of sulfate leached decreased with increased supplementary materials of slag and fly ash and decreased with the Fastrac 300 mixture presumably due to the reaction of supplementary materials with the sulfate phases. The total mass of sulfate leached did not necessarily correspond to mass of nitrate removed for cellular concrete mixtures. Nitrate removal was observed to be greater during first 1-3 pore volumes (0.5-5 hrs) of the breakthrough experiment which may correspond to full saturation of the pores similar to the pH and conductivity trends. Nitrate removal rates decreased at two rates after a maximum removal was achieved possibly indicating different removal mechanisms. The replacement of OPC with Fastrac 300 Type III blended cement or 50% replacement with limestone fines decreased nitrate removal, despite preferential specimen geometry and breakthrough operating conditions. An increase in total nitrate removed was observed with a lower w/c. The 50% replacement of OPC with slag increased the nitrate removal for the 0.5 w/c and could potentially increase the removal for the 0.3 w/c mixture. Further improvements could be made on the breakthrough experiment by testing a wider range of w/c, determine the source of soluble sulfate, and adjusting specimen/breakthrough parameters to optimize removal.

CHAPTER 6

BEADS

It was suspected that the surfactant used in cellular lightweight foamed concrete influenced the nitrate-nitrogen removal of the cementitious media in the breakthrough experiment. Therefore, a permeable, lightweight cementitious media was designed as a new series of permeable reactive media, herein described as O-B. O-B was designed to have a similar amount of reactive material as the foamed concrete previously used. The O-B mixture can be developed with additional stages of removal mechanisms in ways that the permeable reactive concrete and foamed concrete could not.

Concrete Preparation and Mixing

O-B was designed with ordinary portland cement (OPC) at a w/c of 0.27. Hydraulic lightweight aggregate was used as a coarse aggregate. Freshly mixed O-B was mixed in the large mixer until the desired coating of cementitious paste on the aggregate was met. The media was then placed into a plastic container, covered with plastic, and allowed to cure for 7 days. After 7 days of curing, the media was broke apart with a hammer then transferred to the environmental chamber to dry for an additional 14 days. O-B specimen were then stored in a freezer with a constant 50% relative humidity and temperature of 8°C in accordance to ASTM F2520 (ASTM, 2012c). The media was scooped into PVC pipes of 10 cm diameter and 15 cm in length. The media was suspended in the pipe by Ceviaval 100% cotton cheesecloth. Breakthrough experimentation was conducted as described with the cellular concrete and water quality measurements were conducted as described with the permeable reactive concrete.



Figure 26. Freshly Mixed Beads

pH and Conductivity

Figure 27 and Figure 28 show the effluent pH and conductivity for O-B and O.3-F for comparison. The O-B mixture demonstrated a similar trend to the foam mixtures for effluent conductivity and pH. The pH of the beads started lower (12.3) than the cellular mixtures (12.5) and did not increase as great as the cellular mixtures did. Time to reach maximum pH and conductivity of the beads was greater (~4 hrs) than the cellular concrete (~1 hr). The O-B mixture presumably took a longer amount of time to become fully saturated due to the decreased surface area and increased paste thickness. The pH and conductivity at 90% breakthrough were also lower than the cellular concretes as shown in Table 9. The lower final pH and conductivity values of the O-B mixture are due to the longer breakthrough experiment duration when compared to the cellular mixtures, which followed a similar trend.

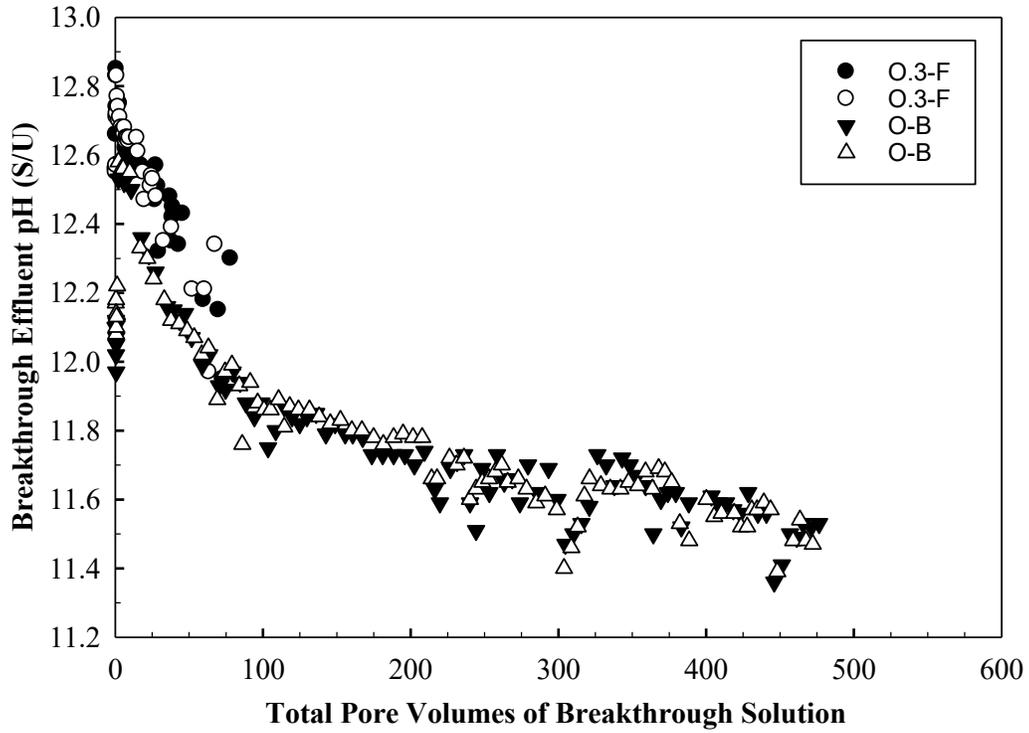


Figure 27. Breakthrough Experiment Effluent pH for Cellular Concrete (O.3-F) and Beads (O-B)

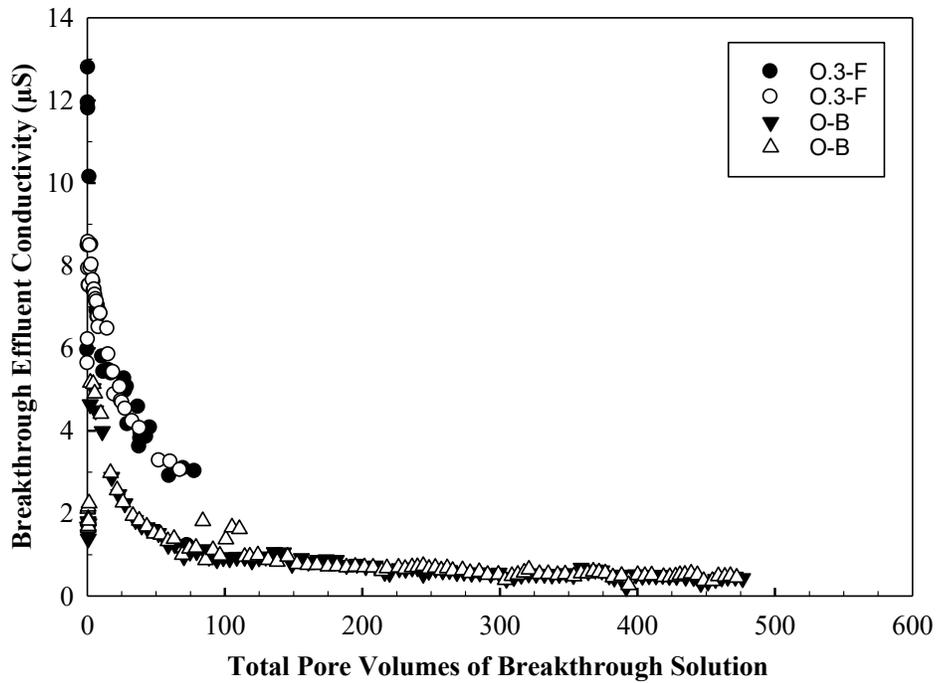


Figure 28. Breakthrough Experiment Effluent Conductivity for Cellular Concrete (O.3-F) and Beads (O-B)

Nitrate-nitrogen Removal Rates

Figure 29 shows the breakthrough curve normalized to an influent concentration of 2.3 mg NO₃-N /L for the O-B compared to the O.3-F mixture. The O-B mixture had three distinct rates of removal increase or decrease similar to that of the cellular concrete mixtures. Maximum removal was observed around 1 day after the start of the experiment. Delayed removal was also attributed to full saturation of the cement paste pores. Maximum removal was delayed longer than that of foam mixtures presumably due to decreased pore porosity. The maximum removal was just above 70% at 10-20 pore volumes (1-3 days), unlike the cellular mixtures which was up to 20% at 2-3 pore volumes (0.5-6 hrs). After maximum removal was achieved, two rates of decrease in removal were observed similar to that of the cellular concrete. The first rate occurred between 20-150 pore volumes (3-15 days). The second rate continued until the experiment was terminated at 475 pore volumes (44 days). The decrease in removal efficiency was not as rapid as what was observed in the cellular concrete. The transition between the first and second rate did, however, occur near a similar percent removal range of 10-15% (C_i/C_o 0.85-0.90). The second rate was much slower than the former. An approximate 100% breakthrough was estimated at 80 total days based on the secondary decrease in removal efficiency. The experiment was then terminated at 44 days as the remaining <10% removal was of little value. A possible modification to shift the breakthrough curve and obtain a greater maximum removal would be decreasing the size of the aggregate as modeled by Shaverdi (2012).

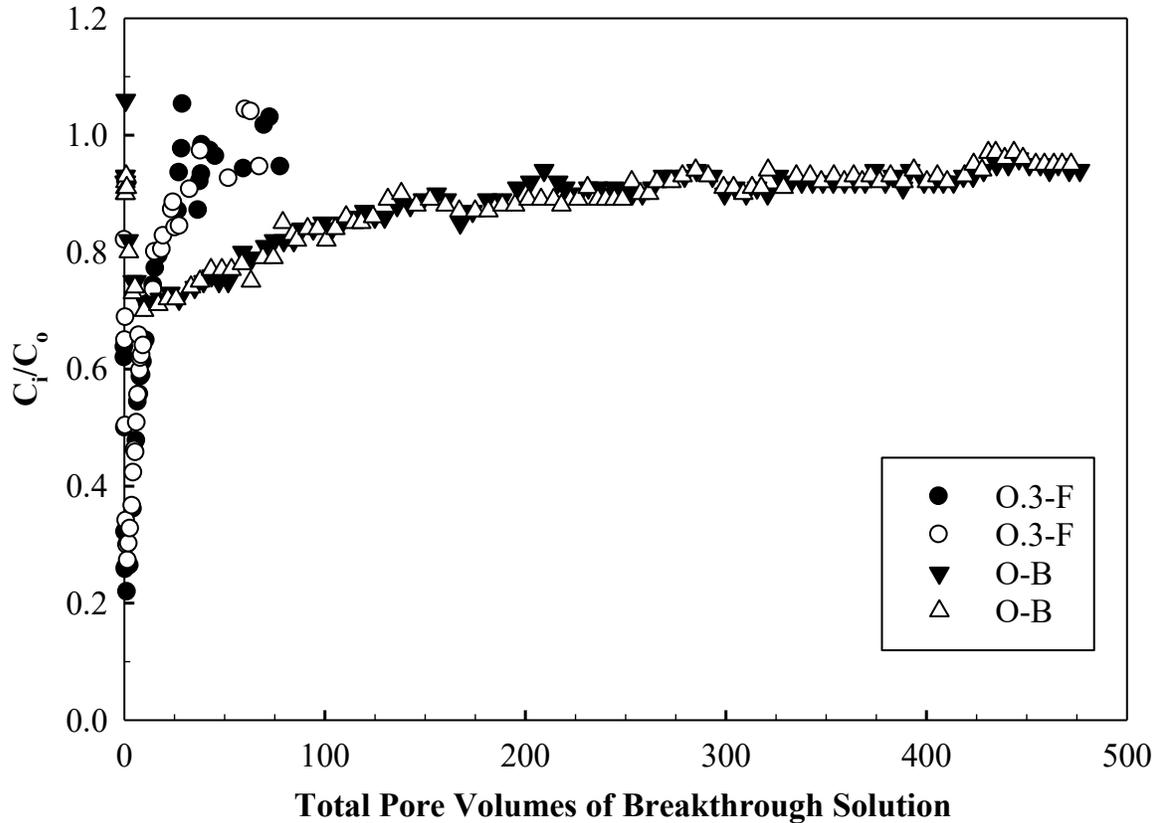


Figure 29. Breakthrough Curve for Cellular Concrete (O.3-F) and Beads (O-F) Normalized to Influent Concentration of 2.3 mg NO₃-N /L

The NO₃-N removal rate and capacity of O.5-F, O.3-F and O-B mixtures are shown in Figure 30. Figure 30 shows the NO₃-N removal normalized to cement mass. The O-B mixture does not perform as well as the cellular mixtures on a mass scale because of the greater density. In Figure 30, however, it is determined that the O-B mixture has a greater removal capacity than the cellular mixtures. Since the O-B and O.3-F had similar w/c ratios, it can be postulated that the foaming agent decreased the removal capacity of the OPC. The surfactant coating the cement particles or increased chemical reaction between the cement particles and foaming agent could result in changes in NO₃-N removal. The rate of removal for the O-B is much slower than the O.3-F, presumably due to the surface area available and denser cement paste of the O-B mixture. Again, the data must be interpreted with caution due to the larger column

and longer residence times for the O-B mixtures. Further details can be seen in Table AI of the appendix. Table 9 shows the $\text{NO}_3\text{-N}$ removed normalized to the proportion of cement mass and volume needed to treat 1 kg $\text{NO}_3\text{-N}$ of for the O-B and cellular OPC mixtures for comparison. Although the beads may have had 90% removal for 10 days, the first instance of 90% removal was used to be conservative. The O-B mixture would require less volume to treat 1 kg of $\text{NO}_3\text{-N}$.

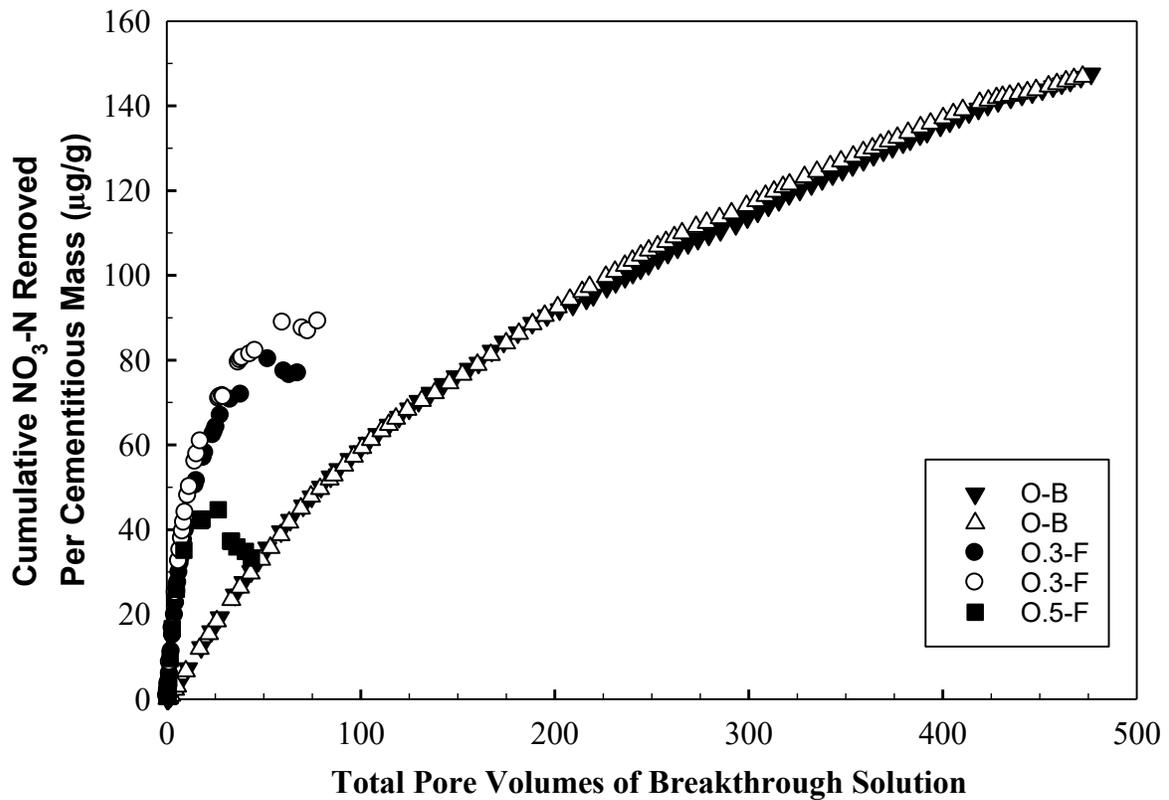


Figure 30. Nitrate-nitrogen Mass Removed During Breakthrough Testing Normalized to Cement Mass

Table 9. Continuous Fixed-Bed Column Parameters at 90% Breakthrough

Mixture	pH	Cond (mS)	NO ₃ -N Mass Removed / Cementitious Mass (µg/g)	Volume of Concrete to Treat 1 kg of NO ₃ -N (m ³)	Sulfate Leached / Cementitious Mass (µg/g)
O.5-F	12.7	6.9	35.1	125	1064
O.3-F	12.5	5.3	70.9	55	1166
	12.5	4.5	66.9	58	1084
O-B	11.7	0.7	88.8	48	488
	11.7	0.7	105.9	39	634

Leached Sulfate

The sulfate leached from O-B during the breakthrough experiment was plotted in Figure 33 with the O.5-F and O.3-F cellular concrete mixtures for comparison. Significantly less sulfate leached from the O-B mixture than the foam mixtures containing only OPC, suggesting a considerable amount of sulfate leaching from the foaming agent. The additional sulfate leached from the cellular concrete may have inadvertently decreased the nitrate removal.

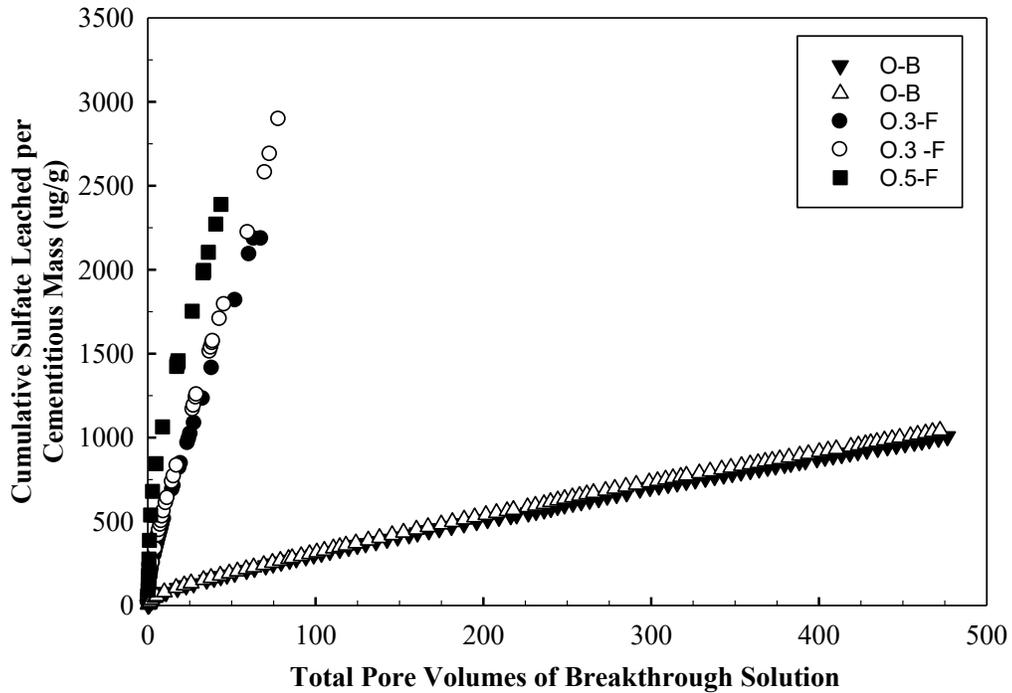


Figure 31. Sulfate Leached During Continuous Fixed-Bed Breakthrough Experiment (O.5-F and O.3-F at 0.15 cm/s and O-B at 0.05 cm/s)

Conclusions

Through the breakthrough experiment of the lightweight aggregate coated in cementitious material, several answers were determined for questions that had arisen during the breakthrough experiments with cellular concrete. Similar trends in effluent pH, effluent conductivity, and removal rates were observed between the beads and cellular lightweight concrete. Although the pH and conductivity of the beads mixture were generally less than that of the cellular concrete, a maximum value followed by a decrease was similar to that of the foamed concrete. Maximum pH, conductivity and nitrate removal may have corresponded with full saturation of the capillary pores similar to that of the cellular mixtures. A similar trend was determined in maximum nitrate removal and decreasing rates of removal between the beads and foamed concrete possibly indicating the efficiency of multiple removal mechanisms.

Overall, a greater removal of nitrate was observed for the beads mixture than the foamed concrete mixtures considering the mass of cement dosed. A lesser amount of sulfate leached from the beads mixture indicating that the foaming agent may have contributed to excess constituents leaching, consequently decreasing nitrate removal. The rate of nitrate removal for the beads was slower than the foamed concrete presumably due to the porosity of the cement paste and decreased reactive surface area of the beads. Further development of the beads could include the addition of supplementary materials, adjustment in water cement ratio, optimization of aggregate size. Overall, the beads were determined to be beneficial for nitrate removal and adaptability for future mixture proportions.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The current research presented utilized laboratory experiments, including batch reactor jar testing and continuous fixed-bed breakthrough testing, to evaluate and compare the removal rates of dissolved inorganic nutrients, nitrate-nitrogen and orthophosphate-phosphorus, by permeable cementitious materials. The current study was intended to investigate the potential of hydrated cementitious products and the effect of supplementary materials on nutrient removal. Previous research has demonstrated how nutrient removal is facilitated through microbial degradation, adsorption, precipitation, and filtration/infiltration by permeable pavement systems. Some laboratory studies have investigated the removal of nutrients by hydrated permeable concrete or cement, but there has been little focus on nitrate-nitrogen. Other laboratory studies have focused on the performance of unhydrated cementitious materials. Thus, the current study was aimed to investigate and optimize the nutrient adsorption capacity of hydrated cementitious media, especially for nitrate-nitrogen.

At the beginning of the study, five permeable reactive concrete (PRC) mixture proportions were tested for nitrate-nitrogen and orthophosphate-phosphorus removal in 72 hr batch reactor testing. PRC specimens were designed as either a control Portland cement or replacement of portland cement with 25% fly ash or DWTR or 3% activated carbon or titanium dioxide. The purpose of the jar testing was to objectively compare the effect of supplementary materials on nutrient removal by PRC mixtures by controlling physical characteristics including water-to-cement ratio, amount of reactive material and reactive surface area. Results of jar testing indicate how permeable cementitious media can be effective at removing and

retaining dissolved inorganic nutrients through chemical and physical adsorption. Orthophosphate-phosphorus removal and retention was effective for all PRC mixtures. The TiO₂ and fly ash mixtures had the greatest removal up to 100%.

Proceeding the jar testing experiments, fixed-breakthrough tests were performed on five cellular lightweight concrete mixtures to evaluate the nitrate-nitrogen removal in specimen with maximum reactive surface area and reactive material. Foamed concrete was designed with either 100% Portland cement (w/c 0.5), 50% replacement with slag (w/c 0.5), 100% Portland cement (w/c 0.3), Fastrac 300 (w/c 0.3), or 50% replacement with limestone fines (w/c 0.5). Results of the breakthrough testing indicated how decreased water-to-cement ratio and the addition of slag can benefit nitrate-nitrogen removal. Multiple rates of removal were observed throughout the duration of the breakthrough experiments potentially indicating multiple removal mechanisms and their efficiencies. Among the five mixture proportions, differences in nitrate-nitrogen removal were not a substantial as expected indicating that the foaming agent may be negatively influencing removal.

To eliminate the probable effects of foaming surfactant on nitrate-nitrogen removal by permeable reactive material, but maintain a low water-to-cement ratio and mass of reactive material, a lightweight aggregate coated in hydrated portland cement (beads) was tested for nitrate-nitrogen removal in a continuous breakthrough experiment and results were compared to the cellular concrete breakthrough experiments. Results concluded how the foaming agent used in generating foamed concrete may have decreased nitrate-nitrogen removal potential hydrated portland cement. A similar trend in pH, conductivity, and nitrate removal was observed between the beads and cellular concrete. The breakthrough curve for the beads followed similar trends for the maximum removal and two decreasing rates of removal. A

maximum removal of 30% was quickly reached, then two rates of decreasing removal were observed. The experiment was terminated after 44 days after a projected 44 days of less than 10% removal was expected. When compared to the cellular mixtures of portland cement (w/c 0.3 and 0.5), the beads removed a much greater mass of nitrate-nitrogen per mass of portland cement.

The results of the current study demonstrate how hydrated cementitious materials can be beneficial for dissolved inorganic nutrient removal in water systems. The results in the current study are limited to cementitious products cured under standard laboratory conditions for a short duration (generally 7 days). Further limitations included the range of nitrate-nitrogen and orthophosphate-phosphorus concentrations tested and the individual testing of either nitrate-nitrogen or orthophosphate-phosphorus as demonstrated by the linear isotherms determined in jar testing. Although the permeable cementitious media demonstrated effective nutrient removal, further testing is needed to optimize and describe the nature of nutrient removal.

APPENDIX

Table A1. Breakthrough Specimen Parameters

Mixture	Wet Density (kg/m ³)	Specimen Mass (g)	Mass Cement (g)	Mass Cementitious (g)	Column Diameter (cm)	Column Height (cm)	PVC Ave. Vol. (cm ³)
O.5-F	24.6	109.8	73.1	73.1	5.1	15.4	321
S.5-F	23.2	102.4	34.1	68.2	5.1	15.0	312
		100.8	33.6	67.1	5.1	15.4	321
O.3-F	22.9	106.4	81.8	81.8	5.1	15.4	321
		105.6	81.2	81.2	5.1	15.1	314
L.3-F	24.7	409.1	157.1	314.2	10.0	20.3	1605
		409.2	157.1	314.2	10.0	20.5	1627
C.3-F	18.4	274.2	-	211.0	10.0	20.5	1624
		274.5		211.3	10.0	20.2	1600
O-B	-	1247.6	379.2	379.2	10.0	20.4	1614
		1277.8	388.4	388.4	10.0	20.4	1614

Table A2. Continuous Fixed-Bed Column Parameters at 90% Breakthrough

Mixture	Cumulative Time (days)	Average Velocity (cm/s)	Average Flow (ml/min)	Residence Time (min)	Effluent Treated (L)
O.5-F	0.5	0.14	3.8	1.8	3
S.5-F	1.0	0.14	2.8	1.9	4
	0.9	0.15	3.2	1.7	5
O.3-F	1.2	0.14	3.5	1.8	8
	2.2	0.12	3.0	2.0	8
L.3-F	4.0	0.05	3.7	7.3	23
	4.4	0.04	3.3	8.1	21
C.3-F	5.1	0.04	3.1	8.7	23
	5.1	0.04	3.3	8.2	20
O-B	17.0	0.04	3.4	7.9	85
	22.5	0.04	3.4	8.0	112

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