

**MARITIME TRANSPORTATION RESEARCH AND EDUCATION CENTER
TIER 1 UNIVERSITY TRANSPORTATION CENTER
U.S. DEPARTMENT OF TRANSPORTATION**



**Exploration of novel multifunctional open graded friction courses
for in-situ highway runoff treatment**

July 1, 2014-June 30, 2016

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Final Report Date

FINAL RESEARCH REPORT

Prepared for:

Maritime Transportation Research and Education Center

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ACKNOWLEDGEMENT

This material is based upon work supported by the U.S. Department of Transportation under Grant Award Number DTRT13-G-UTC50. The work was conducted through the Maritime Transportation Research and Education Center at the University of Arkansas.

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1. Project Description

Pollutants on roadways and parking lots can come from various sources, including the deposition of exhaust, fluid leakage from vehicles, abrasion from the friction between tires and roads, abrasion from brake pads, deicing activities, atmospheric deposition, corrosion of crash barriers, and pavement itself. Storm water runoffs from roadways contain both organic and inorganic contaminants of which large portions are eventually conveyed to the nearby water bodies such as rivers and lakes. Copper (Cu) and Zinc (Zn) have been identified to be the major inorganic contaminants in roadway runoffs (USDOT, 2012). Contaminants from vehicles and activities associated with roadway construction and maintenance tend to be washed from roads and roadsides when it rains or snow melts; large amount of this runoff pollution is carried directly to water bodies. The concentration ranges of Zn and Cu in runoffs are 20-2000 µg/L and 5-200 µg/L respectively according to various studies (Davis et al, 2001; McNamee, 1998). According to Herrera Environmental Consultants (2007), Zn and Cu in runoffs are 13-134 µg/L and 3-18 µg/L respectively. Barrett et al. (1998) studied stormwater samples collected from surface runoff from a highway in Texas and found that concentrations of Zn and Cu were 222 µg/L and 37 µg/L respectively.

U.S. Environmental Protection Agency (EPA) storm water regulations set limits on the levels of pollution in streams and lakes (Pervious Pavement, 2011). Therefore, the U.S. Department of Transportation (DOT) is subjected to increasing pressures by water quality regulatory agencies for the control and treatment of highway storm water runoffs. To meet these regulations, two basic approaches have been considered: (1) to reduce the overall run-off from an area, and (2) to reduce the level of pollutants contained in the runoffs.

Pagotto et al. (2000) investigated the runoffs generated from both porous and non-porous road surface in France and found that the runoff water quality from pervious open graded friction course (OGFC) was better than the non-porous ones such as hot-mix asphalt (HMA). OGFC is an alternative to HMA and is produced by eliminating the fine aggregate from the asphalt mix. Normally, a layer of porous asphalt, approximately 50 mm thick, is placed as an overlay on top of an existing conventional concrete or asphalt roadway surface. Main benefits of OGFC include the improved rain water drainage that reduces hydroplaning, the reduction of splash and spray behind vehicles, the improvement of wet pavement friction and surface reflectivity, and the reduction of traffic noise.

Pervious Concrete Pavement (PCP), as one of OGFCs, has become attractive in roadway and parking lot constructions because of its economic, structural, and environmental advantages. It can facilitate the recharge of groundwater and reduce storm water runoff. PCP is made of large aggregates with little to no fine aggregates and the mixture contains little or no sand, creating a substantial void content. The voids ratio in PCP overlay layer is generally 18% to 22% (Barrett et al, 2008).

The goal of this study is to examine the removal of the major heavy metals Cu and Zn in roadway runoffs through PCP and Modified PCP (MPCP). The latter is a PCP that contains strategically selected additives. The objectives of this study include

- 1) To identify functional additives based on their commercial availability, cost, and potential adsorption capacity of heavy metals,
- 2) To fabricate PCP and MPCP samples with identified additives and test their physical and mechanical properties important for highway pavement, and
- 3) To examine the removal of heavy metals with the PCP and MPCP samples from highway runoffs through batch and dynamic adsorption tests.

2. Methodological Approach

2.1. Materials

To produce PCP and MPCP samples, following materials were used:

- (1) Portland cement. The Portland cement was obtained from a local store. The particle was very fine, and smooth and dark grey in color.
- (2) Crushed lime stones. The aggregates used in the PCP and MPCP were crushed lime stones obtained from a large quarry in Jackson, Mississippi as shown in Figure 2-1. They are of high quality and polish resistant aggregate with a capacity to provide and maintain good frictional characteristics.



Figure 2-1. Crushed lime stones used in PCP and MPCP sample fabrication

- (3) Water. Water is one of the most important elements in cement products. The water used for mixing and curing should be clean and free from injurious quantities of alkalis, acid, oils, salt, sugar, organic materials, vegetable growth and other substances that may be deleterious to bricks, stone, concrete or steel. Potable water is generally considered satisfactory for mixing. The pH value of water should be not less than 6.
- (4) Functional additives. Adsorption different additives including various bentonites, zeolite, activated carbon, diatomite, and lime were used as functional additives to produce modified PCP or MPCP which were intended to have high adsorption capacities for heavy metals in runoffs. These additives were used in the form of mostly powder and had a different texture. Only 5% of these additives were used in making MPCP samples.

2.2. Test of adsorption capacities of functional additives

Different types of functional additives were tested for their absorbing capacities on Zn and Cu. The adsorption test was conducted using a known mass (in g or mg) of each additive with a specific volume of solutions containing heavy metal ions of desired concentrations at constant temperature (20°C). The solid to water ratio was 1:10. The mixtures of additives solution were shaken for 24 h to ensure that the adsorption reaches equilibrium. The concentrations before and after adsorption were measured. The amount of the metal adsorbed was derived. This test was conducted for each additive with different metal concentrations to obtain isotherm parameters. The additives with high Zn and Cu absorbing capacities would be considered as additives in making MPCP samples.

Linear, Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich methods were used to model the experimental data and to determine which model best describes the nature of the adsorption isotherm for each additive.

2.3. PCP sample preparation

The PCP samples were prepared using crushed limestone aggregates, Portland cement, and water as described in Section 2.1. The graduation of the aggregates used in the preparation of the PCP samples is given in Table 2-1.

Table 2-1. Graduation of aggregates in PCP fabrication

Sieve number	Size (mm)	% Passing	% Content
1/2"	12.5	100	0
3/8"	9.5	80	20
No. 4	4.75	10	70
No. 8	2.36	2	8
No. 200	0.075	0-2	2

Two different sizes of samples were prepared for this study. For compressive strength test, sample size was 4 inch in diameter and 8 inch in thickness. For all other test, sample size was 6 inch in diameter and 2 inch in thickness.

The aggregates were dried in oven at 165°C for 2 h and weighed according to the selected gradation (Table 2-1). Cement and water were added to the aggregate in a desired ratio to make the paste of desired consistency. In this study, an aggregate-to-cement ratio of 3:1 and a water-to-cement of 1:3 was used. After mixing it was poured in molds, shaken and compacted. Then the samples were left for setting for 24 h. After setting, the samples were taken out of the molds and sealed in plastic bags for the curing. Water was sprinkled in the bags to keep the humidity above 95%. The curing time used in the study was 14 d. After curing, the samples were ready for various testing. Figure 2-2 shows the pictures of the PCP samples.

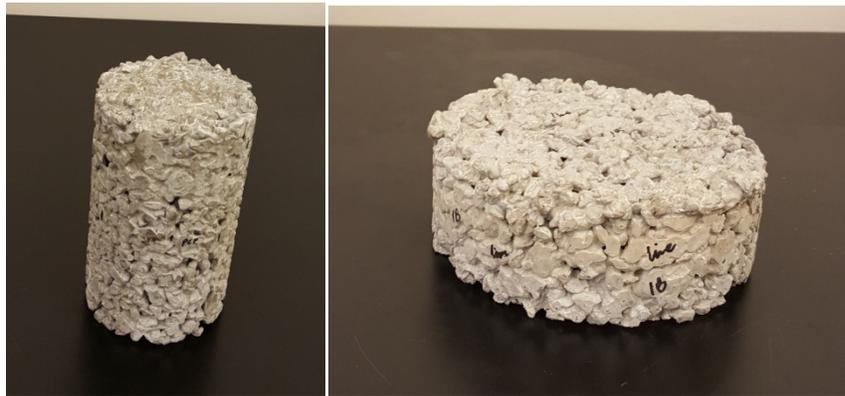


Figure 2-2. PCP samples made for testing

2.4. MPCP sample preparation

The same procedures as used in the PCP preparation were followed except that the identified functional additives were added to the mixtures to replace the fine aggregates (passing No. 200 sieve). The additives used in preparing MPCP samples included 100% pure bentonite, granular bentonite, granular zeolite, and lime. The 100% pure bentonite was obtained from Best Bentonite Company. It has light tan to grey solid color. This is in the form of powder and it has very fine particles. The granular bentonite was obtained from Texas Sodium Bentonite, Inc. and the granular zeolite from Zeo, USA. Lime was obtained from MDOT, Jackson. It has light grey solid color. These additives were identified to be effective in absorbing Cu and Zn through the adsorption test (Section 2.2) and were used as fines at 5% of the total dry materials to make MPCP samples.

2.5. Testing of Physical and Mechanical Properties of PCP and MPCP Samples

The permeability, air void, and compressive strength of the PCP and MPCP samples were tested as described below.

(1) Permeability

Permeability test was conducted according to ASTM Falling Head Laboratory Permeability Test Method (ASTM, 2001). A Permeameter manufactured by Global Gilson was used in this study. Each specimen was put in the rubber container. Petroleum jelly was applied onto the plastic wrapped specimen for lubrication before the specimen was inserted into the stand pipe. Once the apparatus was secured, the Permeameter was filled with water to a height above the top of the specimen. The valve was opened and the time required for the water to drop from the initial head and the final head above the specimen was recorded and used to calculate the permeability using Darcy's Law.

(2) Air Voids

Air voids test was conducted according to ASTM C1754/C1754M standard (ASTM, 2012). The dimensions of a specimen were measured to determine its volume. The PCP/MPCP samples of 6 inch in diameter and 2 inch thick were oven dried at 93 °C for 24 to 48 h to get the actual dry weight. The weights of the samples were measured before and after they were soaked in the water. Specific gravity weight balance was used to measure the weight of sample in water. The air void content was calculated using the difference between the total volume and the displaced volume when submerged.

(3) Unconfined compressive strength

The unconfined compressive strengths (UCS) of the PCP and MPCP samples were tested according to ASTM Standard C 39-96 (ASTM, 1998) to assess the mechanical properties of the samples. The specimens were 4 inch in diameter and 8 inch in length. The sample was loaded axially in the automatic compression test machine at a constant axial strain rate and the applied load resulting deformations was used to calculate the UCS.

2.6. Batch Adsorption Test

The PCP or MPCP samples were soaked in the water containing 0.3 to 0.5 mg/L Zn and Cu for 24 h in room temperature. The solid-to-water ratio was 1:5. The solution was stirred periodically. The initial and final pH values were also measured. After the adsorption, the water was analyzed for Cu and Zn concentrations to determine the adsorption rates by the samples. The batch adsorption test setup is shown in Figure 2-3.



Figure 2-3. Batch adsorption test

2.7. Dynamic Adsorption Test

This test was performed using the same Permeameter as for the permeability test. Water containing Zn and Cu was passed through the PCP sample at constant flow rate of about 0.105 L/h. The effluent was collected at different times. The accumulative weight of the effluent was recorded and effluent samples taken at different times were analyzed for Cu and Zn concentrations and as well as pH. Calcium (Ca) and aluminum (Al) in the effluents were also analyzed. Concentration-versus-time curves were obtained which can be used to evaluate the in-situ removal of heavy metals by PCP or MPCP pavements. The dynamic adsorption test setup is shown in Figure 2-4.



Figure 2-4. Experimental setup for dynamic adsorption test

3. Results/Findings

3.1. Adsorption test results of different additives

From the adsorption test as described in Section 2.2, the equilibrium concentrations of Cu and Zn in water were plotted against their concentrations in the solid phase. For the twelve additives tested. Most adsorption results fit Freundlich isotherm model with a few fit linear model. The Freundlich isotherm model is defined as

$$X = K_f C^{1/n}$$

Where X is the amount of adsorbate (Cu or Zn in this case) adsorbed onto per unit mass of solid; C is the equilibrium solution concentration of the adsorbate; K_f is the Freundlich adsorption constant; and n is a constant. The Freundlich K_f is equivalent to the distribution coefficient K_d in the linear model ($X=K_dC$) and the bigger its value is, the higher is the adsorption capacity of the material. Table 3-1 gives the results from curve-fitting of the equilibrium concentrations for all the twelve additives tested.

Table 3-1 Adsorption test results of functional additives on heavy metals Cu and Zn

Additive Tested	Heavy metal	Correlation coefficient R ²	Isotherm model	K_f or K_d
Granular Bentonite (Texas Sodium Bentonite)	Cu	0.97	Freundlich	1086
	Zn	0.95	Freundlich	735
Pearl Soil (Pearl, Mississippi)	Cu	0.98	Freundlich	156
	Zn	0.94	Liner	66
100% Pure Bentonite (Texas Best Bentonite, Inc.)	Cu	0.66	Liner	591
	Zn	0.57	Liner	737
Zeolite powder ultrafine (Kelpless)	Cu	0.91	Freundlich	796
	Zn	0.97	Freundlich	379
Pure Zeolite clay (Greece)	Cu	0.97	Freundlich	334
	Zn	0.99	Freundlich	314
Sodium Zeolite (Charles B. Crystal Co. inc)	Cu	0.81	Liner	413
	Zn	0.97	Freundlich	298
Sodium Bentonite (Charles B. Chrystal Co. Inc)	Cu	0.67	Liner	997
	Zn	0.75	Liner	1161
Bentonite Seal 0922W (Soil Moisture Equipment Corp.)	Cu	0.87	Freundlich	513
	Zn	0.99	Freundlich	482
Granular Zeolite (Zeo, USA)	Cu	0.85	Freundlich	431

	Zn	0.95	Freundlich	415
Activated Carbon (envirosupply.net)	Cu	0.85	Linear	1982
	Zn	0.93	Freundlich	638
Diatomite (Burney)	Cu	0.87	Freundlich	680
	Zn	--	--	--
Lime (MDOT)	Cu	0.08	Freundlich	1320
	Zn	0.59	Freundlich	1364

The results indicate that 100% pure bentonite, granular zeolite, granular bentonite, and lime had high adsorption capabilities for both Cu and Zn. They were used as additives to make MPCP samples.

3.2. Permeability results for PCP and MPCP samples

The permeabilities for PCP samples and MPCP samples containing 5% of the four selected additives have been tested and results are shown in Table 3-2.

Table 3-1 Permeability results for PCP samples and MPCP samples

Sample	Average Permeability (m/d)
PCP	23.0
MPCP with 5% 100% Pure Bentonite	36.5
MPCP with 5% Granular Bentonite	32.8
MPCP with 5% Granular Zeolite	29.0
MPCP with 5% Lime	30.9

The results indicate that the MPCP samples with bentonite have higher permeabilities. This is due to the swelling property of the bentonite that caused the sample to have more cracks which were observed on the samples. Nevertheless, these permeabilities are within normal range for most PCPs.

3.3. Air voids results for PCP and MPCP samples

The results of air voids for the PCP and MPCP samples are given in Table 3-3.

Table 3-3 Air voids measured for PCP samples and MPCP samples

Sample	Air Voids (%)
PCP	25.8
MPCP with 5% 100% Pure Bentonite	36.8
MPCP with 5% Granular Bentonite	32.1
MPCP with 5% Granular Zeolite	28.3
MPCP with 5% Lime	22.0

3.4. Unconfined compressive strength results

Three types of samples, i.e., PCP, MPCP with 5% lime, and MPCP with 5% 100% Pure Bentonite were tested for unconfined compressive strength and results are given in Table 3-4. The UCS results indicate that lime enhances the strength of PCP and bentonite weakens it. For the PCP samples and MCPC samples with lime added, the UCS's were over 3700 psi which is as good as for normal concrete. However, the MPCP samples with bentonite added, the UCS is only 850 psi which does not meet the strength requirement for pavement.

Table 3-4. Unconfined compressive strength (USC) of PCP and MPCP samples

Sample	Peak Load (lbf)	UCS (psi)
PCP	46853	3730
MPCP (5% lime)	51240	4076
MPCP (5% 100% Pure Bentonite)	10400	850

3.5. Batch adsorption test results for PCP and MPCP samples

Batch absorption test had been performed on PCP samples and MPCP samples with 5% of additives. The solid-to-water ratio was 1:5 and the initial concentrations of Cu and Zn in the water were 0.3-0.5 mg/L. After three days of contact, the concentrations of Cu and Zn in the water were measured and the removals of Cu and Zn were calculated. The results are shown in Table 3-5.

Table 3-5 Batch adsorption test results for PCP and MPCP samples

Sample	Adsorption rate (%)	
	Cu	Zn
PCP	59.3	93.5
MPCP (5% 100% Pure Bentonite)	46.1	86.1
MPCP (5% Granular Bentonite)	21.8	33.6
MPCP (5% Granular Zeolite)	48.0	34.4
MPCP (5% Lime)	31.7	46.8

The results indicate that the addition of the additives do not increase the ability of the PCP samples in absorbing Cu and Zn from water. This further indicates that the cement in the PCP and MPCP samples is the main agent absorbing the heavy metals. Adding the additives does not improve the adsorption capacity. In regard to the removal of Cu and Zn from runoffs, there is no benefit to add these additives and PCP itself already has high absorbing capacity.

3.6. Dynamic adsorption test results

Since the batch adsorption results revealed that the additives do not increase the abilities of the PCP samples in absorbing Cu and Zn, the dynamic adsorption test was performed only on PCP samples. Due to the constraints of test device and time, the dynamic test was performed on only one PCP sample for 60 d. The concentrations of Cu and Zn in the influent were 4.73 and 2.13 mg/L respectively. The effluents were analyzed for Cu and Zn as well as calcium (Ca), aluminum (Al), and iron (Fe). The concentrations of Fe in the effluents were found near zero. The concentrations of Cu, Zn, Ca, and Al with time are plotted as shown in Figure 3-1.

It can be seen in Figure 3-1 that the concentrations of Cu and Zn gradually decreased with time to as low as 5% of the original concentrations while the concentration of Ca maintained high (20-100 mg/L). This indicates that the main mechanism of Cu and Zn removal was ion exchange with Ca, not adsorption. Since there was huge amount of Ca in the sample (mainly in the Portland cement), the removal could continue for a long time. Even for 60 d, the removals of Cu and Zn still maintained high. This can lead to a conclusion that the PCP has long-lasting removal capacities for Cu and Zn in runoffs.

Figure 3-2 is a picture of the PCP sample taken out of the Permeameter after the dynamic adsorption test. The blue color on the top indicates the deposit of Cu salt and the Cu was retained from the influent of the test. This again suggests an ion exchange mechanism for the removal of Cu in the water.

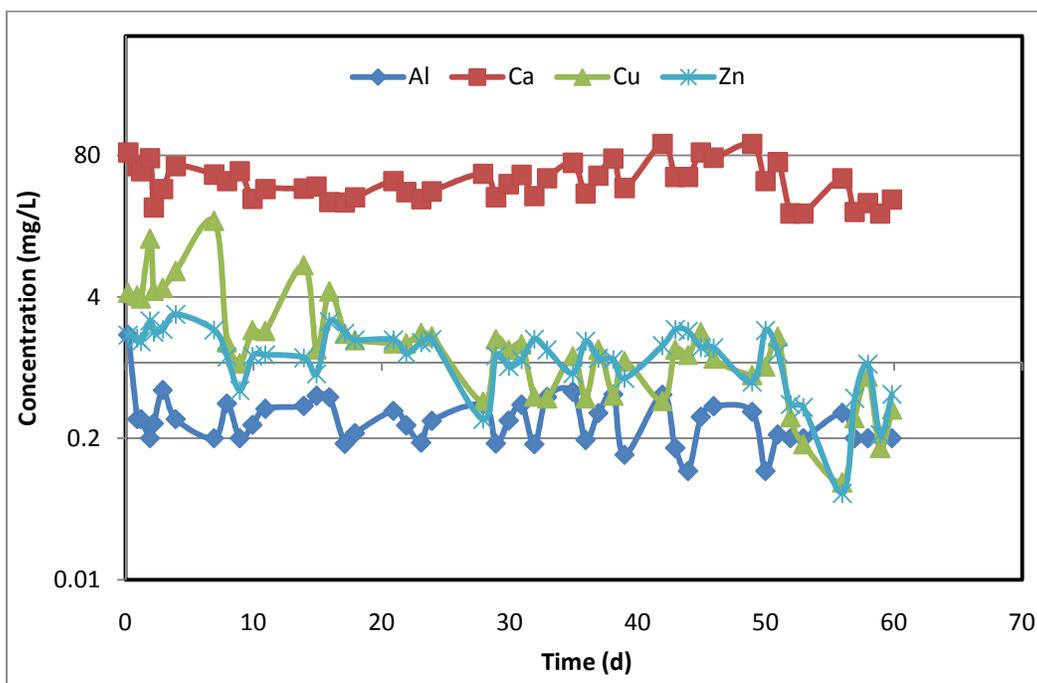


Figure 3-1. Changes of concentrations of metals in effluent of the dynamic adsorption test

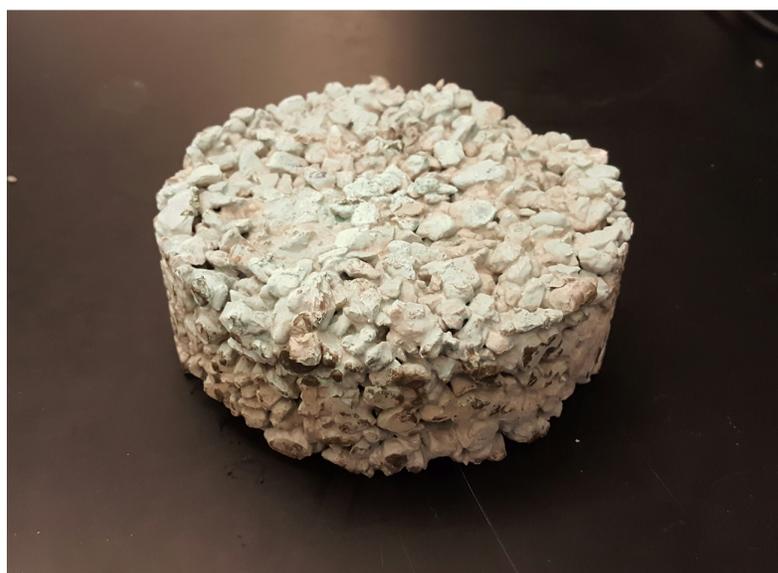


Figure 3-2. PCP sample after dynamic adsorption test

4. Impacts/Benefits of Implementation (actual, not anticipated)

The results of this study bring an important conclusion that not only can the pervious concrete pavement bring the traffic-related benefits, but also environmental benefits because its long-term removal capacities for Cu and Zn, which are the major heavy metal contaminants in roadway runoffs. The use of PCP in roadways and parking lots brings positive impacts for the sake of environmental protection.

5. Recommendations and Conclusions

This study found that the possible functional additives such as bentonite, zeolite, and clay cannot increase the physical and mechanical properties of PCP, neither the removal of Cu and Zn. Lime is effective in enhancing the physical and mechanical strengths of PCP, but cannot improve the removals of Cu and Zn from runoffs. On the other hand, PCP alone has a long-term removing capability for Cu and Zn. The capacity comes from the ion exchange with huge amount of calcium contained in the raw material (cement) in PCP. Therefore, the use of PCP on roadway and parking lots can not only mitigate the storm water runoff, but also provide long-term environmental benefits by removing heavy metals from the runoffs.

It is recommended that a long-term, pilot scale test be further performed to more closely simulate the real-life situation of PCP and quantify the reduction of pollutants in the runoffs.

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