Incorporating Adsorbents into Porous Asphalt Design

A Major Qualifying Project Report:

submitted to the faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

By

Thomas Paul O'Connell II

Benton Cassie

Seth Brewster

Professor John A. Bergendahl, Advisor

Professor Rajib B. Mallick, Advisor

Professor Mingjiang Tao, Advisor

Abstract

Two zeolites, HiSiv 3000 and 5A, were evaluated for usefulness as a sorbent base for porous pavement. Benzene, C_6H_6 , was selected as the contaminant to be studied and column adsorption tests were designed to analyze removal. HiSiv 3000 performed better for removing the benzene from water than the 5A in the thirty hour contact test. Granular Activated Carbon (GAC) performed best overall in the one hour contact test. Structural analyses revealed problems with the use of 5A as a base material. Further analyses and testing with 5A is warranted.

Acknowledgements

The team would like to acknowledge Professors John Bergendahl, Rajib Mallick and Mingjiang Tao of the Civil & Environmental Engineering Department of Worcester Polytechnic Institute for their guidance, advice and time. The team would also like to thank Donald Pelligrino and Dean Daigneault for their assistance with our laboratory experiments.

MQP Capstone Design Requirement

To meet the requirement of the design aspect of the project, the team designed experiments to identify removal efficiency of a contaminant using a sorbent material. The team also used the data to design a porous asphalt layer system with a sorbent material integrated into its layers. Benzene was the contaminant of choice because it constitutes a general contaminant from vehicles. The team designed and built column adsorption tests for three different sorbents, and measured the contaminant using chemical oxygen demand (COD) tests and a spectrophotometer. The experiments were designed and constrained by the goal of identifying absorption capacity. The equipment and material used were chosen due to the literature reviewed and the background yielded by such review. The design and testing took into account both the limitations and restrictions that inherently exist within the experiments.

Current porous asphalt designs were improved with a sorbent material integrated into its layers, and a computational soil mechanics program called "Everstress" was used to analyze its structural integrity. The team utilized a method to allow visualization of the structural study. The structural study equated the strength of the sorbents to the stresses provided by vehicle and pavement loads to check for acceptability. Acceptability was governed solely on those parameters but not without the consideration of limitations that each method contains within it. The design of the experiments and the porous asphalt took into account the scope of the data collected and the limitations of the experiments.

Executive Summary

The amount of impervious surface in a landscape is an important indicator of environmental and habitat quality (Bauer, 2005). Non-point source pollution from stormwater runoff is well-documented as a leading cause of impairment of freshwater lakes, rivers, and estuaries. In 2004, the Environmental Protection Agency published a state integrated assessment report for stream impairment in the Mid-Atlantic declaring that 4,376 miles of stream were considered impaired from urban and storm sewer runoff (EPA, 2004). Along with stream degradation, impervious surfaces decrease the amount of infiltration taking place over an area. A sustainable hydrological cycle requires that rain recharges the groundwater by infiltration. This decrease in local water table from increased runoff changes the mechanics of the native soil and the environment surrounding it. With a focus on sustainable living, these practices cannot continue and must be mitigated or remedied. Porous surfaces can promote infiltration while decreasing the need for stormwater systems (T.H.Cahill, 2003).

Porous asphalt has been in use for forty years with initial failure taking place in the binder. It would migrate downward and created a choker layer impeding infiltration. Currently, binder is mixed with an SBS polymer to negate migration of the binder, and open graded friction coarse (OGFC) are used with impervious sub-layers to direct runoff along the sub-layer into stormwater systems. This design decreases splash, increases lane marker visibility and road friction. However with its impervious sub-layer it does not promote infiltration into underlying soil. The design of completely porous asphalt that promotes infiltration is governed by the permeability of the native soil and the porosity of the hot mix design. Low permeability sites require piping or expensive recharge beds while high permeability sites may only require a filter

layer. The asphalt binder, typically 2% to 5%, and the sieve analysis with no fines, are critical to create a permeable surface that still exhibits structural integrity.

Porous asphalt, once thought only useful in parking lots, has recently been implemented on the Maine Mall Road in South Portland, MA; a road that services 5% heavy trucks, 16,750 AADT and a design hourly volume of 2412 (Portland, 2009). Porous pavement is not without its concerns, for instance, there are possibilities of high levels of contamination and this contamination can infiltrate through the porous pavement and contaminant the local water tables. The concern is not without contention, with studies showing the removal of a high percentage of suspended solids and hydrocarbons (T.Ballestero, 2009) with sand filter layers. There are applications that are not suitable for a completely porous pavement such as truck stops or manufacturing plants, where the possibility of contamination is high. It is the goal of this project to develop a porous pavement system incorporating a sorbent suitable for such an application.

Zeolites are micro-porous crystalline alumino-silicate structures that belong to a class of alkali or alkali earth metals. Zeolites contain three-dimensional, covalently bonded tetrahedrons made up of aluminum and silicon, SiO₄ and AlO₄ (Yang, 2003). The frameworks are generally open and contain channels and cavities. Zeolites are used in many applications around the world. Commercial grade zeolite is meant for water, air filtration, and cat litter (Zeolite, 2004). It's common in laundry detergent and as an additive in hot mix asphalt.

Activated carbon is another adsorbent that was used in this research. Its internal surface can range from $500 - 1500 \text{ m}^2/\text{g}$, which makes it ideal for adsorption. Activated carbon comes in two forms, powder activated carbon (PAC) and granular activated carbon (GAC). It can adsorb organics such as chloride phenol, and BTEX (LennTech, 2009). It's also used for odor, taste control, and for purifying water.

The adsorption process involves three stages. First, the contaminating substances stick on to the surface of the carbon. Next, the substances move into the large pores. Finally, they are adsorbed onto the inner surface of the carbon.

Sustainable living requires the mitigation of effects of development on the environment. Porous surfaces can promote infiltration while decreasing the need for stormwater systems (T.H.Cahill, 2003). However, there are applications where high contamination possibilities may not warrant the use of a porous pavement. It is the goal of this project to develop a porous pavement system incorporating a sorbent suitable for such an application.

Findings

The team designed column adsorption tests to analyze the removal of benzene using two zeolites, HiSiv 3000 and 5A. GAC was also tested, as a bench mark, to compare with the zeolites' removal capacity. The sorbents were placed into columns and samples of known concentrations of benzene were passed through the column and remained for designated time periods. Two control tests, one with aggregate and one without aggregate, identified if outside variables affected results. In preliminary tests, the three sorbents were placed in two different positions, mixed and in a layer, for one hour to identify the optimal sorbent and position. The GAC exhibited the greatest removal capacity, 92%, with the HiSiv 3000 removing 38%, and 5A removing 33%. The mixed layer was identified as the best implementation. The difference in removal capacity between the mixed and bottom position was around 9%. The preceding tests were 3, 18 and 30-hour tests and only the two zeolites were tested and only in the mixed position. Samples were quantified with a COD analysis and absorption was measured with a spectrophotometer at 600 nanometers. The absorption was compared to the concentration curve

for final concentration determination. The overall data was utilized to design a porous asphalt system with a sorbent material integrated into its layers.

Approximately 11% of the sample mass was lost in both control tests. Between the two zeolites, HiSiv 3000 had the greatest capacity for removal of benzene overall. However in 1-hr testing, 5A and HiSiv 3000, had similar removal capacities, 35% and 33%. It was in the timed tests that the HiSiv 3000 showed its greatest removal capacity, 82% as compared to 54% for the 5A (for the 30-hour test). Volatilization was also ruled out of consideration on the grounds that the 5A retained nearly 50% of the initial concentration for the 30-hour test. Nevertheless, the activated carbon exhibited the greatest removal capacity, 92%, in only an hour of interaction time. This vast difference in capacity was associated with the standardization of the experiment in that the same weight of the GAC and zeolite were used (15 g), but due to unit weight differences, a greater surface area was exhibited with the GAC. This was visually clear when the GAC was placed into the column and measured over double the height of the zeolite at 2 in. All three sorbents experienced higher removal capacity in the mixed position.

The question of whether the mixed position is an acceptable design was tested via a "pooling test". If the sorbent was to migrate it could pool into areas and interaction between the contaminant and sorbent would decrease. It was performed by mixing 1-2" aggregate and sorbent material and placing over a large size sieve. The sorbent that fell to the bottom was collected and measured. The test showed that drastic difference in particle sizes may allow migration of sorbent and the mixed position may not suffice.

"Everstress", a program used to obtain strain, stresses and deflections within a pavement at various depths under traffic loading, was used to quantify the potential stress, strain and

vii

deflection that might occur within the sorbent material. A typical car and truck load were used in the software program to identify these parameters.

The team utilized the friction angle of each sorbent to quantify its shear strength. The friction angle was obtained by putting a sorbent into a 1000 mL graduated cylinder with water. The cylinder was tipped past 60° and put back upright. The angle of the slope was then measured. This illustrates the sorbents shear strength based on its critical state friction angle. Each sorbent was measured both intact and crushed. GAC had the highest friction angle while the 5A had the lowest.

Using the principal stresses from Everstress, and the friction angle, the team utilized a method called Mohr's circle to visualize feasibility of structural acceptability. In Mohr's circle, the principal stresses from the car and truck loads are used as S1 and S3 on a graph with the friction angle at the origin. Mohr's circle revealed possible problems with the 5A, which warrants further analysis. However, both the GAC and HiSiv 3000 were shown to be acceptable under both the car and truck loads.

Table of Contents

Introduction	1
Background	2
Infiltration	2
Stormwater Systems	3
Contamination	4
Porous Pavement	6
Current Designs	6
Porous Pavement Design Constraints	9
Column Adsorption Tests	
Selection of Contaminant	
Selection of Adsorbents	
Structural Tests	
"Everstress" Computational Software Program	
Critical State Friction Angle	
Mohr's Circle	
Methodology	
Method of Measurement & The Concentration Curve	
Chemical Oxygen Demand Tests	
Concentration Curve of Benzene	
Column Adsorption Tests	20
Test Procedure	
Material Quantities	
Control	
Control without Aggregate	23
5A Zeolite	23
HiSiv 3000	24
Granular Activated Carbon	24

Kinetic Effects	
Structural Test	
"Pooling Test"	25
"Everstress" Computational Software Program	26
Critical State Friction Angle	27
Results and Discussion	
Column Adsorption Tests Results	
Control & Control without Aggregate	
5A Zeolite Removal Capacity	
HiSiv 3000 Zeolite Removal Capacity	
Granular Activated Carbon Removal Capacity	
Structural Aspect Results	
"Pooling" Test	
Critical State Friction Angle Results	
"Everstress" Computational Software Program	
Mohr's Circle	
Design and Recommendations	41
References	46
Appendix	49
Appendix A – COD & Spectrophotometer Lab Procedure	
Appendix B – Material Lab Data Sheets	49
Appendix C – Control w & w/o Aggregate Lab Procedure	
Appendix D – Sorbent Test Lab Procedure Bottom Position	
Appendix E – Sorbent Test Lab Procedure Mixed Procedure	
Appendix F – Preliminary 1 hour test data	51
Appendix G - Concentration curve data	
Appendix H - 3 -18-30 hour time tests	
Appendix I – Proposal	53

List of Figures

Figure 1 - Impervious Surface Example (Bowles, 2009)	3
Figure 2 - Coefficients of Runoff (Bowles, 2009)	4
Figure 3 - Impervious Cover to Water Quality Graph (Advameg, 2009)	5
Figure 4 - Porous Asphalt (T.Ballestero, 2009)	6
Figure 5 - OGFC with Impervious Sub-Layers (T.Ballestero, 2009)	7
Figure 6 - Typical Sieve Analysis for Porous Asphalt (T.H.Cahill, 2003)	8
Figure 7 - OGFC with pervious Sub-Layers (T.Ballestero, 2009)	9
Figure 8 - Tetrehadral Zeolite Unit Cell (CO2CRC, 2008)	12
Figure 9 - COD Vials	19
Figure 10 - Cary UV Spectrophotometer	19
Figure 11 – Column Adsorption Test	20
Figure 12 - Heater Block	21
Figure 13 - Placement of Sorbent	21
Figure 14 - Recharge Bed Aggregate	25
Figure 15 - Pooling Test	25
Figure 16 - 5A Friction Angle	28
Figure 17 - HiSiv 3000 Friction Angle	28
Figure 18 - GAC Friction Angle	28
Figure 19 - Concentration Curve	30
Figure 20 - Control with Aggregate & Control without Aggregate	31
Figure 21 - 5A Mixed & Bottom	32
Figure 22 - HiSiv Mixed & Bottom	32
Figure 23 - GAC Mixed & Bottom	33
Figure 24 - 1 Hour Time Set Test Graph	34
Figure 25 - Mixed & Bottom for HiSiv & 5A – 1 Hour	35
Figure 26 - Time Test Data HiSiv 3000	36
Figure 27 - Time Test Data 5A	36
Figure 28 - Friction Angle Diagrams	40
Figure 29 - Design Schematic	43

List of Tables

Table 1 – Zeolite Mechanical Data (Aldrich, 2005), (Gas Alarm, 2004)	14
Table 2 - Activated Carbon Information (CarboChem, 2009)	15
Table 3 - Input Data for Everstress	
Table 4 - Input Data for Car Load	27
Table 5 - Input Data for Truck Load	27
Table 6 - Concentration Curve Data	
Table 7 - Column Adsorption Test Table	
Table 8 - HiSiv and 5A Column Adsorption Test Data	
Table 9 - Kinetics Effect Data HiSiv 3000 & 5A	
Table 10 - Friction Angle Data – Intact State	
Table 11 - Friction Angle Data - Crushed Sorbent	
Table 12 - Output Data Car and Truck Loads	
Table 13 - Recharge Bed Sieve Analysis	41
Table 14 - Choker Coarse Sieve Analysis	
Table 15 - OGFC Sieve Analysis	

Introduction

Due to impervious pavements, water collects pollution on the surface, which is diverted into storm drains instead of infiltration into the ground. The lack of infiltration lowers the local water table. The water gathers and runs into a drainage system that empties into water courses. The large volumes of runoff erode stream banks, damage streamside vegetation, and widen stream channels. Urbanization also introduces certain pollutants transported to receiving waters such as oil, grease, pesticides, road salts and heavy metals (EPA, 2010).

One way to help reduce runoff and promote infiltration into the water table is to utilize porous pavement structures. They are made with built-in void spaces that let water and air pass through. These devices can allow stormwater management systems and irrigation systems to be downsized and possibly be eliminated, depending on the area. The recharging of local water tables ensures a sustainable hydrological cycle however; high contamination prohibits the use of porous pavements due to the concern of contamination of the water table.

The objective of this work is to evaluate the feasibility of an adsorbent to be incorporated into a porous pavement structure. Zeolites and activated carbon have a structure of many pores and chambers. This way, some molecules are able to pass through the structure while others are excluded, or broken down. Zeolites and activated carbon have large cavernous pores, which provide a very large surface area, good for removing organics from water. Zeolites are most common in laundry detergents and cat litter.

In order to incorporate a sorbent layer into a porous pavement structure, research was done on infiltration, stormwater systems, contamination, sorbent materials and porous pavement design. First, column adsorption tests had to be done to see whether the zeolites or activated carbon can adsorb a sufficient amount of benzene at certain concentrations. After the column adsorption tests were completed, structural tests were performed to see if sorbents in a pavement structure could withstand a typical load of a car (e.g. sedan) and a truck.

The project required column adsorption tests of adsorbents and the analysis of structural integrity. With this research project, the team developed four goals:

- 1. Analyze the removal capacity of the chosen sorbents.
- 2. Investigate the effect of time on sorbent's sorption.
- 3. Evaluate the structural integrity of a porous asphalt structure with an incorporated sorbent layer.
- 4. Design a porous pavement with an incorporating sorbent layer based on the data.

Background

In order to investigate the removal capacity of the sorbents to be incorporated into a porous asphalt design, the team had to perform research on all three chosen sorbents, contaminants and porous pavements. The team utilized research papers, fact sheets, journal articles, and literature to develop the background needed to execute this project.

Infiltration

Infiltration is the downward movement of water through soil. In any porous surface design, this is the mechanism that is being utilized. In the hydrological cycle, infiltration is the process that recharges the aquifers, but as impervious surface increases, the area of infiltration

decreases. Figure 1 is an example of the effect of impervious surface on an aquifer (Bowles, 2009).



Figure 1 - Impervious Surface Example (Bowles, 2009)

The lack of infiltration lowers the water level of aquifers and ultimately changes the soil properties and landscape environment of the location. This example also reveals another problem associated with impervious pavement and that is runoff. Runoff is managed through stormwater systems.

Stormwater Systems

Since runoff cannot infiltrate into the ground, it's channeled by the impervious surface. Stormwater systems must be developed to mitigate the peak volume and velocity runoff during storms. Figure 2 shows coefficients of runoff for various surfaces, which govern the design of stormwater systems (Advameg, 2009).



Figure 2 - Coefficients of Runoff (Bowles, 2009)

As shown on this chart, concrete and asphalt direct nearly 100% of runoff along its surface. The engineer will calculate the velocity and quantity of the runoff using these coefficients and local storm water values. Watersheds are designated; based on topography, water flow and the area of pervious and impervious surface. With this data, systems are constructed to hold or direct runoff to desired areas such as waterways or other stormwater systems. However, impervious surfaces are often associated with contamination from vehicles and people.

Contamination

Contamination in runoff is called non-point source pollution. The definition of which as stated by the Environmental Protection Agency (EPA, 2008);

The term "point source" means any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged. This term does not include agricultural storm water discharges and return flows from irrigated agriculture.

Non-point pollution has become the leading contamination problem affecting modern society. The most common non-point source pollutants are sediment, microorganisms, nutrients and toxins (Advameg, 2009). Sediments carry with it lawn products, road maintenance products, oil, grease, and gasoline. Microorganisms are hazardous to humans, aquatic life, and nutrients such as nitrogen and phosphorous that ultimately destroys the fertility of farmland. Figure 3 illustrates the quality of a watershed stream as compared to its impervious surface.



Figure 3 - Impervious Cover to Water Quality Graph (Advameg, 2009)

Porous Pavement

Porous asphalt is a transportation asphalt surface that allows water to infiltrate into the underlying soil through voids incorporated into the hot mix design. Porous asphalt replenishes the aquifers, reduces the amount of pollutants carried by stormwater systems, and decreases peak runoff volume and velocity. In previous designs the binder never hardened and migrated to the bottom where it created a choker layer constricting infiltration (Advances in Porous Pavement, 2005). It has been remedied with the use of SBS polymers mixed into the binder. Its cost is comparable to typical dense asphalt, depending on site conditions, and in some cases, takes the place of stormwater systems that require large amounts of earthwork to install. If a recharge bed is needed, the overall cost will increase but it is offset by the decrease in stormwater systems.



Figure 4 - Porous Asphalt (T.Ballestero, 2009)

Current Designs

There are two basic types of porous asphalt, each with its own purpose, Open Grade Friction Coarse (OGFC) with an impervious sub-layer and a porous OGFC with an infiltration bed. The purpose of the OGFC with an impervious sub-layer is to direct runoff along the impervious layer into stormwater systems connected to the pavement.



Figure 5 - OGFC with Impervious Sub-Layers (T.Ballestero, 2009)

OGFC's are used to service high speed and high volume roads. OGFC's increase visibility by decreasing splash and spray, reduce tire noise up to 3 to 5 decibels and reduce hydroplaning (U.S. Department of Transportation, 1990). OGFC's exhibit high friction qualities and increase visibility of pavement markings. With an OGFC surface, there is an increase in stripping, susceptibility to rutting at intersections and adverse geometric locations, and require special snow and maintenance methods that will increase the cost of the surface (U.S. Department of Transportation, 1990). OGFC's are not an impervious surface and are used to improve road conditions and not mitigate infiltration concerns or stormwater construction.

There are different designs for porous asphalt that promotes infiltration, each governed specifically by site conditions. Techniques and procedures vary among site conditions but porous asphalt consists of four main components: OGFC, a choker course, a reservoir coarse and geotextiles, each in their own layer. Geotextiles are used in porous pavement design to promote infiltration and to mitigate sediment entry. Typical geotextiles have a weight of 7 oz/yd² and a

flow rate of around 100 gal/min/ft² (Fabrics, 2009). Geotextiles are placed above and below the recharge bed to keep sediment from moving into other layers. The aggregate should be washed to avoid clogging of the geotextile due to fine sediment from dirty aggregate. Some recent information shows that migration of underlying soil into the recharge bed is less important than sediment from runoff. Still, geotextiles will increase the potential for design success.

The first layer of porous asphalt is on average, 4"-6" thick with no fines below sieve #30 in the hot mix asphalt. The asphalt content is around 6%-8% by weight of the total mix. Figure 6 is a typical gradation for porous asphalt (T.H.Cahill, 2003).

US Standard Sieve Size	Percent Passing
1/2"	100
3/8"	95
#4	35
#8	15
#16	10
#30	2

Figure 6 - Typical Sieve Analysis for Porous Asphalt (T.H.Cahill, 2003)

The void content in this layer is around 16%, as compared to around 2%-5% in impervious asphalt. The second layer is the base for porous asphalt called a choker course, it is around 2"-4" thick and it consists of $\frac{1}{2}$ "- $\frac{3}{4}$ " crushed aggregate (T.Ballestero, 2009). This layer acts as a barrier to sediment and a structural support for the top layer.

There are variations in the recharge bed that depend on site conditions, specifically permeability of underlying soil. If the existing soil is poor in draining quality, than the third layer is typically a recharge bed. The recharge bed is 1'-3' in depth with aggregate sizes around

1"-3" and a void content around 40% (T.Ballestero, 2009). The thickness of the layer depends on local stormwater values and sub-grade permeability rates. The recharge bed stores the runoff, allowing it infiltrate slowly into the low permeability soil. If the underlying soil has high permeability, than a recharge bed may not be necessary which will cut down on material and therefore cost. Instead of a recharge bed, it is possible to add a filter layer of sand around 8"-24" in thickness (T.Ballestero, 2009). It is also possible to utilize both the sandy filter and recharge bed layers. Figure 7 is an example of a sandy filter layer (T.Ballestero, 2009).



Figure 7 - OGFC with pervious Sub-Layers (T.Ballestero, 2009)

Porous Pavement Design Constraints

Site examination is necessary for adequate design of porous pavement. Permeability governs the design and must be identified. Soil should be tested 4' below the recharge bed for permeability of at least ½ inch/hour (District, 2004). It is suggested that visual inspection of the underlying soil take place to help identify the soil characteristics (T.H.Cahill, 2003). The porous surface permeability must be at least 8 inches/hour. The recharge bed must be drained in less

than 72 hours and pore pressure is a concern for structural integrity. Once the permeability is identified, the next step is to identify the stormwater values for the area of concern. This governs the depth of the recharge bed and the aggregate sizes. If permeability is not a concern, it's possible to include the sandy filter layer as opposed to the recharge bed, or to include both. Installation requires leveling of the site to prevent pooling. Pipes can be installed in the recharge bed to disperse the runoff.

Once the needs are identified, there are design guides that must also be met. The current literature is general in the design requirements. The Dauphin County Conservation District developed a fact sheet with design considerations (District, 2004). The bottom of the porous pavement structure should be at least 4' above the seasonal high water table. There should be as little earthwork as possible and the underlying soil should not be disturbed. The recharge bed, as well as the porous pavement should be lightly rolled because an increase in rolling will decrease infiltration qualities. It's not suitable in areas that have been filled less than five years, or on grades higher than 6°.

Another concern is the event of clogging. Vacuuming must be performed periodically to remove sediment from the porous asphalt voids. It's not suitable in areas where high wind erosion supplies significant amounts of windblown sediments. It's possible to patch with traditional patching mix if not more than 10% is repaired. Porous asphalt has been shown to handle freeze-thaw cycles rather well. In the summer the binder becomes softer and in the winter, it becomes stiffer, increasing the void content and allowing water to freeze and thaw without undermining the structural integrity.

Column Adsorption Tests

The selection of the contaminant was determined by common pollutions associated with asphalt surfaces. The selection of the sorbent was governed by the contaminant chosen. Both were constricted by availability and cost. With sufficient research on the topics of concern, the validity of the selections was justified.

Selection of Contaminant

Benzene, also called benzol and cyclohexatriene, is a clear, colorless liquid that is highly flammable with a chemical formula of C_6H_6 . It has a molecular weight of 78.11 grams/mol, with 92.25% carbon and 7.75% hydrogen. It is miscible with alcohol, chloroform, ether, carbon disulfide, carbon tetrachloride, glacial acetic acid, acetone, and oils. The solubility of benzene is around 1750 mg/L (EPA, 2009). The human toxicity is from ingestion or inhalation and it typically irritates the mucous membrane but also can cause restlessness, convulsions, and depression (Merck, 1976). It is a constituent of automobile gasoline; therefore it's a contaminant that is expected to be present in parking lots and roadways.

Selection of Adsorbents

Zeolites are microporous crystalline aluminosilicate structures that belong to a class of alkali or alkali earth metals. Zeolites contain three-dimensional covalently bonded tetrahedrons, aluminum and silicon, SiO_4 and AlO_4 (Yang, 2003). The frameworks are open and contain channels and cavities that are located in the middle of the structure. The SiO_4 and AlO_4 are neutralized by cations (e.g. sodium, water and/or other molecules) within the pores.

The shape selective properties of zeolites are also the basis for their use in molecular adsorption. The tetrahedral can be arranged in many ways, which can result around 800 structural possibilities. Less than 200 have been found in natural deposits or synthesized in laboratories (Yang, 2003). Many zeolites are naturally occurring.

The crystalline structure creates the porous structure with openings. Due to the size of the pores, typically between 3 and 10 angstroms in diameter (Yang, 2003), they are able to selectively take up some molecules into their porous structure while rejecting others. This is called molecular sieving.

The structure of the zeolite is the mechanism of adsorption. As stated earlier, the tetrahedral arrangements of SiO_4 and AlO_4 create numerous lattices where the oxygen atoms are shared with another unit cell. The combination of unit cells form channels or cavities. An example of a zeolite can be seen in figure 8 (CO2CRC, 2008).



Figure 8 - Tetrehadral Zeolite Unit Cell (CO2CRC, 2008)

Different zeolite structures include: a chain-like structure with needle-like prismatic crystals, a sheet-like-structure, where the crystals are flattened, and framework structures where the crystals are more equal in dimensions (Yang, 2003)

Zeolites that are natural, occur in mafic volcanic rock. They are found in various settings such as alkaline lakebeds, soils and land surfaces, marine deposits, and geothermal deposits. Ion exchangeable ions, such as potassium, calcium, magnesium and sodium, the major cations, are held electrically within the open structure (Zeo, 2009). Natural zeolite structures have more acid resistant silica to hold its structure together than synthetic based zeolites.

Synthetic zeolites are very small compared to natural zeolites. This is due to the very long crystallization time of natural zeolites in the earth. Synthetic zeolites vary with silica to alumina ratios. The simplest synthetic zeolite is a Type A zeolite, with one silica: one alumina: one sodium ion ratio. Types A, X and Y zeolites are the most dominant for commercial use. Some examples would be 3A, 4A, 5A Type zeolites (Yang, 2003). The number represents the accessible pore size and the letter represents the framework. Different cations can also change the pore size. Zeolites have specific gravity due to the channels and can be hydrophobic (high silica ratio) or hydrophilic (low silica zeolites) (Wilkinson, 2009).

The chosen sorbents in this research were type 5A molecular sieve, HiSiv 3000, and activated carbon. All three sorbents were chosen due to cost and availability. We believe the two zeolites both had satisfactory adsorption rates of benzene, with HiSiv 3000 having the greater adsorption rate due to the high silica ratio. The activated carbon was readily available in the lab and provided a good bench mark from a well known adsorbent.

Molecular sieve type 5A is an alkali alumino silicate and is the calcium form of the Type A crystal structure. The pore size of 5A molecular sieve is about 5 Å. It is mainly used in separation of the normal and isomerous alkane; pressure swing adsorption (PSA) for gases; co-adsorption of moisture and carbon dioxide (Packing, 2009). HiSiv 3000 is a type Y structure that

is high in silica ratio. The pore diameter is around 6 Å. Table 1 shows information on each zeolite that was used in this research.

Zeolite	Company	Pore Diameter	Bulk Density	Surface Area
HiSiv 3000	UOP	6A	47.9 lb/ft ³	321.9 m ² /g
5A	Sigma Aldrich	5A	44 lb/ft ³	570 m ² /g

Table 1 – Zeolite Mechanical Data (Aldrich, 2005), (Gas Alarm, 2004)

Activated carbon is a form of highly porous carbon that can easily adsorb constituents from fluids. It's processed to have a very large surface area (500-1500 m^2/g) to remove soluble substances from water.

Activated carbon is utilized in the adsorption process, and is most often involved in the purification of drinking water. It can be made from coal, wood, and coconut shells due to the large size of their surfaces and the extent to which they are porous (CarboChem, 2009). The bigger the pores, the longer the activated carbon functions over time. Table 2 shows information about different types of activated carbon (CarboChem, 2009).

Types of Activated Carbon					
	Coal	Coconut	Lignite	Wood (powder)	
Micropore	high	high	medium	low	
Macropore	medium	low	high	high	
Hardness	high	high	low	n/a	
Ash	10%	5%	20%	5%	
Water Soluble Ash	low	high	high	medium	
Dust	medium	low	high	n/a	
Reactivation	good	good	poor	none	
Density	.48 g/cc	.48 g/cc	.4 g/cc	.35 g/cc	
Iodine No.	1000	1100	600	1000	

 Table 2 - Activated Carbon Information (CarboChem, 2009)

As activated carbon is placed in water, the adsorption process works in three stages. First, the contaminating substances stick on to the surface of the carbon. Next, the substances move into the large pores. The adsorption takes place because of the attractive force between the molecules. Molecules at the surface of a solid, attracts other molecules. So, contaminants get adsorbed to the surface of carbon (TheActivatedCarbon.com, 2009). Finally, they are adsorbed onto the inner surface of the carbon.

The main function of the activated carbon is to remove contaminants from water. Activated carbon through adsorption also removes chemical like chlorine that combines with carbon to form chloride ions (TheWaterTreatmentPlant.com, 2009). This reaction helps not only in removing contaminants but also removes objectionable tastes and odors from drinking water.

Structural Tests

Simply incorporating a sorbent layer into a porous asphalt design is not adequate if the structural integrity is not found to be acceptable. The use of a computational program called Everstress yielded mechanical parameters caused by loading and a method of critical state friction angle determined the sorbents strength. The sorbents strength must resist the loading caused by both car and truck loads. Mohr's circle was generated for a visual presentation of the structural analysis.

"Everstress" Computational Software Program

In order to analyze typical stresses and strains from vehicle loadings, a computational software program called "Everstress" was utilized. Both a car load and truck load were used in the program. This yielded the principal stresses at depths within the porous pavement structure.

Critical State Friction Angle

The relationship between the friction angle of each sorbent and its shear strength was used as described in a report by J. Carlos Santamarina and Gye Chun Cho. The report brought together stress-dependant strength analysis in the unifying structure of critical state soil mechanics (Cho, 2001). The cumbersome and time intensive process of tri-axial testing could be replaced with the use of friction angle to quantify shear strength of a sample.

Mohr's Circle

Then both the stresses obtained by Everstress and the friction angles of each sorbent could be applied to Mohr's circle to visualize structural acceptability. Mohr's circle is a geometric representation of the 2-D transformation of stresses and is very useful to perform quick and efficient estimations, checks of more extensive work, and other such uses.

Methodology

The team had to identify:

- 1a. The method of measurement and a concentration curve for benzene.
- 1b. The parameters and procedure of the column adsorption tests.
- 1c. The parameters and procedure of the structural tests.

Method of Measurement & The Concentration Curve

The concentration curve was generated to determine the final concentrations of the test samples. The method of measurement used was a Chemical Oxygen Demand test (COD). The COD test and a spectrophotometer quantified the adsorption rate of each sorbent at different concentrations of benzene.

Chemical Oxygen Demand Tests

The method of measurement was a chemical oxygen demand (COD) test and absorption readings using a spectrophotometer. 2.5 mL of a test sample were added to a 20 mg/L – 900 mg/L COD vile, called standards, and heated at 150 degrees Celsius for two hours on the heater block. A blank of 2.5 mL of distilled water was used to zero the spectrophotometer for each experiment. Figure 9 shows a case of COD vials.



In order to avoid errors in the COD testing, the team used three different vials on each sample. After cooling for 45 minutes all three standards were measured with a spectrophotometer that was zeroed with a blank. At high levels of concentration a precipitate formed inside of the vials and was removed for accurate readings. The standard deviation of all three standards of each test was calculated to estimate the precision of the measurements. The spectrophotometer is shown in figure 10 and the COD and spectrophotometer lab procedure is located in Appendix A;



Figure 10 - Cary UV Spectrophotometer

Concentration Curve of Benzene

A concentration curve was developed using this COD analysis. Samples were made with distilled water and concentrations of benzene in increments of 100 mg/L up to 800 mg/L. Steps were taken to account for solubility and volatilization. Samples were mixed twice for five

minutes on a mixing plate and volumetric beakers and pipettes only were used to negate volatilization. Absorption levels were measured by the spectrophotometer and plotted against their associated concentrations. This curve was used to plot the test samples absorbance to identify their concentration.

Column Adsorption Tests

In order to analyze the removal capacity of the two chosen zeolite structures and the GAC, column adsorption tests were designed to mimic both the infiltration process and the actual structure of the porous pavement. The columns had a radius of 1" and a length of 18". The column is shown in figure 11.



Figure 11 – Column Adsorption Test

Test Procedure

The team had to set parameters to identify how the sample would be introduced into the columns and how long it would remain in the column. The lowest suggested permeability of a native soil is ¹/₂" per hour. However the slow infiltration of the samples through the columns was too complicated to mimic and increased concerns about volatilization and outside factors. To

avoid errors the team decided on letting each sample sit in the column for a designated period of time. The initial tests were set for 1 hour. Each sample was drained into a volumetric beaker and placed into a COD vial. The COD vials were then put into a heating block for two hours at a constant temperature of 150 C°. Figure 12 shows the heater block.



Figure 12 - Heater Block

The absorption was then measured using the spectrophotometer and compared to the concentration curve to yield the final concentration of each sample.

To identify parameters concerning the placement of the zeolite, the team decided to place the zeolite into two locations; first in a 1 in. layer along the bottom and second mixed in with the standard amount of aggregate. Figure 13 is a schematic of the placement of the sorbents.



Figure 13 - Placement of Sorbent

Material Quantities

HydroCAD, a stormwater modeling system, showed that in the New England area for a 2 year storm over a 24 hour period accumulated rainfall was 3 in. and the 100 year storm 7 in. (HydroCAD, 2008). The selection of the quantity of the samples, benzene and water, was dependent on these rainfall quantities but standard amounts would also make the experiment simpler and consequently with less error. 100 mL of a sample measured around 5 in. in depth inside the column and was identified as the standard sample size. The team decided on using an original concentration of 800 mg/L for each sample. This would yield larger changes in the concentration then if a lower concentration were used. However, typical concentrations are not this high.

Next, an aggregate size and amount was identified. Due to the constraints of the column a typical recharge bed aggregate of 1 in. to 2 in. could not be used. Instead we attempted to mimic the void ratio of 40% between the aggregate and column. Aggregate between 1/8 in and 1/4 in. served the required needs. The team decided on using 110 g of aggregate which measured 5 in. inside of the column. The aggregate was washed and oven-dried to remove remaining water.

Then, the team decided on the quantity of the zeolite. There were two types of zeolites: 5A & HiSiv 3000. Since our initial tests were to be 1 hour long and the typical lower bound of permeability of native soil is ½ in/h the team used 1 in of the zeolite in the column. This amount was than measured and rounded off to 15 g. The ratio of zeolite to aggregate is around 13.5%.

To compare the zeolite to a known absorbent a second material was identified to compare results. The sorbent chosen was granular activated carbon and the data would serve as a bench mark for the zeolite. Standards were processed exactly the same as the other experiments and 15 g of the active carbon was used. Lab material data sheets are presented in Appendix B.

Control

The control test consisted of only the standard sample of benzene, 100 mL, with a concentration of 800 mg/L and washed aggregate, 110 g. Aggregate was introduced first then the sample. Parafilm was placed over the column to avoid volatilization. The samples sat for 1 hour, then drained, placed into a COD vile, heated, and absorption was measured using a spectrophotometer. The control was the base that all other tests were compared too.

Control without Aggregate

The team wanted to identify if there was any interaction with the aggregate and benzene. A column adsorption test was developed similar to the control test but without aggregate. The final value would be compared to the control to identify if the aggregate interacted with the benzene. The lab procedure for the control with and without aggregate is in Appendix C.

5A Zeolite

The 5A test consisted of the standard amount of aggregate, 110 g, and sorbents, 15 g, and the samples sat in the columns for one hour. Parafilm was placed over the column to avoid volatilization and the zeolite was tested at both standard placements for 1 hour. Final concentrations were then compared to the control sets and the GAC.

HiSiv 3000

This zeolite was tested the same way as the 5A. Standard samples and material quantities were used and the zeolite was tested in both placements for 1 hour. Final concentrations were then compared to the control sets and the GAC.

Granular Activated Carbon

GAC was tested using the standard samples and material quantities. This sorbent was analyzed for 1 hour and in both positions. The lab procedure for the zeolite and GAC on the bottom is located in Appendix D and mixed in Appendix E.

Kinetic Effects

The team also developed tests to analyze the effect of time on the benzene and zeolite. Procedure and material quantities remained the same but the samples sat for a period of 3 hours, 18 hours and 30 hours and only in the mixed position. The time tests would identify if the zeolite would perform better over time and secondly, if the benzene was effected over this length.

Structural Test

The structural test were chosen to estimate the structural integrity of a sorbent layer within the porous pavement structure. Migration of the sorbent and shear strength was the necessary parameters to identify. This was accomplished by a "pooling test" and a computational program that was compared to the sorbents strength.

"Pooling Test"

The "pooling test" tested whether particle size difference prohibited of restricted migration of the sorbents. The first step to the pooling test was acquiring 1-2" aggregate, sorbent material, 4" cylinder and a sieve. The cylinder was open on both ends and placed on top of a sieve that would stop the aggregate but not the sorbent material. If a large amount of sorbent fell through the sieve then particle size differences may allow migration of the sorbents and the mixed position should be further analyses for acceptability.



Figure 14 - Recharge Bed Aggregate



Figure 15 - Pooling Test

The sorbent material and aggregate were mixed and poured into the cylinder. The amount of sorbent material outside the sieve was measured, which showed the potential of migration when placing the sorbent in a mixed position.

"Everstress" Computational Software Program

"Everstress" computes and displays the stress, strain and deflection within a pavement. This allowed us to analyze the pavement at various levels in order to quantify the stresses and strains within the structure. A pavement with a load on the surface was modeled in Everstress, and stresses and strains at different levels were computed for both a car and truck load. The HMA layer was 22.90 cm thick with a Poisson's ratio of 0.35 and the modulus of elasticity of 2000 MPa. The second layer of aggregate was 45.7 cm thick with a Poisson's Ratio of 0.35 and a modulus of 500 MPa. The ground below these two layers was considered infinite with a Poisson's ratio of 0.40 and a modulus of 50 MPa. The layer inputs for both the car and truck loads are presented in table 3.

Layer	Poisson's	Thickness	Moduli (1)
*	Ratio	(cm)	(MPa)
1	0.35	22.9	2000
2	0.35	45.7	500
3	0.4	*	50

Table 3 - Input Data for Everstress

A car load of 4.450 kN and 242 kPa tire pressure was simulated on the pavement. The radius of contact for the car simulation was 7.65 cm. A truck simulation with a load of 40.05 kN and tire pressure of 689.5 kPa was applied with a radius of contact of 13.597 cm. The stress,

strain and deflection at the sorbent material level were then measured separately for both loads. This allowed us to identify the stress, strain and deflection at that desired location of the sorbent. Table 4 and table 5 show the loading input data for the car and truck loads.

Load No	X- Po`s.	Y- Pos.	Load	Pressure	Radius
*	(cm)	(cm)	(N)	(kPa)	(cm)
1	0	0	4450	242	7.651

 Table 4 - Input Data for Car Load

Table 5 - Input Data for Truck Load

Load No	X- Pos.	Y- Pos.	Load	Pressure	Radius
*	(cm)	(cm)	(N)	(kPa)	(cm)
1	0	0	40050	689.5	13.597

Critical State Friction Angle

To determine the shear strength of each sorbent the team utilized their critical state friction angles. The team was concerned with both the intact state of the sorbent and the possibility of the sorbent being crushed therefore the friction angle was found for both states. The team poured the sorbent into a graduated cylinder at least 1000 mL in volume. The graduated cylinder was then filled with water well above the sorbent line. The graduated cylinder was then tilted passed 60°. Then the cylinder was slowly returned to the vertical position and the angle of repose was measured. Then the stresses from Everstress and the friction angles were applied to Mohr's circle to visually estimate the structural acceptability.





Figure 16 - 5A Friction Angle





Figure 17 - HiSiv 3000 Friction Angle





Figure 18 - GAC Friction Angle

Results and Discussion

The results of each sorbent were compared not only to both control tests, but also to themselves in reference to the placement of the sorbent. Kinetic tests were compared to each other. Both zeolite exhibited higher removal capacity for longer durations of time. However, GAC exhibited the highest removal capacity and only in the hour test. Surface area and unit weight may be a factor in the higher removal capacity for the GAC.

Column Adsorption Tests Results

Table 6 shows the amount of benzene used for the desired concentrations is shown along with the concentration curve. Each amount of benzene was mixed with water to a total amount of 1 L. Then, it was measured and plotted against its concentration. The absorbance readings for the concentration curve are shown in Appendix F. The concentration curve is also shown in figure 19.

Desired Concentration (mg/L)	Amount of Benzene (mL)	Total Amount (mL)
100	0.114	1000
200	0.227	1000
300	0.341	1000
400	0.455	1000
500	0.568	1000
600	0.682	1000
700	0.795	1000
800	0.909	1000

Table 6 - Concentration Curve Data



Figure 19 - Concentration Curve

The concentration curve was developed numerous times until there was a consistent set of values. During the initial test, precipitate was entering into the cuvette and the absorption was not accurate. Once the precipitate was identified as a problem and corrected the data began to conform. However there were problems with grouping of different concentrations and it was only with successive iterations that the team was convinced of the accuracy. This is evident in concentration curve, since only four of the values were used. These were the values that yielded the highest linear relationship congruent with consecutive readings.

Control & Control without Aggregate

The control test was the test without a sorbent that identified if removal capacity was affected by outside variables such as volatilization or the materials used. To test if the aggregate was interacting with the benzene, a second control was performed without aggregate. After an hour of sitting in the column, the samples were drained and added to three COD standards then measured using a spectrophotometer. Shown in Figure 20, are the results for the control with and without aggregate. The table shows the average of the final concentration of the standards.



Figure 20 - Control with Aggregate & Control without Aggregate

There is little interaction between the aggregate and benzene with around 2% difference between the two tests. The 11% loss in the control with aggregate was attributed to volatilization. Also there was around a 10% loss in mass of the sample, which upon visual inspection was attributed to both the aggregate and cylinder.

5A Zeolite Removal Capacity

The 5A zeolite removed 30% of the benzene in the bottom position and 36% in the mixed position. This results in an average of around 22% removal capability, which is less the 11% determined by the control test. Figure 21 shows the results of the 5A in both the mixed and bottom position.



Figure 21 - 5A Mixed & Bottom

HiSiv 3000 Zeolite Removal Capacity

The HiSiv removed 33% in the bottom position and 42% in the mixed position. This results in around a 27% removal capability. Presented in figure 22 are the results for the HiSiv 3000 in both the mixed and bottom position.



Figure 22 - HiSiv Mixed & Bottom

Granular Activated Carbon Removal Capacity

The activated carbon removed more benzene than either of the zeolites. However, this was attributed to the surface area of the granular activated carbon. The zeolite and the activated carbon surface areas are not equivalent on a mass basis,15 g of activated carbon has around 50% more area than the zeolite, effectively rising to a depth of over two inches inside of the column. Presented in figure 23 are the results for the GAC in both the mixed and bottom position. The lab absorbance readings for all 1 hour tests are located in Appendix G.



Figure 23 - GAC Mixed & Bottom

Shown below are all the 1-hour long tests including all sorbent tests in both positions and both control tests. The concentrations are located at the bottom of the bar graph and standard deviations located above each bar graph, which can be seen in figure 24 and table 7.



Figure 24 - 1 Hour Time Set Test Graph

Test	Standard Deviation	Concentration mg/L
Control w/agg.	33.81	706
Control w/o agg	50.52	722
HiSiv 3000 Mixed	7.64	463
HiSiv 3000 Bottom	5.69	534
5A Mixed	1.53	513
5A Bottom	14.93	564
Activated Carbon Mixed	0.58	22
Activated Carbon Bottom	0.58	107

 Table 7 - Column Adsorption Test Table

Also shown is the comparison between the 5A and HiSiv in both positions in a bar chart, figure 25, and table, table 8.



Figure 25 - Mixed & Bottom for HiSiv & 5A - 1 Hour

Test	Standard Deviation	Concentration mg/L
HiSiv 3000 Mixed	7.64	463
5A Mixed	1.53	513
HiSiv 3000 Bottom	5.69	534
5A Bottom	14.93	564

Table 8 - HiSiv and 5A Column Adsorption Test Data

Kinetics Test Results

To analyze whether the zeolite had a greater removal capacity when exposed to the sample for longer periods of time or if the benzene was affected by this duration, the team performed the column adsorption tests for a period of 3 hours, 18 hours and 30 hours. Only the HiSiv and 5A were tested at these time sets and only in the mixed position, which was identified to be the best placement in the preliminary 1 hour test. Present is the data on the kinetics tests, in both a bar chart and table, figure 26 and 27 and table 9. The concentrations and standard deviations of the three standards are shown for both formats. The lab absorbance readings for the time sets are located in Appendix H.



Figure 26 - Time Test Data HiSiv 3000



Figure 27 - Time Test Data 5A

Time	Test	Standard Deviation	Concentration mg/L
3hrs	5A-	10.54	481
	Mixed		
	HiSiv-	13.58	506
	Mixed		
18hrs	5A-	7.51	464
	Mixed		
	HiSiv-	1.73	344
	Mixed		
30hrs	5A-	1.53	368
	Mixed		
	HiSiv-	10.58	147
	Mixed		

Table 9 - Kinetics Effect Data HiSiv 3000 & 5A

The HiSiv performed well as the interaction time increased, removing around 82% of the benzene in the 30 hour test. Volatilization is a concern at this duration but the 5A retained half of the original concentration.

Structural Aspect Results

The pooling test and the strength and stress determination were based on current methods and research associated with pavement analysis. The limitations and restrictions inherent in the methods governed the methods application to this study.

"Pooling" Test

The pooling test revealed the possibility of migration of the zeolite when placed in a mixed position. Approximately 90% of the sorbent fell through to the bottom of the sieve. Even upon visual inspection it was clear that the sorbent sat or pooled in certain areas, effectively lowering the possibility of interaction between the sorbent and contaminant.

Critical State Friction Angle Results

The friction angle provides information on the shear strength of the material. The greater the friction angle, the higher the shear strength the given material will have. There were two sets of tests, one test with each sorbent crushed, and the other with each sorbent intact. For each set, the sorbent angle was tested three times and then averaged. Table 10 shows the angles and standard deviation for each sorbent in the intact state.

Туре	HiSiv	5A	GAC
Angle	29	24	34
	31	23	37
	33	25	39
Average	31	24	36.67
St. Dev	2	1	2.52

Table 10 - Friction Angle Data – Intact State

There were some differences between the crushed and the intact state friction angles as shown in Table 11.

Type Crushed	HiSiv	5A	GAC
Angle	25	36	35
	28	32	39
	30	35	36
Average	27.67	34.33	36.67
St. Dev	2.52	2.08	2.08

Table	11	- Friction	Angle	Data	-	Crushed	Sorbent	t
-------	----	------------	-------	------	---	---------	---------	---

The HiSiv friction angle went down when the material was crushed. The HiSiv is cylindrical in form and when crushed, it became a mix of powder and smaller cylindrical material. The 5A zeolite friction angle went up significantly when crushed. It's normally in a spherical shape, which gave it a low friction angle. Once crushed, the material was no longer uniform, giving it the higher angle. The friction angle of the GAC remained the same after crushing. This is due to the fact the GAC was initially in granular form and it didn't change significantly once crushed.

"Everstress" Computational Software Program

Everstress yielded principle stresses for the desired depth of the sorbent. For the carload, the principal stresses were 2.66 kPa and 6.45 kPa. The truckload had principal stresses of 23.35 kPa and 56.62 kPa. Table 12 is a summary of the outputs for both car and truck loads.

Load Type	Z-Position	Sxx, Syy	Szz	Exx, Eyy	Ezz	S1	S3
	(cm)	(kPa)	(kPa)	(10^-6)	(10^-6)	(kPa)	(kPa)
Car	68.6	6.45 (T)	1.12 (C)	9.16 (T)	11.26 (C)	2.66 (C)	6.45 (C)
Truck	68.6	56.62 (T)	9.91 (C)	80.54 (T)	99.08 (C)	23.35 (C)	56.62 (C)

Table 12 - Output Data Car and Truck Loads

Mohr's Circle

Figure 28 depicts Mohr's circle for each sorbent with both car and truckload stresses. The friction angles used were for the intact state and as shown it is revealed that the 5A zeolite failed for both situations and requires further investigation. Both the GAC and HiSiv passed with GAC yielding the greatest friction angle and therefore the greatest shear strength.



Figure 28 - Friction Angle Diagrams

Design and Recommendations

The design presented here is based on the literature reviewed by the team and results of the experiments conducted. Though the adsorption results were better for the mixed position, the pooling test revealed the possibility of pooling of the sorbent. Therefore, confining the sorbent into one layer prohibits migration of the sorbent. We placed the layer of sorbent 26 in. down for a thickness of 1". A recharge bed was chosen for two reasons. First, it has higher stresses at the layer of sorbent than a non-recharge bed design and second, it is used in areas of large runoff. The recharge bed will consist of a reservoir of crushed stone 3/4" – 2" for a depth of 18 in. Its sieve analysis is present in table 13;

Recharge Bed Aggregate Sieve Analysis			
Sieve Size	% Passing		
2-1/2"	100		
2"	95-100		
1"	0-30		
3/4"	0-5.0		

Table 13 - Recharge Bed Sieve Analysis

The choker layer will be 4" in depth and will act as the structural base for the OGFC. The binder content should be a minimum of 2% and contain a SBS polymer. The majority of aggregate sizes should be between 3/4" and 3/16" with nothing lower than sieve 30. Its sieve analysis is presented in table 14.

Choker Coarse Design Analysis				
Sieve Size	Target	% Passing		
1.48"	100	100		
1"	96	95-100		
3/4"	90	80-95		
1/2"	48	35-70		
No. 4	6	2-10		
No. 8	3	0-5		
No. 25	1.3	0-2.0		
Binder Content	Minimum 2%			

 Table 14 - Choker Coarse Sieve Analysis

The OGFC will be 4" and have a permeability of 8 in./hr. The binder content shall be a minimum of at least 6% and contain a SBS polymer. Its sieve analysis is presented in table 15.

OGFC Design Analysis			
Sieve Size	Target	% Passing	
3/4"	100	100	
1/2'	96	85-100	
3/8"	65	55-75	
No. 4	20	10-25	
No. 8	8	5-10	
No. 25	2.3	2.0-4.0	
Binder Content	Minimum 6%		

Table 15 - OGFC Sieve Analysis

The design schematic is presented in figure 29.



Figure 29 - Design Schematic

Geotextiles will prohibit migration of fine sediment. It will be placed both below the choker coarse and confining the sorbent material. The native soil is to be undisturbed.

The design presented above was based on the results of this MQP project and will be subject to further verifications and modifications.

Procurement of the zeolite was difficult and selection was governed by availability. We would suggest that research on a zeolite for removal of a hydrocarbon consist of a large range of molecular sieve sizes since this is the mechanism of desire. Without becoming too complicated of a project, this team believes that identifying the removal capacity with respect to duration and location is key in optimizing the use in, as of now, untested areas such as within a porous pavement.

Other zeolites could have been used instead of type 5A molecular sieve and HiSiv 3000. In 1998, there were around 200 synthesized and natural zeolites in the world. Different zeolites, with different structures and pore sizes, could possibly give significantly different results.

Contaminants from runoff are found in lower concentrations than what was researched. Using a set of lower concentrations would eliminate the precipitate in the COD vials and may give more steady readings. Also, benzene isn't the only contaminant that pollutes the water in runoff. Other containments include: paint, pesticides, other motor vehicle contaminants and salt. These contaminants could be used to further advance this research.

The team believes the experiment could be performed on a larger scale to make a more realistic situation with fewer limitations. A suggestion would be using 4'x4' box of HMA with 1"-2" base of crushed aggregate and a layer of adsorbent. A pump above could be used to

replicate rainfall falling on the porous pavement structure with a collector at the bottom to gather the test samples.

References

Advameg. 2009. Water Encyclopedia. [Online] 2009. http://www.waterencyclopedia.com/Po-Re/Pollution-Sources-Point-and-Nonpoint.html.

Advances in Porous Pavement. Tara Hun-Dorris. 2005. 2005, Stormwater.

Aldrich, Sigma. 2005. Technical Information Bulletin-Molecular Sieves. *Sigma Aldrich*. [Online] Sigma Aldrich, 2005. [Cited: November 11, 2009.] http://homepages.see.leeds.ac.uk/~chmjbm/safety/msds/Molecular%20Sieves.pdf.

Bauer, Loeffelholz & Wilson 2005. 2005. *Estimation, Mapping and Change Analysis of Impervious Surface Area by LANDSAT Remote Sensing.* Sioux Falls : South Dakota, 2005. GIS Study.

Bowles, Glenn. 2009. Impervios Surface: An Environmental Indicator. [Online] 2009. [Cited: 10 22, 2009.] http://www.uwsp.edu/cnr/landcenter/pdffiles/EnvironmentalIndicatorFactSheet.pdf.

CarboChem. 2009. Activated Carbon 101. *CarboChem*. [Online] 2009. [Cited: November 23, 2009.] http://www.carbochem.com/activatedcarbon101.html.

Santamarina, J. Carlos and Cho, Gye Chun. 2001. *Determination of Critical State Paramters in Sandy Soils.* s.l. : Geotechnical Testing Journal, 2001.

CO2CRC. 2008. Zeolite Unit Cell. *Cooperative Research Centre for Greenhouse Gas Technologies.* [Online] Cooperative Research Centre for Greenhouse Gas Technologies, 2008. [Cited: September 10, 2009.] Picture of zeolite unit cell. http://www.co2crc.com.au/about/co2crc.

Webster's New College World Dictionary. 2009. Activated Carbon. *Your Dictionary*. [Online] LoveToKnow, Corp., 2009. [Cited: November 23, 2009.] http://www.yourdictionary.com/activated-carbon.

Dauphnin County Conservation District. 2004. Best Management Practices Fact Sheet: Porous Asphalt. [Online] 2004. [Cited: 01 14, 2010.] http://www.dauphincd.org/swm/BMPfactsheets/Porous%20Asphalt%20fact%20sheet.pdf.

EPA. 2010. Environmental Protection Agency-Managing Urban Runoff. *EPA web site*. [Online] January 10, 2010. [Cited: January 22, 2010.] Managing urban runoff. http://www.epa.gov/nps/facts/point7.htm.

-. 2004. *Mid-Atlantic Water*. s.l. : EPA, 2004. Environmental.

-. 2008. U.S. Environmental Protection Agency. [Online] 2008. http://www.epa.gov/nps/whatis.html.

...2009. US Environmental Protection Agency. US Environmental Protection Agency-Benzene. [Online] 2009. [Cited: September 1, 2009.] solubility of benzen. http://www.epa.gov/athens/learn2model/part-two/onsite/es.html.

US. Fabrics2009. US Fabrics. [Online] 31 2009. [Cited: 3 15, 2010.] http://www.usfabricsinc.com/media/products/catnonwoven.pdf.

Gas Alarm. Patent Storm, LLC. 2004. s.l. : US Patent 5764150, 2004.

HydroCAD. 2008. Stormwater Modeling System. s.l. : Applied Microcomputer Systems, 2008.

LeFevre, Greg, Gulliv, John S. and Weiss, Peter T. 2008. *Contamination of Soil and Groundwater.* Minneapolis, MN : St. Anthony Falls Laboratory University of Minnesota, 2008. A Literature Review.

LennTech. 2009. Lenntech Water treatment & purification Holding B.V. *A LennTech Web Site*. [Online] 2009. [Cited: December 2, 2009.] http://www.lenntech.com/library/adsorption/adsorption.htm.

Merck Index. 1976. 1976. 9th Edition. Rahway : Merck and Company, Inc., 1976.

AceChemPack Tower Packing. 2009. 5A Molecular Sieve. *AceChemPack Tower Packing Co.* [Online] 2009. [Cited: September 26, 2009.] http://www.tower-packing.com/molecular%20sieve/5a_molecular_sieve.htm.

South Portland. 2009. *Maine Mall Road Porous Pavement.* South Portland : South Portland, 2009. Civil. Personal Communication with Richard Bradford on the 26 of January, 2010

T.Ballestero, R.Roseen, K.Houle, J.Briggs & J.Houle. 2009. *Porous Pavement as a Technology for Salt Reduction.* s.l. : University of New Hampshire Stormwater Center, 2009. Research.

T.H.Cahill, P.E., M.Adams, P.E. & C.Marm. 2003. Porous Asphalt: The Right Choice for Porous Pavements. *cleanwatermn.* [Online] 09-10 2003. [Cited: 01 11, 2010.] http://www.cleanwatermn.org/Documents/MS4% 20toolkit% 20files/Good% 20Housekeeping/Porous% 20 Pavement/Asphalt-Right% 20Choice% 20For% 20Porous% 20Pavements.pdf.

TheActivatedCarbon.com. 2009. Activated Carbon Adsorption. *The Activated Carbon*. [Online] 2009. [Cited: November 27, 2009.] http://www.theactivatedcarbon.com/page/activated-carbon-adsorption/.

TheWaterTreatmentPlant.com. 2009. Carbon Adsortion. *Water Treatment Plant.* [Online] TheWaterTreatmentPlant.com, 2009. [Cited: November 26, 2009.] http://www.thewatertreatmentplant.com/carbon-adsorption.html.

U.S. Department of Transportation, FHA. 1990. FHWA. [Online] December 26, 1990. [Cited: November 11, 2009.] http://www.fhwa.dot.gov/legsregs/directives/techadvs/t504031.htm.

Waikato Enviroment. 2010. EW GOV. [Online] 2010. http://www.ew.govt.nz/environmental-information/Rivers-lakes-and-wetlands/healthyrivers/Waikato-River/Runoff-and-leaching/.

Wilkinson, Angus P. 2009. Introduction to Zeolites. *Georgia Institute of Technology - Department of chemistry and biochemistry*. [Online] 2009. [Cited: September 10, 2009.]

http://web.chemistry.gatech.edu/~wilkinson/Class_notes/CHEM_3111_6170/Introduction_to_zeolites.pdf .

Yang, Ralph T. 2003. *Adsorbents: Fundamentals and Applications.* Hoboken : John Wiley and Sons Inc., 2003.

Zeo. 2009. About Zeolites: Zeolite Structure. *A Zeo Inc. Webste.* [Online] 2009. [Cited: 09 26, 2009.] http://www.zeoinc.com/zeolite_structure.html.

Zeolite. 2004. Zeolite Product. *A Zeolite.com Website*. [Online] Zeolite.com, 2004. [Cited: October 12, 2009.] http://www.zeolite.com/.

Appendix

Appendix A – COD & Spectrophotometer Lab Procedure

- 1. Preheat a COD heater block to 150° Celsius.
- 2. Use the reagent 20-900 mg/L COD test tubes.
- 3. Remove cap from COD test tube and add 2.5 mL of your sample down the side of the vial so it will form a layer on top of the reagents.
- 4. Place cap back on test tube and shake carefully.
- 5. Place the test tube on the COD heater block and leave for two hours.
- 6. After two hour span, take out sample and allow it to cool to room temperature for a half hour.
- 7. Open program "Simple Reads".
- 8. Set the wavelength of the spectrophotometer to 600 nm.
- 9. Zero the spectrometer with a blank using a cuvette.
- 10. Remove any precipitate form the COD vile.
- 11. Replace blank with sample with another cuvette and click "Read".
- 12. Read the absorbance of the sample on the spectrophotometer.

Appendix B – Material Lab Data Sheets

Material	Specs	Notes
Zeolite		
Amt		
type		
Aggregate		
type		
Amt		
size		
Cylinder		
dia.		
height of Zeolite/Agg.		
solution		
Amt		
mg/L of benzene		
pump		
rate of flow		
Results		
amt of loss		
Final Abs		
Concentration		

Appendix C – Control w & w/o Aggregate Lab Procedure

- 1. Prepare an 800 mg/L concentration of benzene to water.
- 2. Put valve on to bottom of cylinder.
- 3. Clamp cylinder to a stand
- 4. Put valve tip partly in a 100 mL volumetric flask and seal with parafilm to prevent benzene from escaping.
- 5. Measure 110 grams of sieve 1/8" and put into cylinder.
- 6. Measure 100 mL of 800 mg/L concentrated benzene and slowly pour into top of cylinder into a funnel so the benzene won't plume.
- 7. Wrap top of cylinder with parafilm immediately after all benzene is in the cylinder.
- 8. Let cylinder sit for designated time set.
- 9. Release valve and let it pour into 100 mL volumetric flask and cover with parafilm.
- 10. Follow the COD analyses and ensure that all sample are place on the heater block within a half hour.

Appendix D – Sorbent Test Lab Procedure Bottom Position

- 1. Prepare an 800 mg/L concentration of benzene to water.
- 2. Put valve on the bottom of cylinder.
- 3. Clamp cylinder to stand.
- 4. Put valve tip partly in a 100 mL volumetric flask and seal with parafilm to prevent benzene from escaping.
- 5. Measure 15 grams of zeolite and put into cylinder on the bottom.
- 6. Measure 110 grams of sieve 1/8" and put into cylinder on top of the zeolite.
- 7. Measure 100 mL of 800 mg/L concentrated benzene and slowly pour into top of cylinder into a funnel so the benzene won't plume.
- 8. Let cylinder sit for the designated time set.
- 9. Release valve and let it pour into 100 mL volumetric flask.
- 10. Follow the COD analyses and ensure that all sample are place on the heater block within a half hour.

Appendix E – Sorbent Test Lab Procedure Mixed Procedure

- 1. Prepare an 800 mg/L concentration of benzene to water.
- 2. Put valve on the bottom of the cylinder.
- 3. Clamp cylinder to stand.
- 4. Put valve tip partly in a 100 mL volumetric flask and seal with parafilm to prevent benzene from escaping.
- 5. Measure 15 grams of zeolite.
- 6. Measure 110 grams of sieve 1/8" and place into the same beaker as the zeolite.

- 7. Gently shake beaker to thoroughly mix then put into cylinder.
- 8. Let cylinder sit for designated time set.
- Release valve and let it pour into 100 mL volumetric flask.
 Follow the COD analyses and ensure that all samples are placed on the heater block within a half hour.

Appendix F – Preliminary 1 hour test data

Test	Standard Deviation	Concentration (mg/L)
Control w/aggregate	33.81	706
Control w/o aggregate	50.52	722
HiSiv 3000 Mixed	7.64	463
HiSiv 3000 Bottom	5.69	534
5A Mixed	1.53	513
5A Bottom	14.93	564
Activated Carbon Mixed	0.58	22
Activated Carbon Bottom	0.58	107

Appendix G - Concentration curve data

abs (x 1000)	Concentration (mg/L)
217	100
277	200
279	300
292	400
344	500
413	600
403	700
455	800

Appendix H - 3 -18-30 hour time tests

3 Hour Test			
HiSiv-Mixed	312	5A- Mixed	296
	323		284
	296		305
Average	310		295
Standard Deviation	13.58		10.54
Concentration	506		481
18 Hour Test			
HiSiv-Mixed	213	5A- Mixed	280
	210		293
	210		280
Average	211		284
Standard Deviation	1.73		7.51
Concentration	344		464
30 Hour Test			
HiSiv-Mixed	86	5A- Mixed	224
	82		226
	102		227
Avg	90		226
STDev	10.58		1.53
Concentration	147		368

Appendix I – Proposal

Porous Asphalt Filtration Design Proposal

Impervious asphalt does not allow infiltration to recharge ground water aquifers. Porous pavement promotes infiltration allowing runoff to recharge the aquifers. However runoff has the possibility of contamination from cars, trucks and other hazardous materials that sit on top of pavements. With ground water being diminished from the increase in impervious surface, porous pavement is a possible solution, but significant research must be done to mitigate possible contamination events.

The objectives of this project are to find a solution to mitigate such contaminants from entering the ground water through porous pavement. The solution must stop a significant amount of contaminants and also hold up to the stresses and strains of a road loads. If the solution cannot meet both of those needs it would be unsatisfactory. The team had to identify;

- 1. Analyze the removal capacity of the two zeolite structures.
- 2. Investigate the effect of time on the zeolite.
- 3. Compute the strength of each sorbent
- 4. Design a porous pavement incorporating sorbent based on the data.

In order to meet these needs the team must analyze the removal capacity of two forms of zeolites and use granular activated carbon as a bench mark. The team must select a contaminant, such as benzene, and test the sorbents in the lab for their absorption capacities. The tests simulate a porous pavement that allows water and benzene to infiltrate for set periods of time. Once the allotted time was over the amount of benzene that had infiltrated the "ground" or gone through the mock pavement will then be measured. The measurements will yield the most optimal remover of the contaminant.

We then must test the sorbent materials for their structural acceptability. First the stresses and strains within the pavement at various levels have to be found. A program called Everstress will be utilized in order to complete this task. The program allows various pressures from cars or trucks to be applied and the stresses and strains at different level to be computed. Once these stress and strains are figured out the, the shear strength of the sorbent materials had to be figured out. Friction angles will be used to identify the shear strengths of the sorbents and Mohr's circle will be used to visual the acceptability. If the friction angle line intersect with the stress circle than the sorbent would be found unacceptable in design.