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A Novel Pervious Cement Reaction Barrier (PCRB) *in Situ* Arsenic Remediation System

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A NOVEL PERVIOUS CEMENT REACTION BARRIER (PCRB) *IN SITU*
ARSENIC REMEDIATION SYSTEM

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Morgan Liane Jones

May 2010

**A NOVEL PERVIOUS CEMENT REACTION BARRIER (PCRB) *IN SITU*
ARSENIC REMEDIATION SYSTEM**

Date Recommended May 13, 2010

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“I can do all things through Christ who strengthens me” Philippians 4:13

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Morgan Jones

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45 Pages

Directed by: Cathleen Webb

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As of 2006, the U.S. Environmental Protection Agency (EPA) lowered the Maximum Contaminant Level (MCL) for arsenic from 50 parts per billion (ppb), to 10 ppb because of links to cancer. Current remediation technologies are expensive; therefore, this change will result in increased economic pressure on rural communities with high levels of arsenic in their drinking water. Lowering of the standard has spurred the development of a novel remediation technology that has shown the ability to reduce arsenic in drinking water at the source. Limestone-based materials appear to be an effective arsenic removal process that has great potential for source reduction in drinking water. This research examined the potential use of pervious concrete as an *in situ* arsenic remediation system. This involved the designated construction of the Pervious Cement Reaction Barrier (PCRB). The research clearly showed that the PCRB has the potential to reduce arsenic in drinking water developed at the source. This is a significant expansion of the technical applications of the arsenic remediation technology. The research also showed that adding a modifier, Fe_2O_3 , did not contribute to the efficiency of arsenic removal.

I. INTRODUCTION

Arsenic contaminated drinking water has become a global health crisis. Approximately 60 million people are at risk for arsenic related diseases due to the consumption of drinking water contaminated with arsenic.¹ According to United Nations Children's Fund, 80 percent of these people are at risk in Asia (Table 1).⁹ Other parts of the world that also have major societal, cultural, and health impacts from drinking water with high levels of arsenic are India, Mongolia, Poland, Hungary, Chile, Argentina, and Mexico.² The most publicized and most endemic situation in a single country is Bangladesh. The situation is especially critical because the primary source of drinking and cooking water for most of its population is groundwater extracted from shallow aquifers. The 8-12 million tubewells³ that extracted water from subsurface aquifers were provided by the Bangladesh government to provide the country with bacteriologically safe drinking water.⁴ Although this achievement has reduced the incidence of waterborne diseases, the tubewells inadvertently created another problem because the groundwater was contaminated with extremely high levels of naturally occurring arsenic.

Arsenic can have adverse effects on human health. The symptoms of arsenic poisoning vary due to the type and level of exposure of the chemical to the body. Immediate symptoms short of lethality during acute arsenic poisoning include vomiting, abdominal pain, and bloody diarrhea.³ The symptoms of acute poisoning resemble other types of diseases; therefore, many patients are initially misdiagnosed. The problem could then become chronic with repeated exposures. During chronic

arsenic poisoning, often after long term exposure through drinking water, commonly the first observed symptoms are changes in the skin: skin lesions, pigmentation changes, and hyperkeratosis (skin thickening).³ A later symptom is cancer, which may impact the kidney, lung, bladder, or liver, and may take more than ten years to develop.⁵ Additionally, higher doses of inorganic arsenic species can lead to a disease known as the black foot disease.² The symptoms of the black foot disease include thickening and discoloration of the skin, lesions, stomach pain, nausea, vomiting, diarrhea, loss of limbs, and hearing impairment.⁶ Most of these symptoms only appear after five to ten years of exposure and can lead to death after fifteen to twenty years.⁶

Due to arsenic's links to cancer and the black foot disease in 2006, the Environmental Protection Agency (EPA) lowered the drinking water standard in the United States for arsenic from 50 parts per billion (ppb) to 10 parts per billion.⁷ Additionally, the provisional guideline value set by the World Health Organization (WHO) for arsenic has also been set at 10 ppb.³

Arsenic can be present from both natural and anthropogenic sources. Most arsenic contamination is due to naturally occurring arsenic in sediments and/or volcanic rocks. Some countries, such as Thailand and Ghana, have developed contamination from mining activities including leaching of mine tailings and waste deposits as well as atmosphere releases during the smelting process. Additionally, gopher eradication efforts have also caused arsenic contamination in the western United States.⁸

Location	Area extent (km ²)	Population at risk ^a	Arsenic range (µg L ⁻¹)
Bangladesh	150,000	35,000,000	<1-2,300
China (Inner Mongolia, Xinjiang, Shanxi)	68,000	5,600,000	40-4,400
India (West Bengal)	23,000	5,000,000	<10-3,200
Nepal	30,000	550,000	<10-200
Taiwan (China)	6,000	(?) 10,000 ^b	10-1,800
Vietnam	1,000	10,000,000 ^c	1-3,100
Myanmar	(?) 3,000	3,400,000	-
Cambodia	(?)<1,000	320,000 ^d	-

- Not available

^a Estimated to be exposed to drinking water with arsenic > 50 µg L⁻¹,

From Smedley 2003 and data sources therein

^b Before mitigation

^c United Nations Children's Fund (UNICEF) estimate

^d Maximum

Table 1: Summary of the distribution and scale of documented arsenic problems (>50 µg L⁻¹) in aquifers in south and east Asia⁹

Arsenic is a toxic metalloid element. It is unique among the heavy metalloids in its ease of mobilization at the pH values typically found in groundwater (pH 6.5-8.5).¹⁰ Arsenic can occur in natural waters as two oxidation states: arsenite (As (III)) and arsenate (As (V)). Arsenite is approximately sixty times more toxic than arsenate and it can easily oxidize and interfere with the metabolic pathway. Understanding the speciation of arsenic is important in determining arsenic chemistry so that effective removal methods for removing dissolved arsenic from water can be designed. The distribution of As (V) and As (III) compounds are significantly influenced by pH and illustrated by a speciation diagram. Figures 1 and 2 indicate the predominant forms of As (V) and As (III) present at any given value of pH. Tables 2 and 3 list the forms of arsenate in aqueous solution and the pH range in which more than 50 percent of that particular arsenate species exists in its correlating pH range with respect to total arsenic concentration. However, for arsenite species as shown in Table 3, pH ranges overlap and the percentage of the arsenite species may not be greater than 50 percent. For example, at pH 13, the percent distribution of arsenite species expected are 17 percent of both AsO_3^{3-} and H_2AsO_3^- and 63 percent HAsO_3^{2-} .

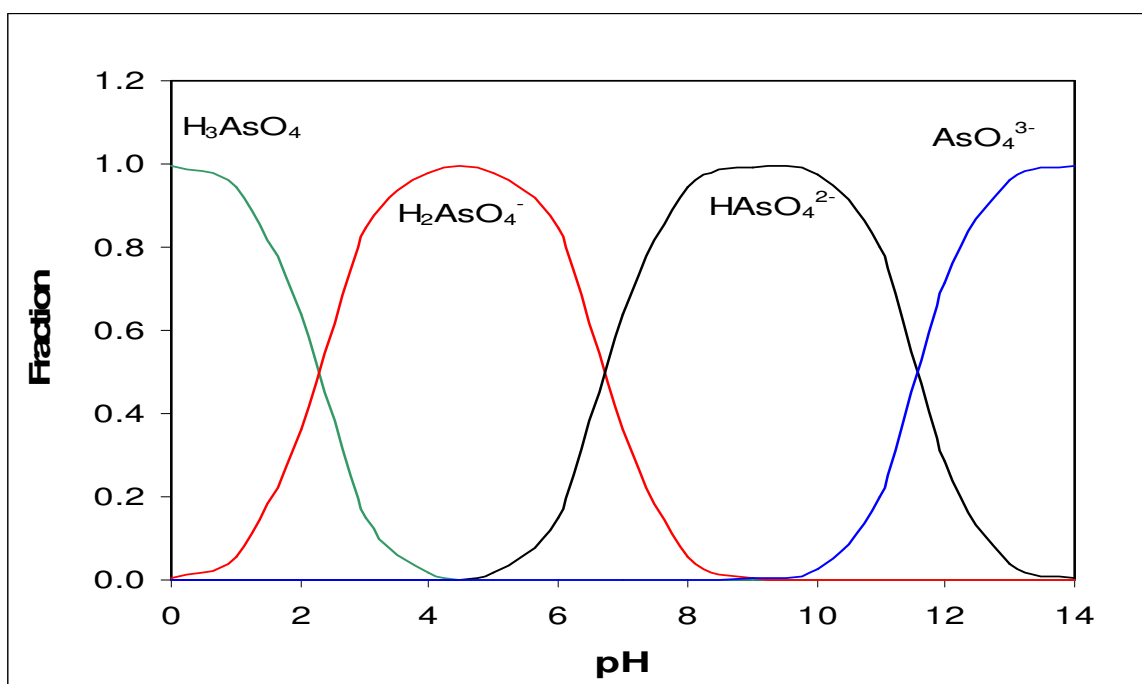


Figure 1: Arsenate speciation diagram (+5 oxidation state).

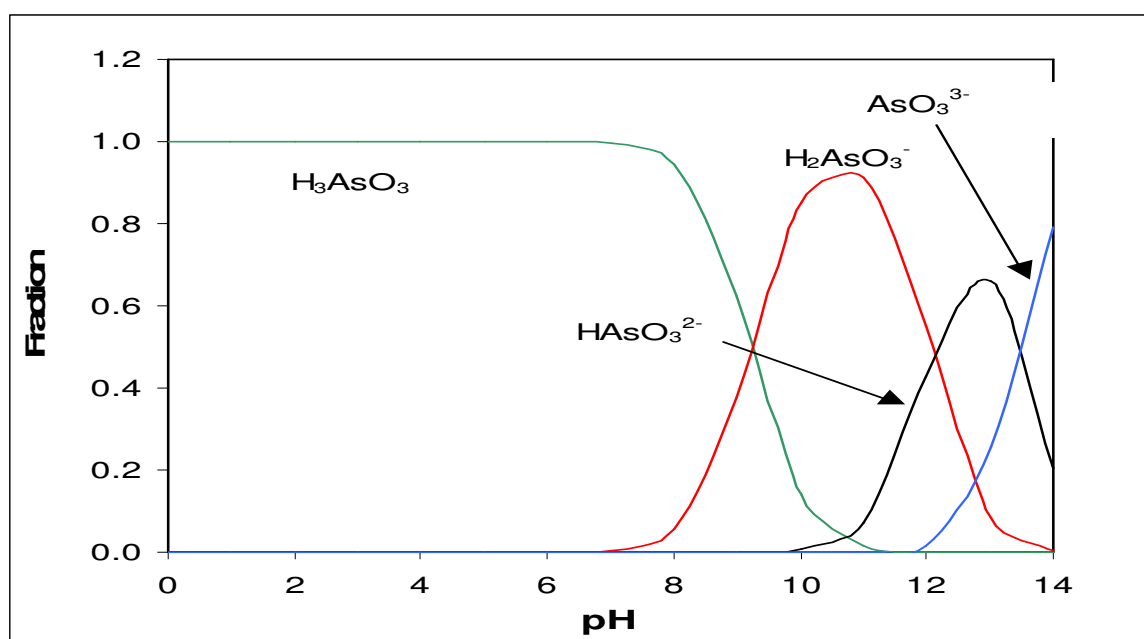


Figure 2: Arsenite speciation diagram (+3 oxidation state).

Arsenic Species	Name	pH stability range
H_3AsO_4	Arsenic Acid	pH 0-2
H_2AsO_4^-	Dihydrogen Arsenate	pH 2-7
HAsO_4^{2-}	Hydrogen Arsenate	pH 7-12
AsO_4^{3-}	Arsenate Ion	pH 12-14

Table 2: Arsenate speciation.

Arsenic Species	Name	pH stability range
H_3AsO_3	Arsenous Acid	pH 0-9
H_2AsO_3^-	Dihydrogen Arsenite	pH 9-12
HAsO_3^{2-}	Hydrogen Arsenite	pH 11-14

Table 3: Arsenite speciation.

Redox potential is also an important factor controlling arsenic speciation.¹⁰

Figure 3 illustrates the pE-pH diagram for arsenic. This diagram summarizes the fields of stability for aqueous arsenic species, and provides a basis for predicting which arsenic species will be present under different environmental conditions. The fields of stability reflect the speciation diagrams and/or oxidizing conditions. The diagram is restricted in range by the stability of water in Figures 1 and 2.

According to the pE-pH diagram (Figure 3), arsenate occurs under oxidizing conditions where H_2AsO_4^- is dominant at a low pH (~2.5-7), and HAsO_4^{2-} is dominant at a higher pH (~7-11.5). Also under these conditions, H_3AsO_4 is present under very acidic conditions, while AsO_4^{3-} is present under extreme alkaline conditions.¹¹

Arsenite occurs under reduced conditions (Figure 3). The dominant species present under reducing conditions is H_3AsO_3 at a pH less than approximately 9.2. The other arsenite species exist in alkaline conditions: H_2AsO_3^- (pH = ~9.5-12.1), HAsO_3^{2-} (pH = ~12.1-13.5), AsO_3^{3-} (pH = ~13.5-14).¹¹

The primary arsenate species found in groundwater are H_2AsO_4^- and HAsO_4^{2-} . In contrast, it is the uncharged form of arsenite (H_3AsO_3) that is found at typical groundwater pH values.¹¹ Since drinking water pH typically ranges from 5.5 to 8.3, any method of removing arsenic must consider using the predominant species present. The method must be robust enough to remove all species. For example, at pH 7, arsenate is nearly an equal mixture of anions; whereas arsenite is virtually all neutral.

Many remediation technologies are more efficient at removing arsenate than arsenite, due to charge electrostatic interactions with arsenate.

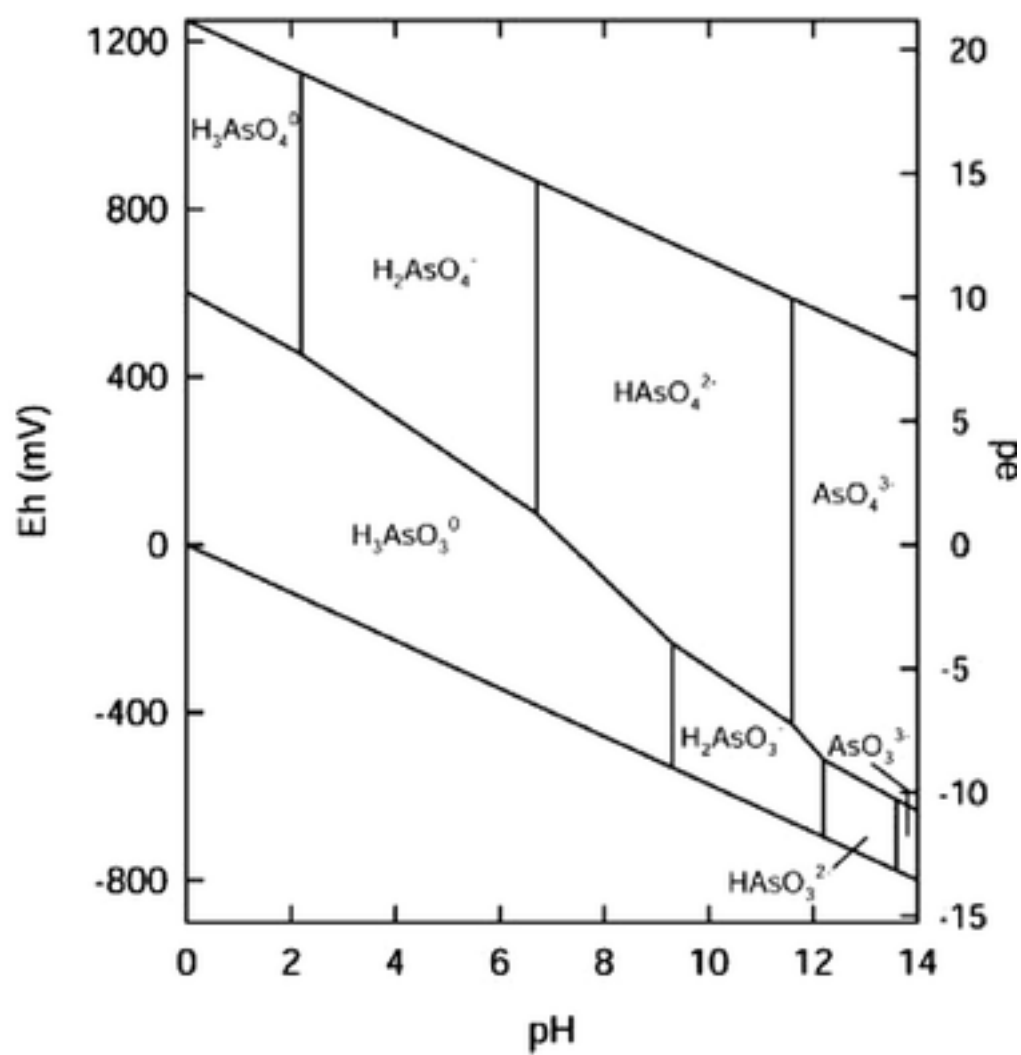


Figure 3: pE-pH diagram for aqueous arsenic species.¹⁰

There are four categories that include most current arsenic removal technologies: ion exchange, membrane process, adsorption, and chemical precipitation.¹² Although these processes can remove arsenic, each has disadvantages. For example, ion exchange treatments involve exchange competition from other anions found in groundwater creating limited ability to efficiently remove arsenic under a wide variety of water quality conditions. Although membrane processes are very effective in removing arsenic from groundwater, the cost is particularly high especially for use in developing areas with limited resources. The two categories of arsenic treatment that are currently utilized more frequently are adsorption and chemical precipitation processes.¹²

One common water treatment methodology using chemical precipitation for arsenic removal is coagulation/ filtration. Coagulation/ filtration is performed by removing suspended and dissolved solids from source water. The coagulation process promotes aggregation of the suspended solids to form flocculants (flocs), which then can be removed through sedimentation and/or filtration. Alum and iron (III) salts, such as ferric chloride, are the most common coagulants used for drinking water treatment.¹³ Ferric salts are more widely used than aluminum salts because of their effective ability to remove arsenite.¹⁴ During the formation of ferric hydroxides, removal of arsenic occurs through chemical adsorption and co-precipitation. The chemical bond that forms between ferric hydroxides and arsenate and arsenite species makes this method less susceptible to competition by background electrolytes.¹⁴ Both ferric salts and alum are more efficient at removing arsenate, therefore pre-oxidation

of arsenite is generally required to achieve maximum removal efficiency.¹² This removal technology is costly and best suited to larger water providers.

Other technologies that are effective at removing arsenic are granular ferric hydroxide (GFH) and zero-valent iron (ZVI). GFH is composed of a poorly crystallized FeOOH phase and is similar to the mineral β -FeO(OH) (akaganeite).¹⁴ It is manufactured by neutralizing and precipitating iron chloride solution with sodium hydroxide, followed by granulation at high pressure.¹⁵ GFH has sorption loadings that are high even at low arsenic concentrations and is effective at a wider pH range (5.5-9).¹⁶ ZVI has also proved to be effective at removing arsenic. It is a strong reducer and has the advantage of being nontoxic and relatively inexpensive. Su and Puls¹⁷ have shown that ZVI is effective at removing arsenic at low pH and in high-sulfide containing water. Although the reducing strength of ZVI decreases significantly at neutral pH, the hydroxide species forming on the surface of ZVI are effective adsorption sites for both arsenate and arsenite at neutral and basic pH.¹²

In 2005, the National Academy of Engineering (NAE) established the Grainger Challenge Prize for Sustainability to accelerate the development and distribution of community or household scale water treatment systems to remove arsenic from the contaminated groundwater found in developing countries.¹⁸ Abul Hussam received the gold award (first place) of one million dollars for his SONO filter. The SONO filter consists of two buckets. Water first flows through a top bucket consisting of locally available coarse river sand and a composite iron matrix (CIM) to filter coarse particles and remove inorganic arsenic, respectively.¹⁹ The water then

flows into a second bucket where it flows through coarse river sand, wood charcoal to remove organics, and fine river sand and wet brick chips to remove fine particles and stabilize water flow.¹⁹ The silver award of \$200,000 was awarded to Arup SenGupta, John Greenleaf, Lee Blaney, Owen Boyd, Arun Deb, and the nonprofit organization Water for the People. The system developed by this team is applied to a community's well head. Water is hand-pumped into a fixed-bed column, where it passes through activated alumina or hybrid anion exchanger (HAIX) to remove arsenic.¹⁹ The water then passes through a chamber of graded gravel to remove particulates.¹⁹ The bronze award of \$100,000 was awarded to the Children's Safe Drinking Water Program at Procter & Gamble Co. This program developed the PURTM Purifier of Water coagulation and flocculation treatment system. This treatment system combines chemicals for disinfection, coagulation, and flocculation in a sachet that can treat small batches for water in the home.¹⁹

In order for these technologies to be effective in developing countries, they must meet certain criteria. Appropriate technologies should be applicable over a wide range of arsenic concentrations and groundwater pH, Eh conditions, easy to use without running water or electricity, and the materials for the treatment should be cheap and readily available, and/or suitable for reuse.¹² Current remediation technologies, including coagulation/filtration and ion exchange, are quite expensive and are typically designed for large water treatment facilities rather than small rural water treatment facilities. Not only are small rural systems at a disadvantage because of the high operating cost, but also often experience difficulty in employing well-

trained operators and in maintaining the optimum operating conditions needed to successfully meet drinking water standards.

The effects of ingested arsenic contaminated water can be severe and maintaining the arsenic standard for drinking water is difficult; therefore, there is an urgency to develop a low-cost remediation technology for arsenic removal that can be easily adapted to rural supply systems. The purpose of this study is to characterize a robust new media for the removal of arsenic in drinking water using limestone as the base material. Limestone-based material provides several benefits to the drinking water community including reasonable removal efficiency, low material cost, compatibility with other water treatment processes, ease of use, and low-cost disposal in landfills.²⁰ Our most recent media uses iron impregnated limestone and has been found to be both efficient and comparable to the best available technologies, such as granulated ferric hydroxide. We are currently using #9 limestone, however, any natural limestone formation will work reasonably well.

One of our primary research goals focuses on development of *in situ* removal of arsenic from groundwater at the source. Our newest technological approach involves the integration of the iron- impregnated limestone with pervious cement. The key characteristic of pervious cement is that it has an open pore structure that allows relatively high rates of water transmission. The preparation of pervious concrete involves carefully controlled amounts of water and cement materials to create a paste that forms a thick coating around aggregate particles. Little or no sand is used in a mixture of pervious concrete in order to create a substantial void content. The use of the

paste to coat and bind the aggregate particles together creates a system of highly permeable, interconnected voids that drains quickly.²¹ During our research, with the help of Mr. Mike Young (College Engineer and Shop Supervisor), we prepared several columns with pervious cement, hereafter known as a pervious cement reaction barriers (PCRB) (Figure 4).



Figure 4: Pervious cement reaction barriers (PCRB).

II. EXPERIMENTAL

Component Mixture of Pervious Concrete:

This project involved the preparation of pervious concrete. The pervious concrete was prepared by mixing 10.0 lbs of #9 limestone, .550 lbs of water, and 1.40 lbs of Type 1 Portland cement. This pervious concrete preparation method was scaled down by a method provided by Irving Material Incorporated (IMI). The IMI method consisted of 3277 lbs of #9 limestone, 180 lbs of water, and 480 lbs of Type 1 Portland cement. The water-to-cement ratio of the pervious concrete batch was fixed at .30 because water-to-cement ratios between 0.27 and 0.30 are used routinely with the proper inclusion of chemical admixtures.²² The water-to-cement ratio is the relative weight of the water to the cement in the mixture. Four mixes were prepared using a portion of this pervious concrete batch procedure and varying amounts of Fe_2O_3 . Each varying amount of Fe_2O_3 was physically mixed into the wet matrix of the pervious cement. Each mix contained .965 lbs of pervious cement from the prepared batch and varying amounts of Fe_2O_3 . Table 4 illustrates the amount of each component per column. Each batch of pervious cement from Table 4 was poured into 2 x 4 inch columns forming the pervious cement reaction barrier (PCRB) (Figure 4). The PCRBs were then cured for 72 hours in a humidity room at $73^\circ \pm 2$ F. Curing the concrete aids in hydration and has a strong influence on strength and volume stability.²³

PCRB Flow Test:

After the columns were cured, flow tests were performed. Five flow tests were performed with a stop watch for each PCRB. The preliminary testing for the flow rate (liter/second) was to establish the pervious cement's level of permeability and to characterize the flow rate of each column prior to testing. The flow rate was conducted by noting the amount of time each sequential liter took to dispense out of a five liter carboy.

Concentration of Arsenic from Standard and Leachate:

Two five liter carboys were used to prepare two standard batches of ~ 200 ppm As_2O_3 . The batches were made by physically shaking a mixture of five liters of de-ionized water and one mL of 1000 ppb As_2O_3 . Both carboys were used to dispense solution through the PCRBs. The third and fourth five liter carboys were used to collect the leachate from the PCRB (leachate). Tygon™ tubing was used to connect both the dispensing carboy and leachate carboy to the PCRB. The leachate and standard were filtered using a 0.45 micron cellulose nitrate membrane filter in a syringe filter apparatus and collected in a 6 mL vial. The pH of both the leachate and standard solution and the conductivity of the leachate were measured using digital pH and conductivity meters. Overall, 10 leachates for each column and 15 standard samples were collected over a three week period. All standard and leachate samples collected were analyzed for arsenic by graphite furnace atomic absorption spectroscopy (GF-AAS).

Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS):

With the assistance of Mr. Rick Fowler at Western Kentucky University's WATERS analytical laboratory, graphite furnace atomic absorption spectroscopy (GF-AAS) was used to measure the amount of arsenic in the collected standard and leachate samples. GF-AAS is an analytical technique designed to perform quantitative analysis of metals in a wide variety of samples. Atomic absorption is a method that measures the concentration of atoms of an element by passing light, emitted by a hollow cathode lamp of that element, through a cloud of atoms from a sample.²⁴ Only those atoms that are the same as those in the lamp will absorb the light from the lamp. A reduction in the amount of light reaching the detector is seen as a measure of the concentration of that element in the original sample. In atomic absorption spectrometry, the light absorbed by atoms of the analyte is proportional to the number of unexcited atoms present.²⁵ This has been referred to as the Beer Lambert Law and can be expressed in the following equation:

$$A = abc$$

Where A= absorbance

a= absorption coefficient

b= length of the absorbance path

c= concentration of absorbing atoms

If a and b are kept constant then A is directly proportional to c , which is an ideal case of Beer Lambert law.²⁵

During the GF-AAS process, an automatic sampler dispenses a small aliquot (usually less than 100 microliters) of a sample onto the L'vov platform of the graphite tube (atomization chamber). After the liquid has been dispensed, the furnace goes through three temperature phases: drying, char, and atomization. The drying step heats the platform 100-120° C for 30 seconds to evaporate the water analyte.²⁶ The char step increases the temperature to 1,800° C for 30 seconds to convert the analyte and other materials to oxides.²⁶ The atomization step further increases the temperature to 2,800° C for five seconds to convert the element being analyzed to an atomic vapor.²⁶ Additionally, during this step, the absorbance is read. These temperature phases heat the graphite furnace to provide the thermal energy needed to break chemical bonds within the sample and produce free ground state atoms. Ground state atoms then are capable of absorbing energy, in the form of light, and are elevated to an excited state. The amount of light energy absorbed increases as the concentration of the selected element increases.²⁶

GF-AAS is the preferred instrument for analyzing arsenic in a sample because it is more sensitive than other atomic absorption methods since it isolates larger populations of atoms in the light path. Additionally, it has low spectral interference and only requires a very small sample size.²⁶

Acid Digestion of Fe_2O_3 :

Acid digestion is a method of dissolving the metal into solution so that it can be analyzed by laboratory methods to determine the amount of metal or element present. Acid digestion involves adding acid to the Fe_2O_3 and heating it until the solid metal has fully dissolved. After heating, the sample is diluted with water and analyzed. The advantage of this process is that it reveals other metals that may be encapsulated in a non-metal housing or hidden in a multiple layer of metal deposits.²⁸ The acid digestion procedure used in this project involved mixing 1.0 g of Fe_2O_3 and 25 mL of nitric acid with a glass stirring rod in a 100 mL beaker. This mixture was covered with a watch glass and heated using a hot plate for two hours. After two hours, the remaining liquid was filtered using a glass filter packed with damp glass wool into a 100 mL volumetric flask. The liquid was diluted with de-ionized water and then a sample of the liquid was placed into three 6 mL vial. All three samples were analyzed for arsenic by GF-AAS to examine whether or not any arsenic impurities were within the Fe_2O_3 .

PCRB	Pervious Cement (lb)	Ferric Oxide Anhydrous (lb) Fe_2O_3
Column 1	.965	0
Column 2	.965	.008
Column 3	.965	.004
Column 4	.965	.010

Table 4: Components of each column.

III. RESULTS AND DISCUSSION

Flow Rate for Pervious Cement Reaction Barrier:

Flow tests were performed with a stopwatch for each PCRB before dispensing a ~200 ppm arsenic solution into each PCRB column. The preliminary testing for the flow rate (liter/second) was to establish the pervious cement's level of permeability and consistency in order to fully characterize the flow rate of each column prior to testing. The flow rate was conducted by noting the amount of time each liter took to dispense out of a 5-liter carboy. Figures 5 through 8 illustrate the flow rates in each PCRB column with 25 liters flowing through. The flow rates were consistent throughout the tests. The flow tests of columns one through four resulted in an average of 36 ± 6 L/sec, 43 ± 4 L/sec, 35 ± 6 L/sec, and 30 ± 2 L/sec, respectively.

There was no significant change in the flow rate from the beginning to end of the experiment as illustrated in Figures 5 through 8. The PCRB columns showed good flow capability and could continue to be used for the upcoming experiment.

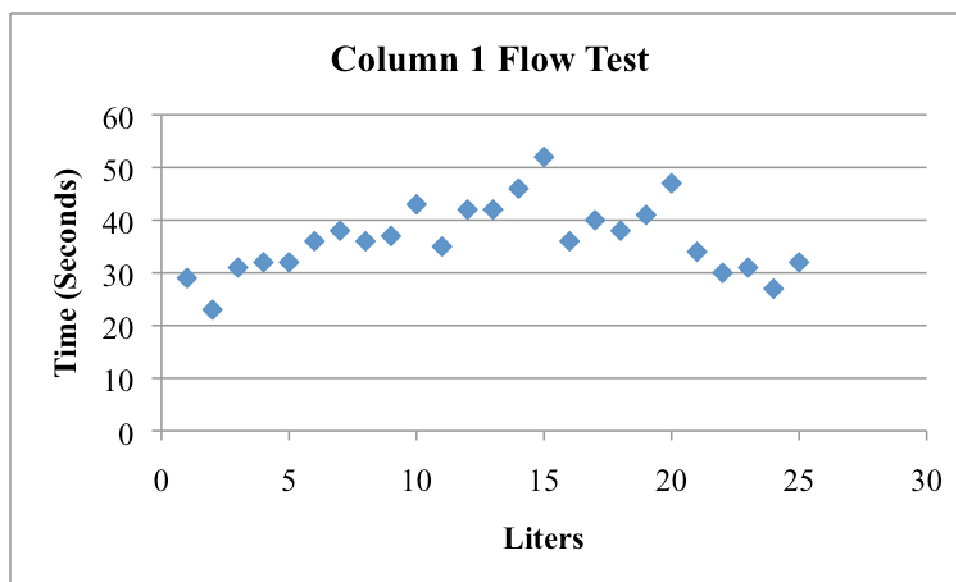


Figure 5: Flow test for PCRB column one
(average: 36 ± 6 L/sec).

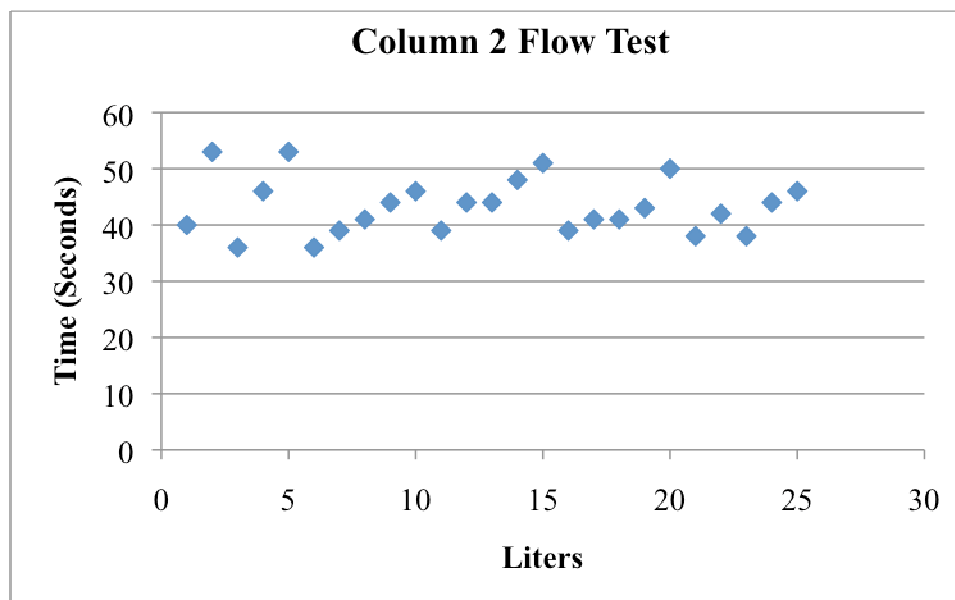


Figure 6: Flow test for PCRB column two
(average: 43 ± 4 L/sec).

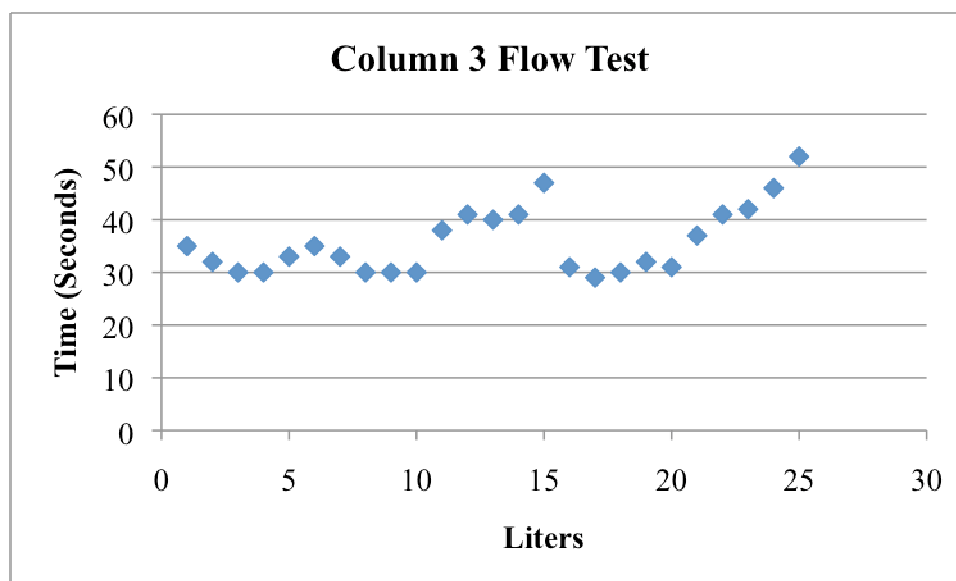


Figure 7: Flow test for PCRB column three

(average: 35 ± 6 L/sec).

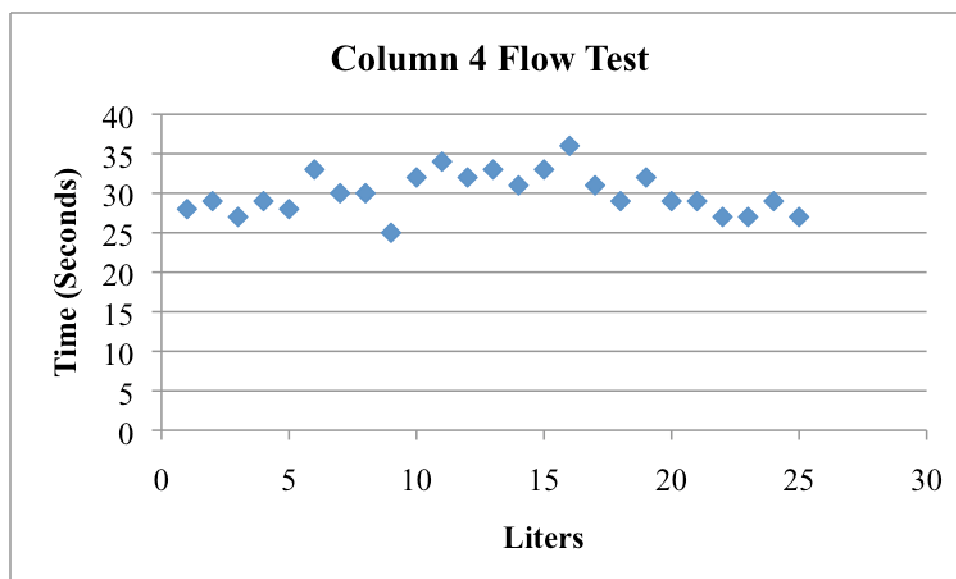


Figure 8: Flow test for PCRB column four
(average: 30 ± 2 L/sec).

Concentration of Arsenic from Standard and Leachate:

After performing flow tests for each PCRB column, each PCRB column was used to conduct initial experiments examining possible removal of arsenic. There were 10 leachate samples collected for each column and 15 standard arsenic samples collected during the experiment.

The 15 standard samples displayed an average concentration of $72 \text{ ppb} \pm 6$ with an average pH of $8 \pm .9$. The leachate samples of columns one through four had an average pH of $8 \pm .4$, $9 \pm .1$, $9 \pm .1$, $9 \pm .5$, respectively, and an average specific conductance of 17 ± 6 , 29 ± 8 , 45 ± 11 , 40 ± 21 , respectively. The leachate samples from columns one through four showed an average concentration of $49 \pm 15 \text{ ppb}$, $77 \pm 5 \text{ ppb}$, $77 \pm 8 \text{ ppb}$, and $72 \pm 7 \text{ ppb}$, respectively. Only columns one and four were shown to remove arsenic. Since 72 ppb of arsenic was in the initial solution and 49 ppb and 72 ppb was in the leachate of columns one and four, respectively, 23 ppb and $.7 \text{ ppb}$ arsenic were removed by the pervious cement columns one and four respectively. This results in 32.8% from column one and $.01\%$ from column four of the initial solution of arsenic being removed. Figures 9-12 show the result of the GF-AA analysis of both the standard and columns one through four leachate samples for arsenic.

Only columns one and four illustrated the potential to remove arsenic. Column one was the standard column that did not contain Fe_2O_3 and Column four contained $.010 \text{ lbs}$ of Fe_2O_3 , the largest amount of any column. As seen in Figure 9, there was

an average of 72 ppb of arsenic in the initial standard solution and as illustrated in Figures 10 and 13, there was an average of 49 ppb and 72 ppb of arsenic in columns one and four leachate, respectively. The PCRB column one removed an average concentration of 23 ppb of arsenic from the initial standard solution. This results in an average of 32.8% of the initial standard solution being removed by PCRB column one. The PCRB column two removed an average concentration of .7 ppb of arsenic from the initial solution. This results in an average of .01% of the initial standard solution being removed by PCRB column four. Arsenic removal was observed in column one because pervious cement is made with limestone. Limestone is an excellent media for arsenic removal because of the presence of Ca^{2+} ions and its buffering capacity. The presence of Ca^{2+} ions in limestone will react with arsenate and precipitate as a calcium arsenate mineral, thereby removing arsenate from water.²⁰ Columns two and three illustrated no removal and higher concentrations of arsenic; and column four showed minimum removal of arsenic than the initial standard leading to the possibility that Fe_2O_3 might have played a role.

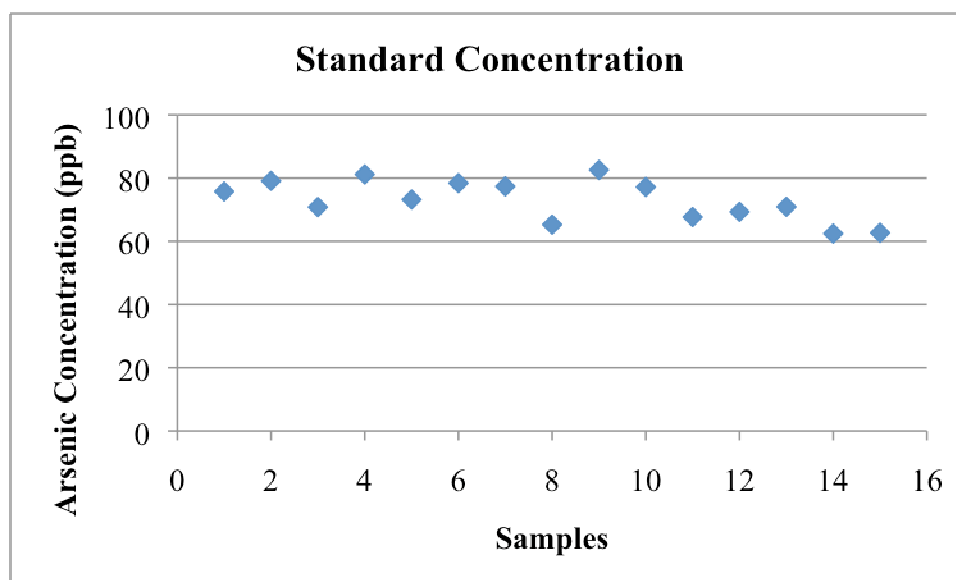


Figure 9: Standard concentration of dispensing solution.

(average concentration: 72 ± 6 ppb)

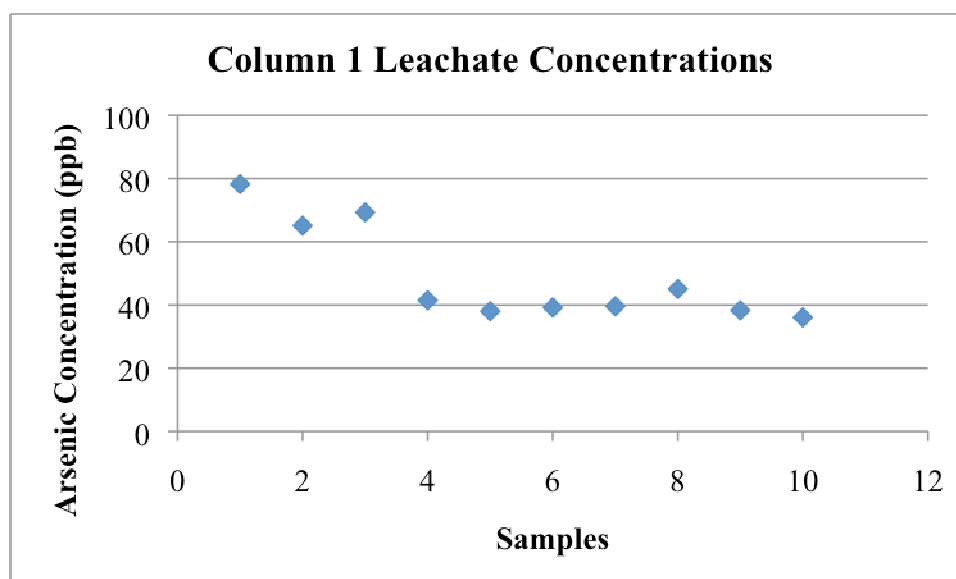


Figure 10: Column one leachate arsenic concentration.

(average concentration: 49 ± 15 ppb)

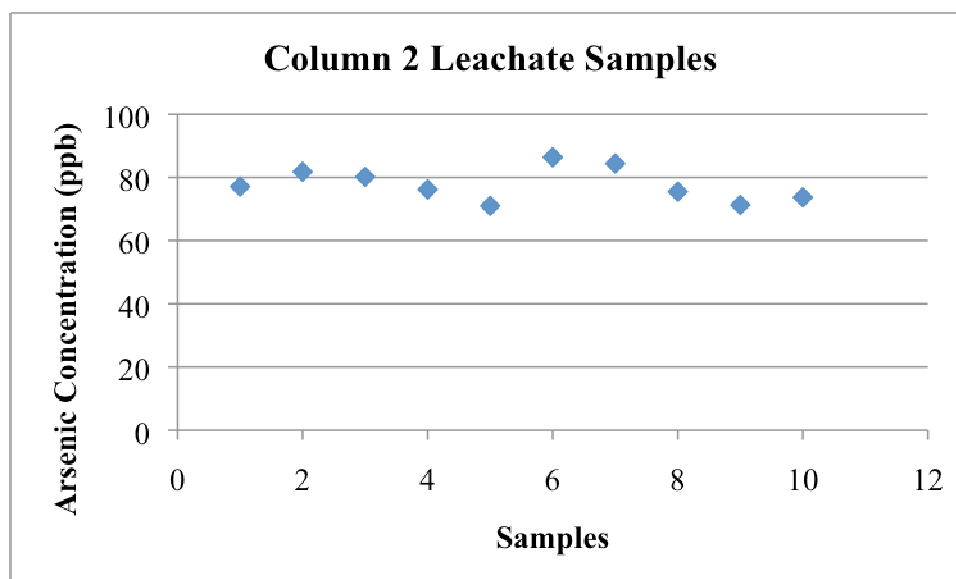


Figure 11: Column two leachate arsenic concentration
(average concentration: 77 ± 5 ppb)

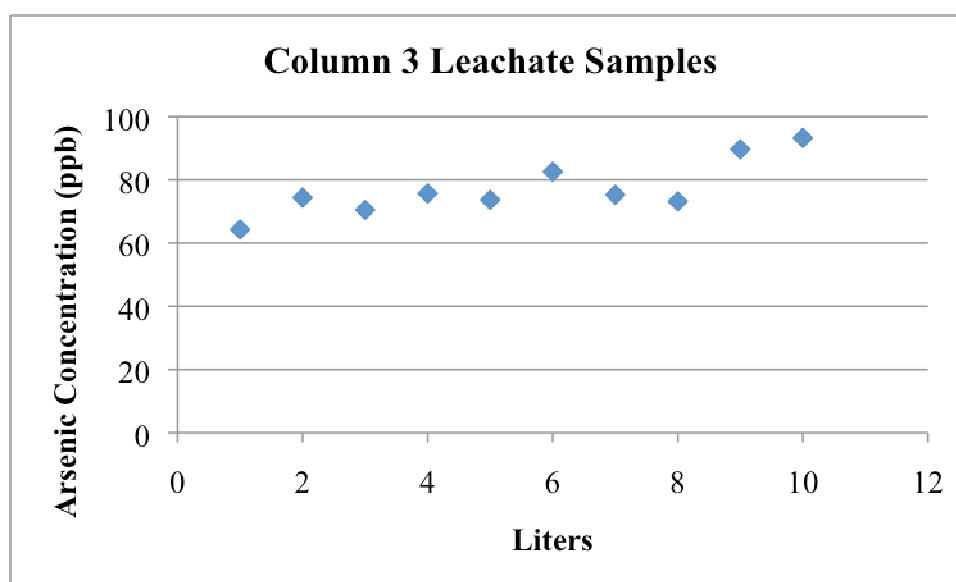


Figure 12: Column three leachate arsenic concentration

(average concentration: 77 ± 8 ppb)

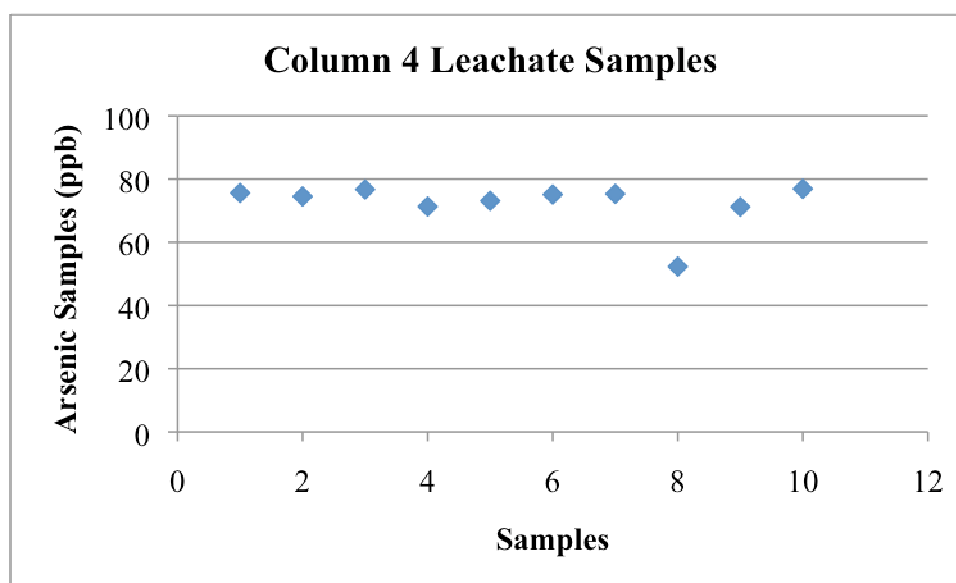


Figure 13: Column four leachate arsenic concentration

(average concentration: 72 ± 7 ppb)

Acid Digestion of Fe_2O_3 :

An acid digestion was performed on the columns additive material, Fe_2O_3 , to examine whether or not it was contaminated with arsenic. There were three samples collected from the acid digestion experiment and all displayed a concentration of less than .001 ppm of arsenic. Therefore, the leachate arsenic concentration from columns two through four with Fe_2O_3 as an additive had no significant contribution from Fe_2O_3 .

IV. CONCLUSION

Arsenic contaminated groundwater continues to be a major concern in the world; and small rural water treatment facilities still face challenges to meet EPA's arsenic standard for drinking water. The studies in this research have provided evidence that there is a possibility that these small rural water treatment facilities can overcome this obstacle by removing arsenic with limestone.

The pervious cement proved to be permeable and an innovative method to remove arsenic at the source. All four PCRB's had good flow capability with an average of 36 L/sec, 43 L/sec, 35 L/sec, and 30 L/sec in columns one through four, respectively.

The PCRB column one displayed an average of 32.8% being removed from the initial solution illustrating the ability to remove arsenic. This arsenic removal is due to the limestone in its composition because the presence of Ca^{2+} ions in the limestone react with arsenate and precipitate as calcium arsenate, thereby removing arsenate from the water.²⁰ However, the other three PCRB columns that included the additive, Fe_2O_3 , were not as efficient in removing arsenic as the column without Fe_2O_3 . An acid digestion of Fe_2O_3 showed that the material contained less than .001 ppm of arsenic, thus illustrating that the material was not contaminated.

Future research on the project involves dispensing the solution through the PCRB against gravity and seeing if longer contact times will effect the removal of arsenic with and without additives. Additionally, the project thus far has only experimented with arsenate, therefore, future studies will use arsenite and explore its

removal efficiency in the PCRB. Arsenite is neutral at typical pH found in drinking water and arsenate is an anion at this pH range, therefore, arsenite is less strongly adsorbed than arsenate on an oxide surface.²⁹ Raven et al.²⁹ has shown that removing arsenic using ferrihydrite not only removes arsenate, but also, arsenite at high pH (approximately greater than 7.5). Since the PCRB contains limestone, which is an excellent media for increasing the pH because of its buffering capacity, the PCRB should remove arsenite as well as arsenate with no pretreatment. The high pH of the PCRB will not only enable arsenate to become hydrogen arsenate and arsenate ion, but also, arsenite will transform into dihydrogen arsenite and hydrogen arsenite. Both these arsenate and arsenite anions will be more likely to absorb onto the oxide than a neutral species.

The overall goal that this project hopes to achieve is the ability to treat arsenic contaminated groundwater at the source. One method of doing this is by placing a slab of the PCRB into the contaminated groundwater and removing it when the PCRB slab has reached its maximum capacity. After the PCRB slab has reached its maximum capacity, the slab will be removed and a new slab will replace it. According to a previous study by the author,³⁰ arsenic limestone waste material is classified as non-hazardous and suitable for disposal in municipal landfills, as verified by Toxicity Characteristic Leaching Procedure (TCLP) and California Waste Extraction Test (CA WET). In addition, compressive strength tests performed on the arsenic limestone waste indicated that the formation of concrete remains a viable option for either disposal or recycling of the limestone waste material at around 5%

levels. Therefore, the maximum absorbed PCRB slab can be recycled in roadways and parking lots.

Limestone-based material in the PCRB provides several economical and sociological benefits to the drinking water community including reasonable removal efficiency, low material cost, compatibility with other water treatment processes, ease of use, and low-cost disposal in landfills.²⁰ Achievement of this goal will enable developing countries such as Bangladesh, which has many impoverished rural communities without the resources or technical training to operate current technologies, to obtain cleaner drinking water for their citizens.

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BIOGRAPHICAL SKETCH

The author was born in Goodlettsville, Tennessee on April 25, 1986. She earned her Bachelor of Science degree with honors and magna cum laude from Western Kentucky University in spring of 2008. In the fall of 2008 she began graduate school at Western Kentucky University where she will earn her Master of Science degree in Chemistry working under Dr. Cathleen Webb. She is expected to defend her thesis on May 13, 2010.

