

SEPARATION OF PHOSPHORUS- AND NITROGEN-NUTRIENTS FROM AGRICULTURAL DEGRADED
WATERS USING PERVIOUS FILTER MATERIAL DEVELOPED FROM INDUSTRIAL BY-PRODUCTS

Progress Report

Submitted to:

Ohio Water Resources Center

Submitted by:

Principal Investigator:

Linda Weavers, Ph.D., P.E., BCEE.

Professor

Department of Civil, Environmental, and Geodetic Engineering

e-mail: weavers.1@osu.edu; Telephone: 614-292-8263; Fax: 614-292-3780

Co-PI:

Chin-Min Cheng, Ph.D., P.E.

Research Associate II-Engineer

Department of Civil, Environmental, and Geodetic Engineering

ABSTRACT

End-of-tail filtration has been suggested as a more aggressive and effective approach to reduce losses of nutrients from crop lands compared to current best management practices (BMPs) focusing on source reduction and minimizing transportation. A number of industrial by-products, e.g., coal combustion by-products and bauxite leaching residual, have been proven chemically effective in trapping P- and/or N-nutrients, and therefore, are potential low-cost nutrient sorbents for the end-of-tail filtration approach. However, the application of these industrial by-products as the filtration media is limited due to unfavorable hydraulic properties, as well as unknown associated environmental impacts. In this proposed study, pervious filter materials owning both reactivity to nutrients and adequate hydraulic properties are developed using fly ash, stabilized FGD materials, and bauxite leaching residual as the feedstock. By modifying the composition of these industrial by-products, the pervious materials are expected to have selective nutrient-sequestering capabilities, which can be used to separate and recycle phosphorus- and nitrogen-nutrients from agricultural drainage waters (ADWs). This study is carried out in three tasks to (1) investigate the adsorption efficiency and service lifetime of selected pervious materials with synthetic ADW; (2) evaluate the physical and chemical integrity of the pervious materials before and after service; and (3) study the interactions between the prepared filter materials and emerging pollutants commonly found in ADW (e.g., estrone). The goal of this study is to demonstrate the feasibility of applying a low-cost and environmentally-sustainable approach to ADW handling and treatment. This alternative to current BMPs is able to convert agricultural and industrial wastes to value-added products containing concentrated and specific nutrients. Currently, the project is still on going. Results obtained from this study will be used to develop a competitive proposal for external funding.

1. Introduction

Eutrophication of water bodies, a result of release of excessive phosphorous (P) and nitrogen (N) from soil to drainages¹, has been an increasing environmental issue in the US, especially in the Midwest, northeast, and Gulf coast area where the watersheds of major freshwater bodies involve rapid growth and intensification of crop and livestock farming². Not only eutrophication posts unpleasant aesthetic characteristics to water bodies, accumulation of toxic, volatile chemicals produced by algae can cause neurological damage in people and animals being exposed to them. Consequently, eutrophication of water resources results in losses of biodiversity, as well as their amenities and services³. For example, the recent outbreaks of Cyanobacteria, or blue-green algae, in the Grand Lake at St. Mary's area in Ohio has led to state officials to issue water contact and fish consumption advisories.

The major cause of many eutrophication incidents can be directly correlated to fertilizer application⁴. To prevent accumulation of nutrients in surface waters, reduction of nutrients present in the agricultural degraded waters (ADW, i.e., livestock wastewater overflow, subsurface drainages, and surface runoffs from cropland) is perceived as necessary approach⁵. Although many best management practices (BMPs) focusing on source reduction and minimizing transportation have been implemented to reduce losses of nutrients from crop lands, these approaches have shown no control on dissolved phosphorus losses^{6,7}, which is the most readily available form of phosphorus to aquatic organisms⁸. Instead, end-of-tail filtration has been suggested as a more aggressive and effective approach⁶. However, the application is limited. Ideal filter materials, i.e., material with both favorable nutrient-sequestering capability and hydraulic property, have yet been identified⁹.

In this study, low-cost pervious sorption materials prepared from a self-geopolymerization process using agricultural wastes and industrial by-products are tested for their potential as an alternative to current BMPs. The self-geopolymerization process enchains agricultural wastes with chemically-effective, nutrient-sorbing industrial by-products (e.g., coal ash, flue gas desulfurization materials, and bauxite residual) and forms pervious materials. By modifying the composition, the pervious materials are expected to have selective sorption capabilities to nitrogen (N-) and phosphorus (P-) nutrients with adjustable hydraulic properties, which can be used to separate and recycle nutrients from ADWs.

2. Objectives

In this study, a geopolymerization procedure is developed to convert coal combustion by-products (i.e., fly ash and flue gas desulfurization (FGD) material) and alkaline bauxite leaching

residual (bauxite red mud) to pervious filter materials. The materials are tested in a bench-scale setting for their effectiveness and capacity on removing nutrients from simulated agricultural drainage waters. The specific objectives of this proposed project are to:

- (1) Assess the performance of the industrial by-product-derived pervious filter materials with respect to their nutrient removal efficiencies, service lifetime, and hydraulic properties;
- (2) Evaluate the chemical and physical integrity of the materials; and
- (3) Study the interactions between the prepared filter materials and other pollutants contained in ADWs (i.e., estrogens).

3. Materials and Method

The work of this proposed study is divided into three tasks. In summary, the first task focuses on preparing and characterizing the pervious filter materials. At least three sets of P-type (i.e., materials selectively adsorb P-nutrients) and N-type (i.e., materials adsorbed nitrate and/or other N-nutrients) are prepared. In the second task, a series of column experiments are setup to (1) evaluate the adsorption efficiency and capacity of the selected pervious materials with a simulated ADW and (2) study the interactions between estrogens and filtration materials. In addition, the physical and chemical integrities of the pervious filter material during and after service are evaluated. The release of metals and metaloids (e.g., mercury, arsenic, selenium, thallium, and boron), as well as sulfate, from the filter materials during filtration are monitored. In addition, surface characterization techniques, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), are applied to investigate the transformations of mineral composition and surface morphology before and after the filtration materials are exhausted.

Pervious Filter Material Preparation and Characterization

Coal combustion by-products (i.e., fly ash and stabilized FGD materials) and bauxite leaching residue (i.e., red mud) are used in the preparation of the nutrient-selective pervious filtration materials (Figure 1). Two different types of pervious filtration materials (i.e., P- and N-types) are prepared using a method modified from Cheng et al.¹⁰ and Jin¹¹. Class F fly ash and sulfite-rich stabilized FGD material provided by coal combustion power plants located in eastern Ohio are used to prepare the phosphorous-capture (P-type) filtration materials. Quick lime

(Carmeus USA, Pittsburg, PA), CaO, is added to provide required alkalinity. The nitrogen-capture materials are prepared from red mud, fly ash, and stabilized FGD material. No quick lime is used in the preparation of N-type filter materials. The bauxite red mud provided by a bauxite processing plant located at southeast Texas is oven-dried before use. In one batch, manganese oxide (MnO₂) is also added in the preparation of N-type material. Woodchip is used in the preparation of both N and P-type filter mixtures to modify the hydraulic properties. The prepared mixtures are then cured in a humidity chamber.

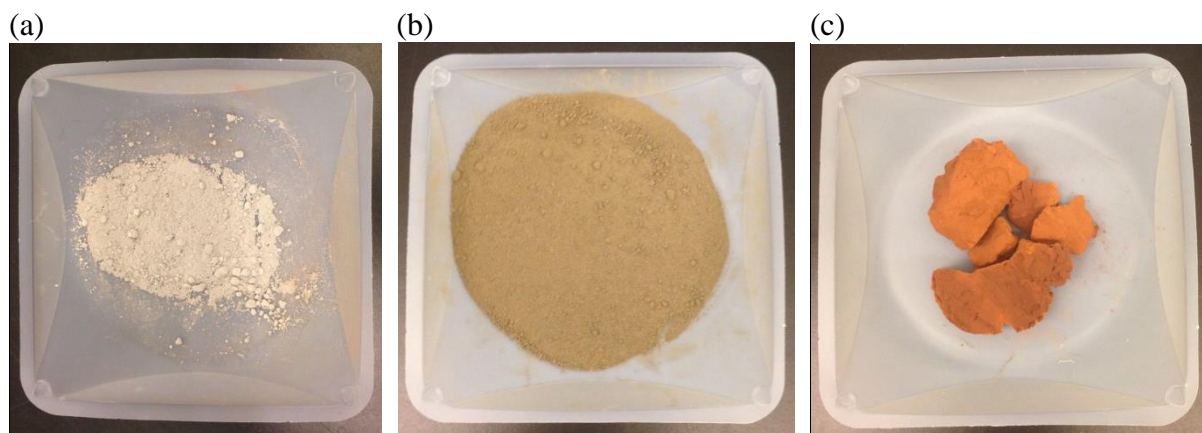


Figure 1. (a) Stabilized FGD material, (b) fly ash, and (c) bauxite red mud used in the preparation of pervious filtration materials.

The cured filter materials are tested for their chemical (i.e., elemental and mineral compositions), physical (density and surface morphology), and engineering (i.e., permeability (k) and/or hydroconductivity (K)) properties as per standard testing protocols. Details on the chemical and physical characterizations of the filter materials are described in the “*Physical and Chemical properties Integrity Evaluation*” section.

Bench-Scale Column Test

A series of column tests are carried out to measure the adsorption capacity and efficiency of prepared pervious materials for P- and N-nutrients with a simulated ADW. In addition to the prepared filter materials, two reference columns, packed separately with granular activated carbon (GAC) and top soil from the OSU’s Waterman Farm Complex, are also included in the column study. A control column, i.e., without packing medium, is included to evaluate the adsorption of nutrients and compounds on the experimental apparatus.

The setup of the column test is illustrated in Figure 2. The ADW used in the column test is synthesized based on formula listed in Table 1. In addition to the constituents listed in the table, one estrogen, e.g., estrone (E1) or 17 α -Estradiol (17 α -E2), commonly found in dairy wastewater¹² is added in selected experimental batches. A peristaltic pump delivers the synthetic ADW to the inlet of a series of two vertically-oriented columns at a constant feed rate (Figure 2). The ADW sequentially passes through the column containing P-type filter material (P-type column) and then the N-Type column. For a given set of filter materials, the column test is carried out under a saturation condition demonstrated in Figure 2.

Table 1. Composition of synthetic dairy wastewater used in this study

Component	Amount (mg/L)
Urea	115.7
NH ₄ Cl	250.0
Na ₂ PO ₄ ·12H ₂ O	385.7
KHCO ₃	257.1
NaHCO ₃	668.6
MgSO ₄ ·7H ₂ O	257.1
FeSO ₄ ·7H ₂ O	10.3
MnSO ₄ ·H ₂ O	10.3
CaCl ₂ ·6H ₂ O	15.4

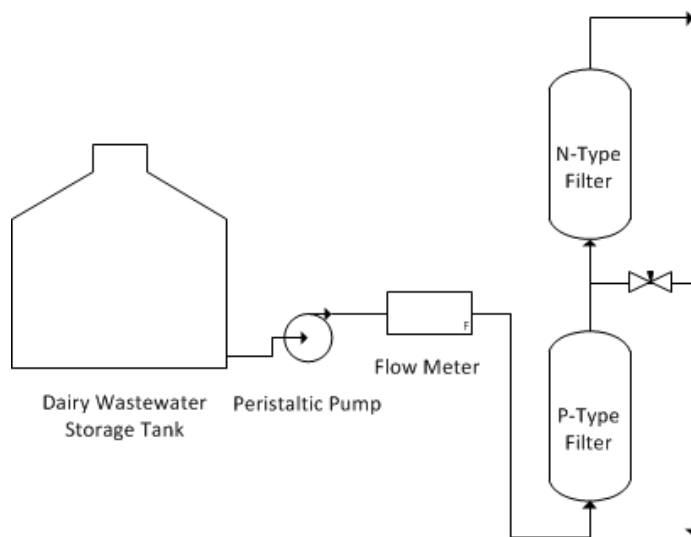


Figure 2. Setup of bench-scale column test

Effluent samples are collected periodically from the outlets of P-type and N-type columns for a list of chemical analyses shown in Table 2. After collection, sample is immediately separated into four sub-samples. The first sub-sample is for pH, conductivity, and redox potential measurements. In the selected batches when estrogen is included in the synthetic ADW, an aliquot of the first subsample is filtered with 1.2µm glass fiber and concentrated by solid-phase extraction for estrogen analysis. Any compounds remained on the sample collection bottle or filter is desorbed by rinsing the bottle and filter with methanol. The concentrated sample is analyzed using a high-performance reverse-phase liquid chromatography tandem electrospray ionization mass spectrometry (HPLC/MS/MS). Deuterated internal standards is added to the samples to correct the interferences caused by the matrix of the sample.

The second sub-sample is filtered and analyzed for alkalinity, total dissolved solids, Cl⁻, SO₄⁻², PO₄⁻³, total Kjeldahl nitrogen, ammonia, and NO₃⁻. The third sub-sample is preserved with 5% HNO₃ and analyzed for “total” elements in the solution. The final sub-sample is filtered through a 0.45-µm syringe filter and preserved with 5% HNO₃ before being analyzed for “dissolved” elements.

Table 2. List of monitoring parameters and respective analytical methods for aqueous samples

Subsample	Parameter	Detection Methods	Instruments	Locations
Subsample I	Conductivity	AWWA Sec. 2510	Thermo Orion 1234	<i>in-situ</i>
	pH		Thermo Orion 1234	<i>in-situ</i>
	Redox Potential		Thermo Orion 1234	<i>in-situ</i>
	Estrogen ^c	HPLC/MS/MS	Micromass Q-TOF II	CCIC ^b
Subsample II	Alkalinity	AWWA Sec. 2310	-	CEGE EER Lab/ OARDC STAR Lab
	Total dissolved solid	AWWA Sec. 2540	-	
	Chloride (Cl)	AWWA Sec. 4110C	Dionex 2100	
	Sulfate (SO ₄ ⁻²)	AWWA Sec. 4110C	Dionex 2100	
	Phosphate(PO ₄ ⁻³)	AWWA Sec. 4110C	Dionex 2100	
	Nitrate (NO ₃ ⁻)	AWWA Sec. 4110C	Dionex 2100	
	Ammonia (NH ₄ ⁺)	AWWA Sec. 4110C	Dionex 2100	
Total Kjeldahl Method	AWWA Sec. 4500 N _{org}	-		
Subsample III/ Subsample IV	Mercury (Hg)	CVAFS	Varian CVAAs,	
	Selected Elements ^a	AWWA Sec. 3120B	Varian VISTA-AX	
	Arsenic (As)/ Thallium(Tl)	AWWA Sec. 3120B	Varian GFAAs, Varian 880Z	
	Selenium (Se)	AWWA Sec. 3120B	Varian GFAAs, Varian 880Z	

^a Aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorous (P), sodium (Na), silver (Ag), zinc (Zn).

^b Campus Chemical Instrument Center at The Ohio State University

^c On selected experimental batches

Chemical and Physical Integrity Evaluations

The exhausted filter materials are preserved using liquid nitrogen and freeze-dried before being analyzed for the mineral and chemical compositions, surface morphology, and forms of adsorbed phosphorus by the methods listed in Table 35. The mineral compositions and morphology of the selected N- and P- type filters materials before and after service are characterized using X-ray diffraction (XRD) and scanning electronic microscopy (SEM), respectively. A Bruker D8 Advance X-ray diffractometer or equivalent is used to identify the mineral composition. The mineral patterns in the diffractograms are matched using the DIFFRACplus EVA software with ICDD Power Diffraction File (PDF2+) database. The complete elemental composition analysis is measured with the assistance of the digestion procedure described in EPA method 3052. A reference coal fly ash, 1633b, provided by the National Institute of Standards and Technology (NIST), is included for analytical quality control. A list of the analyses performed on the materials can be seen in Table 4.

The release potential of trace elements from filter materials before and after service will also be characterized. Standard protocols, i.e., EPA Standard Method 1311, Toxicity Leaching Characteristic Procedure (TCLP), the EPA Standard Method 1312, Synthetic Precipitation Leaching Procedure (SPLP), are used.

Table 3. Physical, mineral, and chemical analyses for selected pervious filter materials

	Method	Instrument	Location
Permeability	ASTM D4525-08		CEGE Soil Lab
Hydraulic Conductivity	ASTM D7100-06		
Morphology	Scanning Electron microscopy	Hitachi S-3000 SEM	OSU Nanotech West Lab
Mineral Composition	X-ray Diffraction	Bruker D8 Advance X-ray diffractometer	SENR Soil Lab ^c
Selected Elements ^a	ASTM D-6357	Milestone Microwave Digestor/ Varian VISTA-AX	CEGE EER Lab ^b
Mercury	ASTM D-6414	Varian CVAAs, Varian 880Z	CEGE EER Lab
Selenium	ASTM D-4606	Varian CVAAs, Varian 880Z	CEGE EER Lab
Arsenic, Thallium	ASTM D-3683	Varian GFAAs, Varian 880Z	CEGE EER Lab

^a aluminum (Al), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorous (P), sodium (Na), sulfur (S), and zinc (Zn).

^b Environmental Engineering Research Laboratory at Department of Civil, Environmental, and Geodetic Engineering of The Ohio State University

^c Soil Lab at School of Environment and Natural Resources of The Ohio State University

4. Current Progress and Tasks to be completed

Characterizations of Industrial By-products

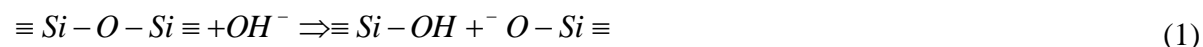
The chemical compositions of fly ash, stabilized FGD material, and bauxite red mud are first characterized and the results are summarized in Table 4. As shown in the table, calcium (Ca) and sulfur (S) are the two most abundant elements in the stabilized FGD material, which is associated with the presence of hanebachite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), portlandite ($\text{Ca}(\text{OH})_2$), and enttringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) in the material. The X-ray diffractogram and mineral composition of stabilized FGD material can be seen in Figure 3. Iron (Fe), aluminum (Al), sulfur (S), and silicon (Si) are the major elements in fly ash. Based on XRD analysis, the fly ash used in this study is comprised of amorphous glass, aluminum silicates (e.g., mullite), and iron oxides (hematite, magnetite, and maghemite). Bauxite red mud is consisted of Al, Fe, and Ca. The X-ray diffractograms of fly ash and red mud are not shown.

By properly coalescing fly ash, stabilized FGD material, and red mud under high alkaline environment, fly ash acts as an inorganic polymer binder to enchain active ingredients through a geopolymerization process. After being alkali-activated, the Si-O-Si or Al-O-Si bonds in fly ash and stabilized FGD material are disassociated and subsequently form network-like crystalline and/or amorphous alkaline aluminosilicates with structural framework similar to zeolite¹³. In a previous project, it has been demonstrated that a geotextile material derived from the geopolymerization process with a mixture of fly ash and stabilized FGD material, has effective phosphorus sorption capability by forming Ca- and Fe-precipitates^{10,14,15}. However, the fly ash/stabilized FGD material mixture did not show observable effect on nitrate mitigation¹⁰.

The addition of bauxite red mud is to enhance the nitrogen-nutrients adsorption capability of the fly ash/FGD mixture. Bauxite red mud contains minerals, e.g., iron (III) (hydr)oxides and hydrous aluminum oxides, that have high affinities for nitrate¹⁶. As a result, the material has been shown to be an effective nutrient sorbent¹⁷. Cengeloglu et al¹⁷ used original and acid-treated bauxite red mud to remove nitrate from aqueous solution and reported 70% and over 90% of removal, respectively. They found the alkaline property of bauxite red mud hindered the adsorption performance.

In this study, bauxite red mud is used as the sole alkalinity source in the geopolymerization process, which might promote the nitrate adsorption capacity. During geopolymerization, the OH⁻ ions from bauxite red mud is consumed (eq. 1) and redistribute the electron density around the silicon atom in fly ash, which weaken the strength of Si-O-Si bond¹⁸

and progress the polymerization process. The reaction neutralizes the negative surface charge of red mud particles, and therefore, might promote the nitrate sorption.



Preparation of P- and N-type pervious filtration

A series of P- and N-type pervious filtration materials have been prepared based on the formulas listed in Tables 5 and 6. Currently, the prepared materials are undergoing a 21-day curing process. The images of two selected prepared materials can be seen in Figure 4. The hydraulic property of the filtration materials are adjusted by the addition of woodchip. Two different sizes of woodchip, i.e., <2.3mm and 2.3-3.6mm, are used. The addition of woodchip creates larger capillary routes for water to pass through. During the geopolymerization process, active ingredients are coated on the surface of woodchip, which allows the nutrients in ADW to react with the active ingredients while passing through the void space.

Table 4. Chemical compositions of fly ash, stabilized FGD material and bauxite red mud used in this study

		Fly Ash	Stabilized FGD material	Red Mud
Phosphorus	P	531	177	1054
Potassium	K	2986	1307	310
Calcium	Ca	9836	172906	33055
Magnesium	Mg	1528	10026	227
sulfur	S	11827	85746	2867
Aluminum	Al	27050	9705	62817
Boron	B	531	313	<3
Copper	Cu	42	<0.4	<0.8
Iron	Fe	59824	18855	240960
Manganese	Mn	85	73	139
Molybdenum	Mo	22	<13	<0.5
Sodium	Na	18851	5296	32412
Zinc	Zn	109	40	22
Arsenic	As	143	36	28
Barium	Ba	177	137	61
Beryllium	Be	<0.18	<0.11	<0.18
Cadmium	Cd	2	6	5
Cobalt	Co	23	4	15
Chromium	Cr	74	25	1397
Lithium	Li	167	106	55
Nickel	Ni	48	7	6
Lead	Pb	28	8	46
Antimony	Sb	<1.5	17	<1.5
Selenium	Se	20	18	1
Silicon	Si	4771	1481	184
Strontium	Sr	229	212	117
Thallium	Tl	129	38	871
Vanadium	V	2	<1.1	<0.6
Mercury	Hg	NA	0.318	NA

NA:Not Available
Unit: mg/kg

Table 5. Formulas of Prepared P-type Filtration Materials

	P-Control	P-type I	P-type II	P-type III
Fly Ash	10.0	10.0	10.0	10.0
Stabilized FGD material	6.0	6.0	6.0	6.0
Quick Lime (CaO)	1.2	1.2	1.2	1.2
Deionized Water	10.5	10.5	10.5	10.5
Wood Chip (<2.3 mm)	0	2.5	5.0	0
Wood Chip (2.3-3.6 mm)	0	0	0	2.5

Unit: g

Table 6. Formulas of Prepared N-type Filtration Materials

	N-type I	N-type II	N-type III	N-type IV
Fly Ash	10.0	10.0	10.0	10.0
Stabilized FGD material	6.0	6.0	6.0	6.0
Red Mud (dried weight)	8	8	8	8
Deionized Water	10.5	10.5	10.5	10.5
Wood Chip (<2.3 mm)	0	2.5	5.0	2.5
MnO ₂	0	0	0	2.0

Unit: g

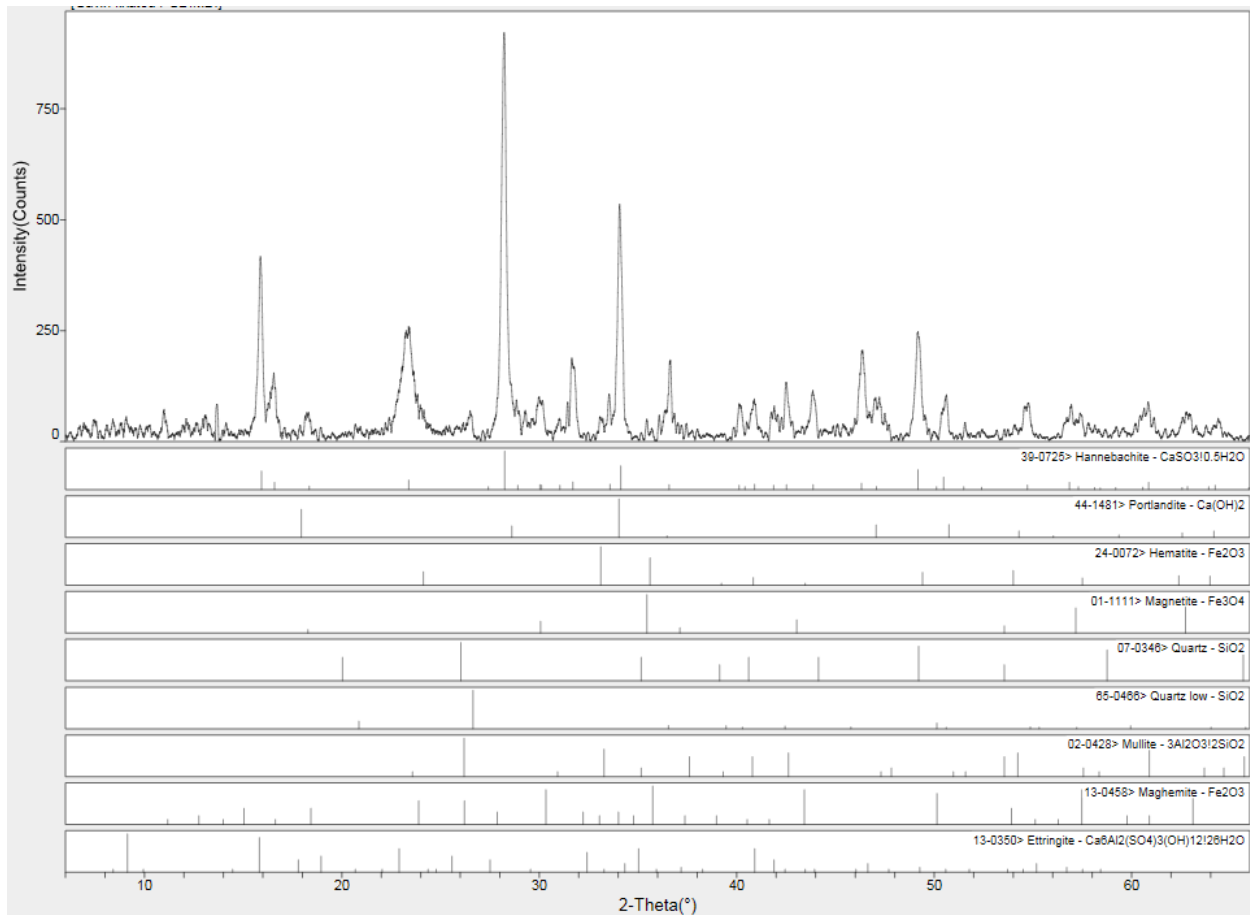


Figure 3. Mineral composition of stabilized FGD material

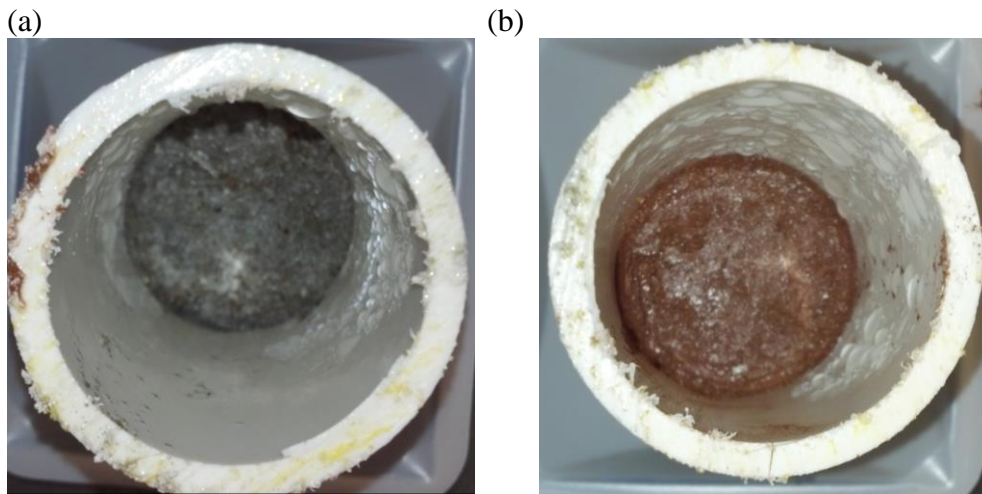


Figure 4. Prepared Pervious filtration materials. (a) P-type and (b) N-type.

These two types (i.e., P- and N-types) of pervious materials are expected to have selective sorption capacity, which can be used to sequentially separate and recover soluble phosphorous and nitrogen in agricultural drainage waters. In practice, two different pervious filter materials can be used in series. The dissolved phosphorous is expected to be selectively retained in the first pervious material (P-type) containing only fly ash and FGD material while allowing nitrate to pass through. Nitrate is captured in the second pervious material (N-Type) containing bauxite red mud, fly ash, and stabilized FGD material.

Tasks to be completed

The bench scale column test described in the “*Materials and Methods*” section is to be carried out soon after the curing of pervious filtration materials is completed. In addition, the integrities of physical and chemical properties of the pervious materials after adsorption will be evaluated.

Despite the great potential for the proposed filtration application, the major concern of reutilizing these by-products is the release of trace elements contained in the materials after being contacted with water. Cheng et al.^{Error! Bookmark not defined.} investigated the water quality impacts associated with using stabilized FGD material as a low permeability liner for a swine manure storage pond. Based on five-year worth of field monitoring data, the concentrations of arsenic (As), boron (B), chromium (Cr), copper (Cu), and zinc (Zn) were consistently found lower in the water passing through the liner than the water collected from the pond. Other trace elements, such as Cd, Se, and Hg were often below the analytical detection limits. Ruyter et al.¹⁹ investigated the red mud accident occurred on October 4th 2010 in Ajka, Hungary by testing the

plant toxicity and trace element availability with mixtures of red mud and non-contaminated soil. They observed the concentrations of trace elements in the leachate of red mud were either non-detectable or less than 20µg/L. In addition, Peters and Basta^{Error! Bookmark not defined.} added bauxite red mud directly to soil to reduce the bioavailable phosphorus. No excessive soil pH and increases of soil salinity, extractable Al, or heavy metals in soils were found in their study. Based on available field data, the application of coal combustion by-products and bauxite red mud has not been suggested to post adverse impacts on the environments.

However, to comprehend the overall benefits of reusing these by-products, it is vital to understand the leaching properties of the prepared pervious materials under different application scenarios.

Expected Outcomes and Significances

The outcome of this study is expected to provide:

- (1) Initial feasibility evaluation of a potential beneficial utilization for by-products produced from coal combustion and aluminum production processes
- (2) Insights regarding the interaction between nutrients and an agricultural emerging pollutant (i.e., estrogen) of FA zeolite-like material and the properties of biopolymers, and
- (3) Results to be transferred in forms of peer-reviewed publications and conferences, and be based upon in preparing competitive proposal for external funding.

The advantage of using selective sorption materials in the filtration approach is the potential to recycle and reutilize nutrients and industrial by-products, which promotes agricultural production to be in accord with the principles of sustainability. FGD gypsum and stabilized FGD material have shown to improve the yield of crops by providing necessary elements (e.g., calcium), changing soil physical properties, and increasing water infiltration and storage when they are applied as soil amendments^{20,21}. Hylander et al.²², used different filter materials (i.e. limestone, Polonite®, and sand) to capture soluble phosphorus and evaluated the subsequent suitability for plant production. They observed some of recycled phosphorus achieved 76% of the yield increased by commercially available P-fertilizer. As demand for food increases, which results in more land to be used for agricultural purpose and a requirement for increased crop yields, the fertilizer demand have been projected to increase faster than world population²³. With foreseeable increase in demand and depletion in reserve, use of recycled nutrients rather than a raw material is important step toward sustainable agricultural

development. Currently, the majority of phosphate rock from mining goes into artificial fertilizer production²⁴. It estimates that sources of high-grade phosphate ore deposits could disappear within the next 100 years at current use rates²⁵.

5. References

- ¹ Alexander, R. B., Smith, R. A., Schwarz, G.E., Boyer, E.W., Nolan, J.V., Brakebill, J.W. (2008) Differences in phosphorous and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environ. Sci. Technol.*, 42, 822-830.
- ² Mueller, D.K., Helsel, D.R., Nutrients in the Nation's Waters--Too Much of a Good Thing?. U.S. Geological Survey Circular 1136, <http://pubs.usgs.gov/circ/circ1136/circ1136.html#PUBS>, accessed 2/4/2011.
- ³ Smith, V.H., Tilman, G.D., Nekola, J.C. (1999) Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems, *Environ. Poll.*, 100, 179-796.
- ⁴ Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food*. The MIT Press, 2001, Cambridge, U.K.
- ⁵ Sharpley A, Foy B, Withers P (2000) Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. *J. Environ. Qual.*, 29, 1-9.
- ⁶ Kleinman P.J.A., Sharpley, A.N., Buda, A. R., McDowell, R.W., Allen, A.L. (2011) Soil controls of phosphorus in runoff: Management barriers and opportunities. *Can. J. Soil Sci.* 91, 329-338.
- ⁷ Sharpley A., Kleinman, P., and Weld J. (2010) Assessment of best management practices to minimize the runoff of manure-borne phosphorous in the United States, *New Zealand J. Agric. Res.*, 47, 461-477.
- ⁸ Sonzogni, W.C., Chapra, S.G., Armstrong, D.E., Logan, L.T. (1982) Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.*, 11, 555-563.
- ⁹ King, k.W., McDonald, J., Moore, J.F., Agrawal, S.G., Fischer, E.N., Balogh, J.C. (2010) Nutrient and pesticide removal from laboratory-simulated tile drainage discharge, *Trans. ASABE*, 53, 769-777.
- ¹⁰ Cheng, C.-M., Tu, W., Behrad, Z., Tarunjit B., Wolfe, W., Walker, H. (2007) Beneficial Reuse of FGD Material in the Construction of Low Permeability Liners: Impacts on Inorganic Water Quality Constituents, *J. Environ. Eng.*, 133, 523-531.
- ¹¹ Jin, N. fly ash Applicability in Pervious Concrete, Master Thesis, The Ohio State University, Columbus, OH 2010.
- ¹² Gall, H. E., Sassman S.A., Lee, L.S., and Jafvert, C.T., Hormone discharges from a Midwest tile-drained agroecosystem receiving animal wastes. *Environ. Sci. Tech.*, 2011, 45, 8755-8764.
- ¹³ Buchwald A., Dombrowski, k., and Weil, M. Influence of geopolymer binder composition on conversion reactions at thermal treatment, in *Developments in porous, Biological and Geopolymer Ceramics: A collection of Papers Presented at the 31st international conference on advanced Ceramics and Composites*, eds. Brito, M., Case, E., Kriven, W.M., Ceramic Engineering and Science Proceedings Volume 28. 257-271. Florida 2007,
- ¹⁴ Allred, B. (2010) Laboratory batch test evaluation of five filter materials for removal of nutrients and pesticides from drainage waters. *Transactions of the ASABE*, 53, 39-54.

- ¹⁵ Bryant, R.B., Buda A.R., Kkeinman, P.J.A., Church, C.D., Saporite, L.S., Folmar, G.J., Bose, S., Allen, A. (2012) Using fluegas desulfurization gypsum to remove dissolved phosphorus from agricultural drainage waters. *J. Environ. Qual.* 41, 664-671.
- ¹⁶ Yao, W., Millero, F.J. (1996) Adsorption of phosphate on manganese dioxide in seawater, *Environ. Sci. Technol.*, 30, 536-541.
- ¹⁷ Cengeloglu, Y., Tor, A., Ersoz, M., Arslan, G. (2006) Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol.*, 51, 374-378.
- ¹⁸ Duxson P, Lukey G.C., Separovic F. van Deventer J.S.J., (2005) Effect of alkali cations on aluminium incorporation in geopolymeric gels, *Ind. Eng. Chem. Res.*, 44, 832-839.
- ¹⁹ Ruters, S., Merten, J., Vassilieva, E., Dehandschutter, B., Poffijn, A., Smolders, E. (2010) The red mud accident in Ajka (Hungary): plant toxicity and trace metal bioavailability in red mud contaminated soil. *Environ. Sci. Technol.*, 45, 1616–1622.
- ²⁰ Chen L., Dick W., Nelson S., (2001) Flue Gas Desulfurization by-product additions to acid soil: Alfalfa productivity and environmental quality, *Environ. Poll.*, 114, 161-168.
- ²¹ Punshon T., Adriano D.C., Weber, J.T. (2001) Effect of flue gas desulfurization residue on plant establishment and soil and leachate quality, *J. Environ. Qual.*, 30, 1071-1080.
- ²² Hylander, L.D., Kietlinska, A., Renman, G., Siman, G. (2006) Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production. *Biores. Technol.*, 97, 914-921.
- ²³ Haar, A. The Reuse of Phosphorus. Eureau Position Paper EU2-04-SL09, 2005; http://eureau.org/sites/eureau.org/files/documents/2005.02.21_recovery_of_phosphorus_from_sludge.pdf. Accessed 10/6/2012.
- ²⁴ Jasinski S.M., Phosphate rock, 2006 Minerals Yearbook. United States Geological Survey, 2007, http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/myb1-2006-phosp.pdf, accessed 10/2/2012.
- ²⁵ Christen, K. (2007) Closing the phosphorus loop, *Environ. Sci. Technol.*, 41, 2078.