EVALUATION OF METALS LEACHING FROM GRAY IRON FOUNDRY AND COAL COMBUSTION BYPRODUCTS

By

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ABSTRACT:

This report is summarizes the results of two separate studies on the leaching of metals from industrial byproducts. The first section of the report describes a comparative study on the leaching of metals from field and laboratory tests on industrial byproducts used as highway construction materials. The second section describes a study on the leaching of metals from high-carbon fly ashes used to stabilize organic soils.

SECTION A:

This study was conducted to provide a comparison between the leaching of metals from field and laboratory tests on industrial byproducts used as highway construction materials. Materials used in this study were from a gray iron foundry (foundry sand and foundry slag) and a coal burning power plant (bottom ash and fly ash). The field tests consisted of lysimeters installed beneath the working platform of a section of Wisconsin State Highway 60, approximately 45 km northwest of Madison, WI, USA. Laboratory tests included column leach tests (CLTs) and water leach tests (WLTs). All samples from field and laboratory testing were analyzed for Cadmium, Chromium, Selenium, and Silver. The elution patterns from the field tests showed two distinct behaviors: first flush and lagged-response leaching. The leaching patterns and peak concentrations from the CLTs and lysimeter tests showed few similarities. The WLTs did not closely replicate the peak concentrations from the CLTs or the lysimeter tests. In several cases the peak concentrations from the CLTs and lysimeters exceeded United States Environmental Protection Agency maximum contaminant levels. However the CLTs and lysimeter tests represent pore fluid concentrations directly below the byproduct layers. Cases in which the byproducts are used above the groundwater table will likely have lower impacts on the groundwater due to adsorption on to soil surfaces and dispersion and diffusion. The use of laboratory tests such as WLTs and CLTs may

be insufficient to evaluate the impacts on groundwater from the use of industrial byproducts. A systematic approach incorporating the physical and chemical properties of the material and the hydrogeological features of the area and should be implemented before a byproduct is used.

SECTION B:

This study was conducted to investigate the potential of metals leaching from soft organic soils stabilized with high carbon fly ashes. Metal leaching was assessed through a series of water leach tests (WLTs) and column leach tests (CLTs) conducted on soil alone, fly ash alone, and soil-fly ash mixtures. Leachate from these tests was analyzed for cadmium (Cd), chromium (Cr), and silver (Ag). The concentrations from WLTs on soil-fly ash mixtures were lower than the concentrations from WLTs on fly ash alone, indicating that metals release is reduced due to adsorption onto fine-grained soil particles. The WLT concentrations can be multiplied by a scaling factor of 50 to provide a generally conservative estimate of the peak concentrations from the CLTs. The effluent concentrations from the CLTs showed two distinct patterns: first-flush, and lagged response leaching. A significant number of cases (29 of 60) had inconclusive leaching patterns because concentrations were consistently below the detection limits. These cases pose low risk to groundwater, because the detection limits of the analysis were at least 10 times lower than the USEPA MCLs. No relationship was found between leaching pattern and soil type (except Lawson soil tended to show inconclusive leaching patterns). However, trends were found between leaching patterns and both fly ash and element. The first-flush leaching behavior was more likely to occur from CLTs on fly ash with higher CaO content. Cr was likely to follow the first-flush leaching pattern, and Ag was likely to show lagged-response behavior. Cd was generally present at lower concentrations, showing inconclusive leaching patterns. The leaching patterns can be explained by the complexation as shown in Pourbaix diagrams from Brookins (1988). Further study is needed to better understand the conditions present in the CLTs, and identify the specific complexes present. Although several CLTs produced leachate with concentrations exceeding NR 140 limits, using HCFA to stabilize organic soils more than 1 m above the groundwater table should pose little risk to groundwater due to sorption onto soil solids as the effluent migrates from the stabilized layers.

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SECTION A

METALS LEACHING FROM FOUR HIGHWAY TEST SECTIONS CONSTRUCTED WITH INDUSTRIAL BYPRODUCTS

1. INTRODUCTION

Soft soils encountered during road construction often are removed and replaced with crushed rock to form a sturdy working platform for pavement construction. This construction practice can be costly, particularly if the rock needs to he hauled to the construction site. As a result, transportation agencies are seeking less costly methods to stabilize soft soils and construct working platforms. In some cases, industrial byproducts can be used to construct lower cost working platforms that provide equal support as those constructed with crushed rock (Tanyu et al. 2004). Use of industrial byproducts in this manner also facilitates sustainable construction by re-using materials currently being landfilled and reducing the use of virgin natural resources. A concern, however, is that contaminants leached from byproducts may contaminate underlying groundwater.

Five test sections were constructed along a 1.4 km stretch of Wisconsin State Highway (STH) 60 near Lodi, Wisconsin (USA) in Summer 2000 to evaluate alternative working platforms for highway construction on soft subgrades. For three of the test sections, coarse-grained industrial byproducts (foundry sand, foundry slag, or bottom ash) are being used as a working platform placed between the subgrade and the granular base course material. Fly-ash-stabilized subgrade (a mixture of existing subgrade and 10% fly ash by dry weight blended *in situ*) was used as the working platform in the fourth test section. The fifth test section is a control where crushed dolostone, a granular material commonly used in Wisconsin, was used for the working platform. Profiles of the test sections are shown in Fig. 1. Thicknesses of the byproduct layers were selected so that each test section had equal structural capacity as the



Fig. 1. Profiles of the test sections constructed using foundry slag, foundry sand, bottom ash, fly ash, and crushed rock (control) at STH 60, Lodi, WI (AC = asphalt concrete).

control section. Procedures defined in the *Guide for Design of Pavement Structures* published by the American Association of State Highway and Transportation Officials (AASHTO 1993) were used to determine the structural capacity. Details of the structural design are described in Edil et al. (2002).

During construction, two pan lysimeters were placed beneath each test section to monitor the quality and quantity of water discharged from the base of the pavement. Samples were collected from these lysimeters over a 5-year period and analyzed for concentrations of cadmium (Cd), chromium (Cr), selenium (Se), and silver (Ag). Batch water leach tests (WLTs) and column leaching tests (CLTs) were also conducted on the byproducts in the laboratory to evaluate their potential to leach Cd, Cr, Se, and Se. This report describes the field leaching data and compares the leaching patterns observed in field to those from the WLTs and CLTs. Peak concentrations observed in the field and laboratory tests are also compared with ground water quality standards stipulated by the State of Wisconsin and the United States Environmental Protection Agency (USEPA).

2. PAST LEACHING STUDIES ON BYPRODUCTS

2.1 Gray Iron Foundry Sand

Foundry system sand is a mixture of silica sand, a binding agent (clay or chemical), and other finishing additives that is used to form molds and cores for casting metals. When clay (typically sodium bentonite, calcium bentonite, or kaolinite) is used as the binder, the mixture is referred to as "green sand" (Abichou et al. 2000). A portion of the mixture is discarded after each use (Bastian and Alleman 1998). Some of this waste sand is used in a variety of construction and agricultural applications (Javed and Lovell 1994, Kleven et al. 2000, Abichou et al. 2000, Naik et al. 2001, Goodhue et al. 2001, Tanyu et al. 2004, Lee and Benson 2005). However, most waste foundry sand is landfilled. In Wisconsin, more than 800,000 Mg (1 Mg \approx 1 US ton) of green sand is landfilled annually (Lee and Benson 2005).

Bastian and Alleman (1998) used Microtox[™] microbial bioassay tests to characterize the environmental suitability of foundry sands from iron foundries (11 sands), a steel foundry (1 sand), and an aluminum foundry (1 sand). Thirteen virgin sands (clean sands without any binders or other additives) were also subjected to bioassay testing. Leachate for the bioassays was produced from batch tests conducted with a 2% NaCl solution with a liquid-to-solid (L-S) ratio of 4:1. Leachate from three of the iron foundry sands caused a quantifiable depression in microbial activity (i.e. less light emitted from the bacteria) compared to tests on the virgin sands. Leachate from the other iron foundry sands caused less inhibition of microbial activity than leachate from virgin sands. Leachate from the aluminum and steel foundry sands caused greater inhibition of microbial activity than leachates from the iron foundry sands or the virgin sands.

Partridge et al. (1998) evaluated groundwater samples and leachates from an embankment constructed with foundry sand and an adjacent embankment constructed with natural sand. Chemical analyses (Zn, Ni, Cd, Cr, Pb, and Cu) and Microtox[™] and Nitrotox[™] bioassays were conducted on the water samples. The foundry sand was from a gray iron foundry that uses organic binders. Samples were collected from 6 groundwater monitoring wells (4 adjacent to a highway embankment constructed using waste foundry sand, 2 near an embankment constructed using natural sand) and from 2 lysimeters (one in the foundry sand embankment, and one in the natural sand embankment). Samples from the lysimeters and monitoring wells in and adjacent to the foundry sand embankment showed negative inhibition relative to leachate and groundwater samples from the natural sand when tested with the Microtox[™] bioassays (i.e., the samples enhanced microbial activity). Samples from the monitoring wells and lysimeters did not enhance microbial activity during Nitrotox[™] bioassays. However, the bioassay results also showed no differences were observed in bacteria growth for samples up-gradient and down-gradient from the foundry sand layers. Only Cd, Ni, and Zn were detected in any of the leachates, and the metals concentrations observed were generally below USEPA drinking water standards. Samples that exceeded the drinking water standards were below requirements for the use of industrial byproducts as defined in Indiana Administrative Code.

Lee and Benson (2006) conducted water leach tests (WLTs) and column leach tests (CLTs) on 12 foundry green sands, a sandy silt, and a clean sand using the procedure in ASTM D 3987, which employs a L-S ratio of 20:1 using deionized water. Concentrations of AI, Ag, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, TI, and Zn from the WLTs were compared with maximum permissible concentrations specified in Wisconsin Administrative Code for industrial byproducts placed below the water table. None of the materials, including the sandy silt and the clean sand, met the criteria for use below the water table. Metals concentrations in leachate from the CLTs were higher than concentrations from the WLTs, but in all cases the concentrations were below USEPA maximum contaminant levels (MCLs).

2.2 Gray Iron Foundry Slag

Slag is a byproduct of the metal processing industry that consists of impurities that float to the surface of molten material. This floating material is skimmed off and cooled to form the solid referred to as slag. Annual blast furnace slag production in the United States is approximately 13 million Mg (Proctor et al. 2000). Although the majority of slag is landfilled, some slag is used in civil engineering applications (Shen and Forssberg 2002).

Lind et al. (2001) studied leaching of metals from two roads constructed using a ferrochrome steel slag. One road consisted of an older roadway resurfaced with a 750-mm-thick layer of slag overlain by hot mix asphalt pavement. A control section was also included where the road was overlain only with asphalt (no slag layer). The other road was a new road constructed only with a 450-mm-thick layer of slag (no asphalt pavement).

At both sites, groundwater monitoring wells were installed adjacent to the paved and unpaved areas, and adjacent to the asphalt control. The wells were installed 1 m and 4 m from the edge of the road. The wells closer to the road were 3.45 m deep, whereas those farther away were 3.04 m deep. Groundwater samples were collected 3 times from each location. For the unpaved road, Cr concentrations in the samples collected from the control monitoring wells (area surfaced with macadam) were comparable to Cr concentrations in the samples collected from the monitoring wells near the slag layers (all < 6 μ g/L). For the road with a hot mix asphalt surface, the Cr concentrations in the samples from the monitoring well 4 m from the slag layer typically were one-half of the concentrations in samples from the monitoring well 1 m from the slag layer.

Ham and Boyle (1990) investigated the characteristics of samples collected from 7 ferrous foundry landfills that contained a mixture of foundry sand, foundry slag, and dust. Samples were collected from monitoring wells up-gradient and down-gradient (at waste boundary) of the landfills. None of the samples analyzed had concentrations of As, Cd, Cr, Pb, Hg, Se, or Ag above USEPA MCLs at the time of the study. Ham and Boyle (1990) also performed USEPA batch extraction procedure (EP) tests (L-S ratio = variable) as well as deionized water leach tests (L-S ratio = 5:1) on samples of foundry wastes collected from the landfills. Leachate from the EP test on three of the foundry wastes had concentrations exceeding the MCL for Cd. However, Cd was not detected in groundwater at any of the landfills containing these foundry wastes.

2.3 Coal Bottom Ash

Bottom ash is a coarse residual composed of mineral oxides in crystalline or glass form that is collected from dry bottom boilers used at coal-fired power plants (Siddiki et al. 2004). Bottom ash is angular, has a porous surface texture (Seals et al. 1972), and appears similar to well-graded coarse sand (Tanyu et al. 2004). According to the American Coal Ash Association (ACAA), approximately 18 million Mg of bottom ash is produced annually in the United States, and 46% of the ash is re-used in applications such as structural fill and roadway construction.

Thayumanavan et al. (2001) conducted an algal bioassay on leachate from WLTs conducted on bottom ash and bottom ash in an asphalt pavement mixture. The water leach tests were one part solids and 4 parts distilled water (L-S ratio = 4:1) and were shaken for 24 h. They found significantly less algae growth in tests with bottom ash leachate compared to control tests with water. However, when bottom ash was

incorporated as an aggregate in asphalt, algal bioassays on the leachate from the bottom ash produced similar results to the control tests.

Goodarzi and Huggins (2001) used a sequential leaching procedure to evaluate leaching of As, Cr, and Ni from coal combustion bottom ash. The bottom ash was exposed to deionized water, ammonium acetate ($NH_4C_2H_3O_2$), and hydrochloric acid (HCl). The concentrations of the $NH_4C_2H_3O_2$ and HCl were not specified. No As was leached from the bottom ash exposed to deionized water and $NH_4C_2H_3O_2$, but 37.5% of the total As was leached after the bottom ash was exposed to HCl. Ni was not leached in water, but 25.7% of total Ni was leached when in $NH_4C_2H_3O_2$. All but the final remaining 0.4% of the Ni was leached in HCl. Cr in the bottom ash was leached by ammonium acetate (4.1%) and hydrochloric acid (95.9%).

2.4 Coal Fly Ash

Fly ash is fine-textured particulate that is removed from the exhaust from coal combustion. Fly ash particles are spherical and have particle sizes ranging between 1 and 150 μ m. Most tend to be silt size, between 2 μ m and 75 μ m (Gutierrez et al. 1993, Bin-Shafique et al. 2006). According to the American Coal Ash Association (ACAA), 70 million Mg of fly ash was produced in 2003 in the United States and 39% was reused in a variety of applications. The remainder was disposed in waste containment facilities such as landfills.

Theis et al. (1977) conducted WLTs on 11 fly ashes at pH 3, 6, 9, and 12 using 200 g of fly ash per liter of deionized water (L-S ratio = 5:1). The batches were shaken for 24 h. pH was controlled with sodium hydroxide and perchloric acid. The leachates were tested for As, Cd, Cr, Cu, Pb, Ni, and Zn. Average concentrations observed for all 11 fly ashes were highest for the tests at pH 3, with the exception of As, which had the highest concentration at pH 12. For instance, Cr release at pH 3 was 3.9 times greater

than the Cr release at pH 12, and the Cd release was 6.1 times higher at pH 3 compared to pH 12.

Praharaj et al. (2002) performed WLTs on 4 fly ashes from a power plant burning sub-bituminous coal. The WLTs were conducted using synthetic rainwater (pH 5.6) at L-S ratios of 4, 8, 12, and 16. The leachate was analyzed for Al, Ca, K, Mg, Na, P, S, Si, As, Ba, Fe, Mn, Mo, Ti, V, Pb, Zn, Co, Cr, Cu, Ni, and Cd. Cd, Cr, Co, and Ni did not leach from the ashes at any L-S ratio. As, Mn, and Mo leached at concentrations between 1 and 26 times above drinking water standards recommended by the World Health Organization and As, Fe, and Mn leached at concentrations between 1 and 6 times higher than USEPA MCLs. Concentrations were highest for most of the metals at the lowest L-S ratio, with concentrations decreasing with increasing L-S ratio.

Bin Shafique et al. (2006) performed WLTs and column leach tests (CLTs) on soils mixed with sub-bituminous fly ashes. The CLTs were conducted to evaluate metals leaching under flow-through conditions more typical of that occurring in the field and to provide a comparison to concentrations from the WLTs. WLTs were performed on the soils alone, fly ashes alone, and on mixtures containing 10% and 20% fly ash (by weight). The WLTs contained 70 g of solids and 1400 ml of deionized water (L-S ratio = 20:1). CLTs were conducted on the soils alone and with mixtures containing 10% and 20% fly ash (by weight). Leachate from the WLTs and CLTs was analyzed for Cd, Cr, Se, and Ag.

Analysis of the CLT data showed that release of Cd, Cr, Se, and Ag was adsorption controlled, with initial concentrations approximately 50 times the WLT concentrations for Cd and Ag and 10 times the WLT concentrations for Cr and Se (Bin Shafique et al. 2006). Metals concentrations in leachate from the WLTs and CLTs varied with fly ash content, which was attributed to the variation in pH with fly ash content.

3. MATERIALS

A summary of the index and physical properties of the byproducts and the subgrade soil at the field site can be found in Table 1 along with classifications of these materials according to the Unified Soil Classification System (USCS) and the AASHTO classification system. Particle size distribution curves for the materials are shown in Fig. 2. The foundry slag, foundry sand, and bottom ash are coarse-grained materials in the Unified Soil Classification System (USCS), and the fly ash and subgrade soil are fine-grained in the USCS. Additional information on the mechanical properties of the foundry sand, foundry slag, and bottom ash can be found in Tanyu et al. (2004).

Water leach tests (WLTs) were conducted on the foundry sand, foundry slag, bottom ash, fly ash, and on the fly ash-soil mixture following the procedure in ASTM D 3987. Based on these analyses, all of the byproducts meet the requirements in Section NR 538 of the Wisconsin Administrative Code for byproducts used in confined geotechnical applications (e.g., materials placed covered with pavement, as in Fig. 1). Results of the WLTs are discussed in Section 5.

3.1 Foundry Sand

Grede Foundries of Reedsburg, WI provided the foundry sand for this study. The foundry produces grey iron castings using a mixture of sand, 10% bentonite, and $\approx 4\%$ sea coal (powdered coal used as a combustible additive). The foundry sand is black in color and classifies as clayey sand (SC) in the USCS and A-2-7 in the AASHTO system. Although the sand is coarse-grained (percent fines = 29%, see Fig. 2), the bentonite gives the material cohesive properties and plasticity (e.g., plasticity index = 9, Table 1).

 Table 1. Physical properties and USCS and AASHTO classifications of the foundry sand, foundry slag, bottom ash, fly ash, and soil used in the study.

Material	Specific Gravity	D ₁₀ (mm)	D ₆₀ (mm)	Cu	Percent Fines (%)	USCS Symbol	AASHTO Symbol
Foundry Sand	2.55	0.0007	0.25	357	29	SC	A-2-7
Foundry Slag	2.29	0.2	2.5	13	9	SW-SM	A-3
Bottom Ash	2.65	0.2	1.5	8	3	SW	A-3
Fly Ash	2.70	0.001	0.07	70	98	ML	A-4
Subgrade Soil	2.70	0.0006	0.02	33	96	CL	A-6



Fig. 2. Particle size distribution curves for foundry sand, foundry slag, bottom ash, fly ash, and subgrade soil used at STH 60 and for the laboratory tests.

3.2 Foundry Slag

The foundry slag is coarse-grained (9% fines) and classifies as well-graded sand with silt (SW-SM) in the USCS and A-3 in the AASHTO soil classification system. The foundry slag was provided by Grede Foundries in Reedsburg, WI, which uses a cupola furnace to prepare molten iron. A cupola furnace is tall cylindrical blast furnace that is typically fed with raw metals and a fluxing agent such as limestone or dolomite (Sun and Sahajwalla 2004). The raw metals fed into the cupola furnace at Grede Foundries come from recycled material, scrap steel, and pig iron. Non-metallic additives used in the melt process include coke, limestone, and coke fines.

3.3 Bottom Ash

The bottom ash used in this study is from a dry bottom furnace at Alliant Energy's Columbia Power Station in Portage, WI that burns sub-bituminous coal from the Wyoming Powder River Basin. The bottom ash is coarse-grained material that classifies as well-graded sand (SW) in the USCS and A-3 in the AASHTO system.

3.4 Fly-Ash-Stabilized Soil

The test section with a fly-ash-stabilized subgrade was constructed with fly ash from Alliant Energy's Columbia Power Station that was blended into the existing subgrade (10% fly ash by dry weight) to a depth of 300 mm using a reclaimer. Immediately after mixing, the mixture was compacted to 15.4 kN/m³ using a tamping foot, steel drum, and rubber tire compactors. The water content was 21% \pm 2% when the mixture was compacted. Details on the construction can be found in Edil et al. (2002).

Columbia Power Station captures the fly ash using electrostatic precipitation and stores the ash in a dry silo. The fly ash contains 98% fines and classifies as elastic silt (ML) in the USCS, A-4 in the AASHTO system, and Class C in ASTM C 618,

The subgrade soil at the STH 60 field site is low plasticity clay (CL) in the USCS and A-6 in AASHTO. The natural water content of the subgrade soil is 23%.

4. METHODS

4.1 Field Lysimeters

Two pan lysimeters (3.75 m x 4.75 m) were installed beneath each section at the STH 60 site to collect leachate draining from the bottom of the profile. A schematic of a typical set of lysimeters is shown in Fig. 3. One lysimeter was located directly under the centerline of the highway and the other was located at the edge, with one-half of the lysimeter under the highway shoulder. The lysimeters were constructed with 1.5-mm-thick textured HDPE geomembrane overlain by a geocomposite drainage layer. Water collected by the lysimeters drains to 120-L HDPE drums located below ground surface adjacent to the highway. Additional information on the lysimeters can be found in Bin Shafique et al. (2002).

Water samples were collected from the lysimeters on a periodic basis. The sampling frequency depended on the rate of drainage from the lysimeters, which varied seasonally. Sampling was least frequent in the winter when freezing occurred and most frequent in the spring when snowmelt and rainfall are more common. During each sampling event, water contained in each drum was removed with a pump, the total volume of water in the drum was recorded, and samples were collected for chemical analysis. Methods used for filtering, preserving, and storing the samples are described in Section 4.4.

4.2 Water Leach Tests

Water leach tests (WLTs) were conducted on the byproducts following the methods in ASTM D 3987, where 70 g of dry solid is mixed with 1400 ml of ASTM Type II water (L-S ratio = 20:1) in 2 L HDPE bottles that are rotated continuously for 18 hr at 29 rpm. After rotation, the solution was allowed to settle for 5 min and the supernatant





Fig. 3. Plan view (A) and cross-section (B) of lysimeters located at STH 60 in Lodi, WI. The foundry slag, foundry sand, and bottom ash sections were constructed similar to the control section, with profiles shown in Fig. 1.1.

was collected, filtered, and the pH was recorded. Samples of the supernatant were stored in sealed HDPE bottles with no headspace.

4.3 Column Leach Tests

Column leach tests (CLTs) were conducted on each of the industrial byproducts to evaluate leaching under flow-through conditions. CLTs on the cohesionless materials (foundry slag and bottom ash) were conducted using rigid-wall permeameters, whereas flexible-wall permeameters were used for the cohesive materials (foundry sand and flyash-stabilized-soil). Schematic drawings of the rigid-wall and flexible wall CLTs are in Fig. 4.

4.3.1 Columns

The rigid-wall procedure was adapted from the procedure described in Lee and Benson (2005). Specimens were compacted directly into a PVC column having the same size as a standard Proctor mold (101.6 mm in diameter and 114.3 mm tall). Non-woven needle-punched geotextiles were placed on the top and bottom of the specimen to ensure uniform flow and to prevent solids from entering the influent and effluent lines. Acrylic end plates with o-rings were used to seal the ends of the column. Upward flow was imposed using a peristaltic pump set at 30 mL/hr (9 mm/d) for the first 1.5 pore volumes of flow (PVF) and 7 mL/hr (2 mm/d) for the remainder of the test. The flow rate was reduced after 1.5 PVF to permit practical sample collection intervals.

The procedure described in Bin Shafique et al. (2002) was used for the flexiblewall tests. Flexible-wall permeameters meeting the criteria in ASTM D 5084 were used for the tests. Test specimens were placed in the permeameter between acrylic end caps and sealed with a latex membrane. Non-woven needle-punched geotextiles were placed between the ends of the specimen and the end caps to promote uniform flow and



Fig. 4. Schematic drawings of rigid-wall (a) and flexible-wall (b) CLTs.

to prevent solids from entering the influent and effluent lines. A hydraulic gradient between 7-12 was used to drive the flow in an upflow mode. An effective confining pressure of 15 kPa was applied to simulate the stress existing in the field.

A 0.1 M LiBr solution was used as the influent for all column tests. The solution was prepared by dissolving LiBr salt (99+% pure, from Aldrich Chemical Company) in de-ionized water followed by exposure to the atmosphere until pH 6 was reached. The concentration was selected so that the ionic strength was similar to pore water in pavement layers (Karczewska et al. 1996). Effluent from the columns was collected in sealed Teflon bags that were emptied after approximately 30~60 mL of flow accumulated (≈ 0.1 PVF). Volume and pH of the effluent were recorded each time a bag was emptied and a 45 mL sample was collected for chemical analysis. Methods used to handle, preserve, and store the samples for chemical analysis are described in Section 4.4.

4.3.2 Preparation of Column Test Specimens

Slag and bottom ash used in the rigid-wall CLTs was crushed by hand through a No. 4 sieve (4.8 mm openings) to remove large particles before preparing test specimens. Large particles (< 5% for slag, 0% for bottom ash) that could not be crushed though the sieve were discarded. The materials were tamped into the PVC molds in 3 lifts. Each lift was tamped using a standard Proctor hammer and then vibrated to achieve approximately the same dry unit weight used in the field (12.4 kN/m³ for foundry slag, 17.1 kN/m³ for both bottom ash).

The soil-fly ash mixture was prepared using standard Proctor methods (ASTM D 698) at a molding water content approximately 2% dry of optimum water content to simulate conditions that existed during construction of the test sections (Bin Shafique et al. 2002). A mixture containing 90% air-dried soil and 10% fly ash (by weight) was

blended by hand until uniform and then sprayed with deionized water until the desired water content (17.3%) was reached. The mixture was compacted one hour after mixing to simulate the delay between mixing and compaction that occurs during construction. After compaction, the specimens were extruded from the compaction molds, sealed in plastic, and cured for 7 days in a 100% humidity environment prior to testing to simulate the condition existing in the field (Edil et al. 2002). The specimen was compacted to a dry unit weight 15.4 kN/m³, which is the same dry unit weight obtained in the field.

The foundry sand was prepared at a water content of 23% and a dry unit weight of 15 kN/m³ to simulate the condition existing in the field (Edil et al. 2002). Prior to compaction, the material was dried and crushed through a No. 4 sieve (4.8 mm openings) followed by re-moistening by spraying and blending with tap water until the desired water content was obtained. The foundry sand was tamped into a Proctor mold to reach the required density. The foundry sand was placed in 3 lifts, and tamped with a standard Proctor hammer. After compaction, the specimen was extruded and placed into the flexible-wall permeameter.

4.4 Chemical Analysis of Effluent

Procedures described in Bin Shafique et al. (2002) were followed for sample handling, preservation, analysis, and quality control. All samples were filtered through a 0.45- μ m membrane filter as required in ASTM D 3987, acidified to pH < 2 using metals-grade nitric acid, and stored in sealed HDPE bottles at 4°C prior to testing. Blanks were prepared and handled using the same protocol used for the other samples.

All samples from the CLTs and lysimeters were analyzed for Cd, Cr, Se, and Ag. Samples collected from the lysimeters later in the study (after 6/2002) and samples from the water leach tests on the foundry sand and foundry slag were also analyzed for Fe and Pb. Samples were analyzed by atomic adsorption (AA) spectrometery or inductively coupled plasma optical emission spectrometery (ICP-OES). AA was used earlier in the study, and ICP later in the study. A switch was made to the ICP to make testing more efficient.

The AA analyses were conducted using a Varian SpectrAA-800 atomic adsorption (AA) spectrometer equipped with a GTA-100 graphite tube atomizer, an automated sample dispenser, and a Varian SpectAA-800 Data Station. Procedures described in USEPA Standard Methods 213.2, 218.2, 270.2, and 272.2 were followed for the AA analyses. The AA was calibrated using 4 standard dilutions to create a calibration curve. Duplicate tests were conducted on each sample and samples with a relative standard deviation (RSD) > 5% were re-tested. The calibration curve and replicate samples were re-analyzed every 10 samples. The detection limits for the AA analysis are in Table 2.

Samples analyzed using ICP-OES were analyzed at either CT Laboratories in Baraboo, WI or at the water chemistry laboratory at the University of Wisconsin-Madison. The UW laboratory was equipped with a Perkin Elmer Optima 4300 DV ICP-OES with an AS 90 Plus autosampler. CT laboratories used a Thermo Jarrell Ash ICAP 61E Trace Analyzer for ICP analysis. ICP-OES analysis was conducted following USEPA Method 6010B. Blanks were included every 10 to 20 analyses and the calibration was verified every 10 analyses. A reagent blank was tested every 20 samples and a spiked sample was analyzed every 10 samples. The limits of detection for the ICP analysis are in Table 2. Table 2.Limits of detection from ICP-OES and AA analysis performed at CT
Laboratories (Baraboo, WI), and at the University of Wisconsin-Madison.

Element	CT Laboratories (ICP-OES)	UW-Madison (ICP-OES)	UW-Madison (AA)	
	Detection Limit (µg/L)	Detection Limit (µg/L)	Detection Limit (µg/L)	
Cd	0.7	0.2	0.1	
Cr	1.7	1.0	2.0	
Se	4.0	10.0	2.0	
Ag	0.8	2.5	0.2	

5. RESULTS AND DISCUSSION

5.1 Lysimeters

5.1.1 Hydrologic Data

Volumetric flux in each lysimeter over the 5-year monitoring period is shown in Fig. 5. The lysimeters were not monitored between July 2002 and June 2003 due to lack of funding. Precipitation data from the National Oceanic and Atmospheric Administration (NOAA) station in Prairie du Sac, WI (approximately 16 km from the site) are shown in Fig. 6.

Box plots showing the volumetric flux (mm/d) from each section of the field site are shown in Fig. 7. Data from the inner and outer lysimeters in each section were combined when preparing the box plots. Volumetric fluxes from the test sections constructed with cohesive or fine-grained materials (foundry sand, fly-ash-stabilized soil) are lower, on average, than the volumetric flux from the lysimeters in the test sections constructed with granular materials (foundry slag, bottom ash, and control section). The average flux from the foundry sand test section (0.09 mm/d) was 1.9 times lower than the average flux from the fly-ash-stabilized-soil test section (0.17 mm/d), and 2.9 times lower than the flux from the bottom ash layer (0.26 mm/d). The average fluxes from the foundry slag (0.22 mm/d) and control (0.20 mm/d) sections were 1.2 to 2.4 times higher than the average flux from the foundry sand and fly-ash-stabilized-soil sections, but not as high as the average flux from the bottom ash section.

Liquid did not appear in the collection drums from the foundry sand section for the first 8 months. The lower average flux and the longer time for leachate breakthrough from the foundry sand layer are likely due to the relatively high bentonite content (10%) of the foundry sand. Laboratory tests conducted by Abichou et al. (2002) on this foundry sand indicated that the saturated hydraulic conductivity can be as low as 10⁻⁸ cm/s.



Fig 5. Volumetric flux from lysimeters in (a) foundry sand, (b) foundry slag, (c) bottom ash, (d) fly-ash-stabilized-soil, and (e) control sections.



Fig 6. Monthly precipitation data collected by the National Oceanic and Atmospheric Administration for Prairie du Sac, WI.



Fig. 7. Box plots of volumetric flux from control, fly-ash-stabilized soil, bottom ash, foundry slag, and foundry sand test sections. Volumetric flux from the inner and outer lysimeters in each section are combined. Average volumetric flux is as follows: control – 0.20 mm/d, fly-ash-stabilized subgrade – 0.17 mm/d, bottom ash – 0.26 mm/d, foundry slag – 0.22 mm/d, and foundry sand – 0.09 mm/d.

5.1.2 Metals Concentrations

Metals concentrations in leachate from the lysimeters over the monitoring period are shown in Figs. 8-11. Peak concentrations observed in the lysimeters along with the number of pore volumes of flow to reach the peak concentration are summarized in Table 3.

Cd and Cr concentrations in leachate (Figs. 8 and 9) are highest in the early portion of the monitoring period and then steadily decrease, a pattern referred to as "first-flush" leaching (Edil et al. 1992). Two exceptions are the Cd and Cr elution patterns from the leachate collected from the foundry sand lysimeter, which gradually climbed throughout the monitoring period ("lagged-response" leaching, Edil et al. 1992). Data for the foundry sand lysimeter are not shown until 6/2002, because too little water was discharged from the foundry sand to permit analysis during the earlier portion of the monitoring period.

Peak concentrations of Cd and Cr in leachate from the foundry slag, bottom ash, and fly-ash-stabilized-soil sections are higher than the peak concentrations in leachate from the control section (3.4-5.2 times higher for Cd, 6.1-15.0 times higher for Cr). For the foundry sand section, the peak Cr concentration was also 1.8 times higher than the peak concentration in the control section, whereas the peak Cd concentration was 2.2 times lower than that for the control section. However, after 3 years, the Cd and Cr concentrations from all test sections were comparable (~5 µg/L for Cd and Cr). The peak Cd and Cr concentrations occurred after an average of approximately 0.2 PVF, with a minimum of 0.01 PVF and a maximum of 0.51 PVF (Table 3). Creek and Shackelford (1992) observed first-flush and lagged-response elution patterns in leachate from CLTs on fly ash, fly ash-sand mixtures, and fly ash-bentonite mixtures. They concluded that elements with higher charge densities tended to elute earlier than species with lower charge densities. The specific species present in the leachate from

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Fig. 8. Cd Concentrations in leachate from lysimeters in (a) foundry sand, (b) foundry slag, (c) bottom ash, (d) fly-ash-stabilized-soil, and (e) control sections.



Fig. 9. Cr Concentrations in leachate from lysimeters in (a) foundry sand, (b) foundry slag, (c) bottom ash, (d) fly-ash-stabilized-soil, and (e) control sections.


Fig. 10. Se Concentrations in leachate from lysimeters in (a) foundry sand, (b) foundry slag, (c) bottom ash, (d) fly-ash-stabilized-soil, and (e) control sections.



Fig. 11. Ag Concentrations in leachate from lysimeters in (a) foundry sand, (b) foundry slag, (c) bottom ash, (d) fly-ash-stabilized-soil, and (e) control sections.

the field tests in this study have not been identified, but Creek and Shackelford (1992) observed first-flush leaching patterns for both Cd and Cr.

The elution pattern for Se (Fig. 10) sharply contrasts the patterns for Cd and Cr (Figs. 8 and 9). Se concentrations are lower during the first 18 mos and higher concentrations during the final 24 mos, with the peak concentration typically reached between 0.9 and 3.4 PVF. The average PVF at peak concentration for Se was 2.2 times higher than the average PVF at peak concentration for the other elements studied. The exception is the foundry sand section, where no distinct peak concentration occurred and only 0.05 PVF was transmitted. Peak Se concentrations from each section were similar (89-151 μ g/L), although the fly-ash-stabilized-soil test section typically had lower Se concentrations than the other test sections throughout the monitoring period (i.e., Se is more likely to leach from working platforms constructed using traditional construction materials and the other alternatives than from fly-ash-stabilized soil). At the end of the monitoring period, Se concentrations from all sections were comparable (~80 μ g/L). The one exception is the Se concentration in the leachate from the inner lysimeter in the fly-ash-stabilized-soil section the fly-ash-stabilized soil).

The lagged-response elution pattern observed for Se may be the result of transformation from Se(IV) to Se(VI) as a result of changing redox conditions in the system. Neal and Sposito (1989) report that Se(IV) is strongly adsorbed by soils, but Se(VI) is weakly sorbed and leaches easier. Se (VI) commonly forms anionic complexes, which are not attracted to the surface of the soil solids (e.g. positively charged clay particles). However, no tests were performed to identify the Se species present in leachate, and the redox conditions present in the field are also unknown.

Ag showed both first-flush and delayed-response leaching patterns. The leaching behavior for Ag was similar for the foundry slag, bottom ash, and control

sections (first-flush elution) and the leachate from all three test sections consistently had a concentration less than 3 μ g/L for the final two years of the monitoring period. The Ag concentrations in the leachate from the foundry slag, bottom ash, and control sections reached peak levels within 0.5 PVF. The Ag leaching pattern from the foundry sand section was not defined because only one sample had a concentration greater than the detection limit (2.5 μ g/L, July 2003). The Ag elution patterns in the leachate from the two lysimeters in the fly-ash-stabilized-soil section were remarkably different. The Ag concentrations in the leachate from the outer lysimeter never exceeded 5 μ g/L, but the Ag concentrations in the leachate from the inner lysimeter increased to over 100 μ g/L after 3 years, and remained above 20 μ g/L for the remainder of the test. The peak Ag concentration in the leachate from the inner lysimeter in the fly-ash-stabilized soil section

Peak concentrations of Cd, Cr, Se, and Ag in each test section constructed with byproducts were divided by peak concentrations from the control section to define normalized peak concentrations (Table 3). Normalized peak concentrations less than 1.0 represent cases where leachate from the control section had a higher peak concentration than leachate from a byproduct test sections. Three (of 16) cases had normalized concentrations less than 1.0, indicating that in these instances the impact on groundwater resulting from the use of industrial byproducts should be no greater than impact from traditionally accepted highway construction materials. Cases in which the normalized concentration is greater than 1.0 indicate that the concentration in leachate from the byproduct layer is higher than the concentration from the control section. The normalized Se concentrations range from 0.9 (fly-ash-stabilized soil) to 1.5 (foundry slag). The highest normalized concentrations of Cd (5.2), Cr (15.0), and Ag (24.7) were at least 3.5 times higher than the highest normalized Se concentration. No pattern was

Cd				Cr		Se			Ag			
Material	Peak Lysimeter Conc. (μg/L)	Normalized Conc.	PVF to Peak Conc.	Peak Lysimeter Conc. (μg/L)	Normalized Conc.	PVF to Peak Conc.	Peak Lysimeter Conc. (μg/L)	Normalized Conc.	PVF to Peak Conc.	Peak Lysimeter Conc. (μg/L)	Normalized Conc.	PVF to Peak Conc.
Foundry Sand	2.8	0.45	0.16	6.1	1.85	0.01	105	1.05	0.05	2.6	0.67	0.14
Foundry Slag	32.1	5.18	0.29	49.6	15.03	0.17	151	1.51	0.87	8.2	2.10	0.24
Bottom Ash	21.2	3.42	0.17	32.1	9.73	0.33	141	1.41	0.98	15.2	3.90	0.17
Fly-Ash- Stabilized Soil	32.1	5.18	0.01	20.2	6.12	0.26	89	0.89	3.37	96.4	24.72	1.89
Control	6.2	1.00	0.51	3.3	1.00	0.44	100	1.00	1.23	3.9	1.00	0.51

Table 3.Peak Cd, Cr, Se and Ag concentrations found in the leachate from lysimeter tests on foundry sand, foundry slag, bottom ash,
fly-ash-stabilized soil, and crushed rock (control), along with the PVF to reach the peak concentration.

observed for the normalized concentrations in terms of byproduct or element (except that normalized Se concentrations tended to be low).

5.2 Comparison of Elution in Lysimeters and WLTs

Cd, Cr, Se, and Ag concentrations in the leachate from the WLTs summarized in Table 4. Concentrations from the WLTs are below the detection limit for 8 of 16 cases, whereas peak concentrations in the leachate collected in the lysimeters are always above detection limits (Table 3). A graph of peak concentrations from the lysimeters vs. corresponding concentrations from the WLTs is shown in Fig. 12. Peak concentrations from the lysimeters generally are higher than those from the WLTs; in only one case is the peak concentration from the WLT higher than the peak concentration from the lysimeters (Cr from fly-ash-stabilized soil). The highest Cr and Se concentrations observed in the field were from the foundry slag test section, whereas the WLT on the foundry slag had Cr and Se concentrations below detection limits. The WLT and lysimeter tests on fly-stabilized-soil produced leachate with the highest Cd concentrations. Ag concentrations in the leachate from the WLTs were all below 2.5 μ g/L, and the highest Ag concentration in the leachate from the field tests was from the fly-ash-stabilized soil section. The peak Ag concentration in the fly-ash-stabilized soil section was at least 6.3 times higher than the peak Ag concentrations observed in the leachate from the other lysimeters.

The disparity between peak concentrations from lysimeters and the concentrations from the WLTs may be due to the different liquid-solid ratios or differences in liquid-solid contact times. Kosson et al. (2002) define two leaching release mechanisms: equilibrium controlled and mass transfer rate controlled. Equilibrium controlled release is typical for cases of slow percolation through porous or granular materials. The field tests on foundry sand and fly-ash-stabilized-soil may fit into

Table 4. Cd, Cr, Se, Ag, Fe, and Pb concentrations in leachate from lysimeters, CLTs, and WLTs on foundry sand, foundry slag, bottom ash, and fly-ash-stabilized soil.

Matorial	Peak Lysimeter Conc. (μg/L) Peak CLT Conc. (μg/L) WLT pH and Concentration (μg/L)							ug/L)							
Waterial	Cd	Cr	Se	Ag	Cd	Cr	Se	Ag	Cd	Cr	Se	Ag	Fe	Pb	рΗ
Foundry Sand	2.8	6.1	105	2.6	32.9	<1.7	<4.0	6.7	0.3	<1.0	<10	<2.5	430	8	9.0
Foundry Slag	32.1	49.6	151	8.2	<0.7	6530	<4.0	16.8	0.2	<1.0	<10	<2.5	48.3	12	10.7
Bottom Ash	21.2	32.1	141	15.2	10.3	961	24.1	4.4	<0.2	1.1	32.5	<2.5	-	-	10.3
Fly-Ash- Stabilized Soil	32.1	20.2	89.0	96.4	4.6	62.9	32.4	5.8	0.6	46	16.2	1.8	-	-	11.0
Fly Ash Alone	-	-	-	-	-	-	-	-	0.7	95	26	2.2	-	-	11.8

Note: Hyphen indicates that test was not conducted. <X.Y indicates concentration is below the detection limit (X.Y µg/L).



Fig. 12. Comparison of WLT Cd, Cr, Se, and Ag concentrations with the peak concentrations found in the leachate from lysimeter tests.

this category. Mass transfer rate controlled release is typical of situations with rapid percolation (i.e. short contact time) relative to the mass transfer rate of the species being leached. Leaching from the granular materials (foundry slag, bottom ash, and the control sections) may be mass transfer rate controlled. No investigation into the mechanisms causing the different leaching results from field tests and WLTs was performed in this study.

5.3 Comparison of Elution in Lysimeters and CLTs

Peak concentrations from the CLTs are summarized in Table 5. A comparison of peak concentrations from the lysimeters and peak concentrations from the CLTs is shown in Fig. 13. No relationship is apparent between peak concentrations from the CLTs and peak concentrations from the lysimeters. Peak concentrations of Cd and Se from the lysimeters are higher than peak concentrations from the CLTs, except for peak Cd concentration from the foundry sand lysimeter, which was 11.8 times lower than the peak concentration from the CLT. Peak concentrations of Ag in the leachate from the lysimeters were both higher and lower than peak concentrations from the CLTs. Except for the fly-ash-stabilized soil, peak concentrations of Ag from the lysimeters and CLTs were within a factor of 3.5. Peak Cr concentrations from the CLTs typically (3 of 4) were higher (3.1 to 131.7 times) than peak concentrations from the lysimeters. Only foundry slag had a peak concentration of Cr in the lysimeter that was higher than the peak concentration in the CLT.

Elution curves for Cd from the test sections and CLTs are shown in Fig. 14. Similar elution patterns for Cd were obtained in the field and the CLTs for the test sections constructed with foundry sand (delayed leaching) and fly-ash-stabilized soil (first flush leaching), except for two outlier points for the CLT on foundry sand. In fact, the Cd elution patterns for fly-ash-stabilized-soil are nearly identical in the field and

Table 5. Peak Cd, Cr, Se, and Ag concentrations, leachate pH, and PVF to peak concentration from CLTs on foundry sand, foundry slag, bottom ash, and fly-ash-stabilized soil.

		Cd		Cr			Se			Ag		
Material	Peak CLT Conc. (μg/L)	pH at Peak Conc.	PVF to Peak Conc.									
Foundry Sand	32.9	8.4	0.1	ND	-	-	ND	-	-	7.0	8.5	1.6
Foundry Slag	ND	-	-	6530	7.4	0.6	ND	-	-	16.8	8.6	28.7
Bottom Ash	10.3	8.5	22.9	961	7.7	0.7	24	9.1	16.5	4.4	8.5	6.9
Fly-Ash- Stabilized Soil	4.6	NT	0.8	62.9	NT	0.8	32.4	NT	0.3	5.8	NT	0.3

ND: Not Detected.

NT: Not Tested.



Fig. 13. Comparison of CLT Cd, Cr, Se, and Ag concentrations with the peak concentrations found in the leachate from lysimeter tests.



Fig. 14. Cd elution curves from CLTs and lysimeters: (a) foundry sand, (b) foundry slag, (c) bottom ash, and (d) fly ash stabilized soil.

CLTs. In contrast, elution of Cd from the foundry slag and bottom ash test sections followed a first-flush pattern, whereas the CLTs yielded concentrations below the detection limits over the same range of PVF. The pH was not measured during the field tests and the CLT on fly-ash-stabilized soil. However, pH at the peak Cd concentration in the leachate from the other CLTs was slightly basic, between 8.4 and 8.5.

Elution curves for Cr from the test sections and CLTs are shown in Fig. 15. The elution curves from the CLTs on foundry slag, bottom ash, and fly-ash-stabilized-soil exhibit a similar pattern as those from the field, although the peak Cr concentrations from the CLTs were 3.1 to 131.7 times larger than those in the field. In contrast, for foundry sand, Cr concentrations from the CLT were always less than the detection limit (1.7 μ g/L), whereas concentrations from the lysimeter were as high as 6.1 μ g/L.

Elution curves for Se from the test sections and CLTs are shown in Fig. 16. Similar curves were obtained from the CLTs and the field only for the fly-ash-stabilizedsoil. For the other materials, Se concentrations from the CLTs were nearly always less than the detection limit (4.0 μ g/L), whereas peak concentrations of Se in the field ranged from 89 μ g/L to 151 μ g/L. One possible explanation for the elevated concentrations of Se in the field is that the primary source of Se is the base course layer (Fig.1) rather than the byproduct layer. The base course was crushed from the same dolostone used for the working platform in the control section, and elevated concentrations of Se were observed in the control section (Table 3 and Fig. 10). Although the Se concentrations from the CLTs were generally below the detection limit, the peak concentration from the CLT on bottom ash occurred at a pH of 9.1.

Elution curves for Ag from the test sections and CLTs are shown in Fig. 17. Similar elution patterns were obtained from the field and CLTs for bottom ash and flyash-stabilized soil. For the fly-ash-stabilized soil, however, Ag concentrations increased



Fig. 15. Cr elution curves from CLTs and lysimeters: (a) foundry sand, (b) foundry slag, (c) bottom ash, and (d) fly ash stabilized soil.



Fig. 16. Se elution curves from CLTs and lysimeters: (a) foundry sand, (b) foundry slag, (c) bottom ash, and (d) fly ash stabilized soil.



Fig. 17. Ag elution curves from CLTs and lysimeters: (a) foundry sand, (b) foundry slag, (c) bottom ash, and (d) fly ash stabilized soil.

in one lysimeter and decreased in the other during the latter portion of the monitoring period, whereas the CLT concentrations remained relatively constant over the same range of PVF. Concentrations of Ag from the CLT on foundry sand tended to be much higher than those measured in the field, which generally were below the detection limit (2.5 μ g/L). However, the one sample from the foundry sand lysimeter that was above the detection limit (2.6 μ g/L) was within the range of concentrations obtained from the CLT (1.0-2 6.7 μ g/L). Concentrations of Ag from the foundry slag test section varied considerably and intermittently, ranging from below the detection limit up to 8.2 μ g/L. A similar variation in concentrations of Ag was observed from the CLT on foundry slag. The pH at the peak CLT Ag concentrations was similar to the pH at peak Cd concentration (pH = 8.5 to 8.6). Due to the lack of field pH data, no comparison of the pH and subsequent leaching conditions could be made between the field and CLT tests.

6. IMPLICATIONS FOR GROUNDWATER QUALITY

A field site was constructed along a stretch of STH 60, 45 km northwest of Madison, WI, USA. The test site was designed to evaluate the leaching of metals from foundry sand, foundry slag, bottom ash, and fly-ash-stabilized soil used as working platform materials. Groundwater quality standards applicable to the field site are defined in Section NR 140 of Wisconsin Administrative Code, *Groundwater Quality NR 140*. The standards in NR 140 are similar to, or lower than USEPA MCLs. A comparison of the NR 140 standards for Cd, Cr, Se, and Ag and peak concentrations from the test sections is in Table 6.

Cd concentrations in the leachate from the foundry slag, bottom ash, and control sections exceeded the NR 140 standard (5 μ g/L) by a factor of 1.2-6.4 for the first 18 mos of the field test. However, in all cases, the Cd concentrations were below the NR 140 standard after 16 mos and 0.6 PVF. Se concentrations exceeded the NR 140 standard (50 μ g/L) for all test sections by a factor of 1.8 to 3.0. Moreover, in all cases except for the fly-ash-stabilized soil, the Se concentration increased and then leveled off at a concentration exceeding the NR 140 standard over the last 24 months of monitoring.

In contrast to Cd and Se, leachate concentrations exceeding the NR 140 standard for Ag (50 μ g/L) were only observed in the fly-ash-stabilized soil section (peak = 96 μ g/L). Ag concentrations of this magnitude were only recorded in one lysimeter in the fly-ash-stabilized soil section, and the concentration in this lysimeter fluctuated between 19 and 113 μ g/L over the last 24 months of the monitoring period. None of the test sections had Cr concentrations exceeding the NR 140 standard (100 μ g/L).

Leachate collected in the lysimeters is representative of pore fluid at the bottom of the pavement profile and represents water reaching groundwater only if the

Table 6.Peak lysimeter concentrations observed in field tests, and estimated concentrations after 1 m and 5 m of migration
from the byproduct layers based on Bin Shafique et al. (2002).

Matorial	Pea	k Lysimete	er Conc. (µ	ιg/L)	Conc. after 1 m migration (µg/L)				Conc. after 5 m migration (µg/L)			
Wateria	Cd	Cr	Se	Ag	Cd	Cr	Se	Ag	Cd	Cr	Se	Ag
Foundry Sand	2.8	6.1	105	2.6	0.6	1.2	21.0	0.5	0.3	0.6	10.5	0.3
Foundry Slag	32.1	49.6	151	8.2	6.4	9.9	30.2	1.6	3.2	5.0	15.1	0.8
Bottom Ash	21.2	32.1	141	15.2	4.2	6.4	28.2	3.0	2.1	3.2	14.1	1.5
Fly-Ash- Stabilized- Soil	32.1	20.2	89	96.4	6.4	4.0	17.8	19.3	3.2	2.0	8.9	9.6
NR 140 Requirements	5	100	50	50	5	100	50	50	5	100	50	50

groundwater table is at the base of the pavement profile. In many roadways, the water table will be deeper. Processes such as sorption, diffusion, dispersion, and dilution occurring in soils between the base of the pavement and the groundwater table will result in lower concentrations by the time the groundwater table is reached. Bin Shafique et al. (2002) conducted a modeling study to simulate the transport of contaminants from working platforms constructed with byproducts to the groundwater table using a variably saturated model of flow and transport that was validated using data from field lysimeter studies. Their findings indicate that the maximum relative concentration decreases with increasing depth to the groundwater table. In particular, the maximum concentration 1 m below the pavement layer typically was 20% of the peak concentration at base of the byproduct layer and 10% of the peak concentration 5 m below the byproduct layer. Estimated concentrations at the groundwater table were obtained by applying these factors (Table 6). In all cases, the estimated concentrations of Cd, Cr, Se, and Ag at the water table are below the NR 140 standards when the groundwater table is at least 5 m below the byproduct layer. For cases where the groundwater table is 1 m below the byproduct layer, the NR 140 standards for Cd, Cr, Se, and Ag would be met for the foundry sand and bottom ash sections. However, for the test sections with foundry slag and fly-ash-stabilized soil, the Cd concentrations are 1.3 times the NR 140 limit. The Cr, Se, and Ag concentrations for the case in which the groundwater table is 1 m below the byproduct layer for foundry slag and fly-ashstabilized soil were all at least 40% lower than the NR 140 limits.

The re-use of industrial byproducts in Wisconsin is regulated based on WLT concentrations. WLTs were conducted on foundry sand, foundry slag, bottom ash, fly ash alone, and fly-ash-stabilized soil. The bottom ash and fly ash used in this study meet NR 538 Category 4 requirements and can be used in confined geotechnical fills. Foundry sand and

foundry slag meet the NR 538 requirements for Cd, Fe, and Pb, but the WLT leachate must be tested for Ba and Hg before the materials can be approved for use in confined geotechnical fills. The WLT concentrations tended to be well below the NR 538 Category 4 requirements (Table 4). However, leachate collected in the lysimeters commonly had concentrations exceeding groundwater standards for Cd, Cr, Se, and Ag specified in Section NR 140 of the Wisconsin Administrative Code. The WLTs did not produce leachate with Cd, Cr, Se, and Ag concentrations that were comparable to the leachate concentrations observed in the field. WLTs may be an insufficient index test to characterize the potential for leaching of metals from industrial byproducts in the field.

CLTs have been used as an alternative to WLTs, with the thought that the flow-through conditions of the CLTs more closely represents the conditions in the field. However, the concentrations in the effluent from the CLTs performed in this study did not closely simulate the concentrations found in the leachate from the field tests. The use of laboratory tests such as WLTs and CLTs may be insufficient to evaluate the impacts on groundwater from the use of industrial byproducts. The local soils, depth to the water table, and the amount of precipitation all play an important role in the migration of metals from industrial byproducts used as construction materials. A systematic approach incorporating the physical and chemical properties of the material and the hydrogeological features of the area and should be implemented before a byproduct is used.

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SECTION B

LEACHING OF HEAVY METALS FROM ORGANIC SOILS STABILIZED WITH HIGH CARBON FLY ASH

1. INTRODUCTION

Deformation of soft soils is a frequent problem during road and building construction in Wisconsin (Tanyu et al. 2004). A common solution in Wisconsin is to excavate the soft soil and fill the excavation with crushed rock known as "breaker run". This cut-and-fill process can be disruptive, time consuming, and expensive, especially when the rock must be hauled from considerable distance to the site. An alternative approach is to improve the soft soil *in situ* by blending in cementitious materials, such as cementitous fly ashes. Previous studies have shown that blending cementitious fly ashes into soft and moist inorganic fine-grained soils can result in substantial increases in strength and modulus (e.g., Acosta et al. 2003, Ferguson 1993, Sridharan et al. 1997).

Stabilizing soft organic soils is particularly problematic, because many cementing agents can be ineffective for organic soils (Clare and Sherwood 1954, 1956). However, Acosta et al. (2003) found that a fly ash with high organic carbon content (e.g., unburned carbon or activated carbon added during pollution control operations), herein referred to as a high-carbon fly ash (HCFA), was effective at stabilizing a soft organic soil. Although only a limited number of tests were conducted, Acosta et al. (2003) showed that increases in strength and stiffness as large as 7 times were achieved using HCFA. This application may prove to be fruitful, because HCFAs generally are landfilled rather than reused. HCFAs also are a large waste stream. Approximately 42 million Mg (1 Mg \approx 1 US ton) of HCFA is generated annually in the United States by the electric power industry (ACAA 2004). Thus, finding reuse applications for HCFAs may provide substantial economic savings.

Based on the findings in Acosta et al. (2003), a research program was initiated regarding the mechanical properties and leaching characteristics of soft organic soils stabilized with HCFAs. This report summarizes the portion of the research program focused on leaching characteristics. Background information on high carbon fly ashes, organic soils, and leaching of metals from fly ash stabilized soils is provided in Section 2. Section 3 of this report describes the soils and fly ashes that were used in the study. Physical and chemical methods employed in the study are described in Section 4. Section 5 presents the results and discusses the findings. A summary and conclusions are in Section 6.

2. BACKGROUND

2.1 FLY ASH

Fly ash is fine textured unburned or non-combustible particulate material that is removed from exhaust emanating from coal combustion. Common fly ash collection methods include electrostatic precipitators, fabric filters, and cyclone (or centrifugal) separation (EERC 2005). Fly ash particles generally range between 1 and 150 μ m and are similar in size and shape to silt particles (Gutierrez et al. 1993). According to the American Coal Ash Association (ACAA), 70 million Mg (1 Mg \approx 1 US ton) of fly ash was produced in 2003 in the United States. Currently 39% of the fly ash produced in the United States is reused in applications such as concrete additives, flowable fill, road sub-base stabilization, snow & ice control, etc (ACAA, 2004). The remainder typically is stored in waste containment facilities such as landfills.

ASTM C 618 defines a classification system for fly ash based on chemical composition $(SiO_2, Al_2O_3, Fe_2O_3, SO_3, moisture content, and loss on ignition) and physical properties (fineness, activity, soundness, etc). The classification criteria specified in ASTM C 618 are shown in Table 1. There are two major classes of fly ash: Class C and Class F. Fly ashes that do not meet the criteria for Class C or Class F are considered to be "off-specification." The majority of the fly ash currently being landfilled is off-specification fly ash (ACAA 2004). High carbon fly ashes, defined here as ashes with LOI > 6%, fall into the off-specification category and comprise as much as 60% of the fly ash produced in the United States (ACAA 2005—personal communication).$

The type of fly ash produced by a plant depends on the coal source, combustion process, and pollution prevention measures. Normally Class F fly ash is produced by power plants burning anthracite or bituminous coal, and Class C fly ash is from plants burning lignite or

Chomical Boguiromonts	ASTM Requirements				
Chemical Requirements	Class F	Class C			
$SiO_2 + AI_2O_3 + Fe_2O_3$, min (%)	70	50			
SO ₃ , max (%)	5	5			
Moisture Content, max (%)	3	3			
Loss on Ignition, max (%)	6	6			

Table 1. Requirements for Class C and Class F fly ash as defined in ASTM C 618.

Physical Paguiromonts	ASTM Requirements				
Filysical Requirements	Class F	Class C			
Fineness, max (%)	34	34			
Pozzolanic Activity @ 7 Days, min (%)	75	75			
Pozzolanic Activity @ 7 Days, min (%)	75	75			
Water Requirement, max (%)	115	105			
Autoclave Expansion, max (%)	0.8	0.8			
Density Variation, max (%)	5	5			
Variation of % Retained on 45-um filter, max (%)	5	5			

sub-bituminous coal (ASTM C 618). Class F fly ash contains more silicates and aluminous material, and Class C fly ash has higher calcium oxide content (Wang 2004).

Although fly ash commonly is an alkaline material (Ghosh and Subbarao 1998; Khanra et al. 1998; Bin Shafique et al. 2002), fly ash can be either acidic or basic. Iyer (2002) indicates that the pH of fly ash depends on the relative amounts of CaO and SiO₂ in the ash. Fly ash with high CaO content tends to be basic, with lime hydration reactions producing hydroxide anions (Iyer 2002):

$$CaO + H_2O \rightarrow Ca^{+2} + 2OH^{-}$$
(2.1)

Acidic conditions may be generated by protons released by alumina or silica reactions (Iyer 2002):

$$SiO_2 + 2H_2O \rightarrow H_2SiO_4 + 2H^+$$
(2.2)

Thus, fly ash that is high in aluminum or silicon oxides may be acidic if the concentration of protons from alumina or silica reactions exceeds the alkalinity associated with the lime hydration reactions. For example, Praharaj et al. (2002) report an acidic pH from a subbituminous coal fly ash. The ash was mixed with water to form slurries with a solid-solution ratio of 1:10 or 2:5. The final pH for the slurries, regardless of solid solution ratio, was between 4-5.

The silicon and aluminum oxides present in fly ash have pozzolanic properties. A pozzolan is siliceous or aluminous material that possesses no independent cementing ability, but will form cement compounds in the presence of an activator (commonly calcium hydroxide)

and water (Mamlouk and Zaniewski 1999). Heating or NaOH can also induce activation of pozzolans. Both Class C and Class F fly ash are pozzolanic materials. Class C fly ash also has self-cementing properties due the presence of lime, which reacts with water to form calcium hydroxide.

2.2 ORGANIC SOILS

According to ASTM D 2487, a soil is considered organic if there is enough organic material present to influence the properties of the soil. For example, a fine-grained soil is referred to as organic if oven drying reduces the liquid limit of the soil by 25% or more. Many organic soils are too soft to adequately support most roads or buildings. Thus, when organic soils are encountered, they are removed and replaced with stronger material or stabilized in place using physical or chemical methods (Hampton and Edil 1998).

A common method to chemically stabilize organic soils is to blend in lime, Portland cement, or fly ash. Clare and Sherwood (1954, 1956) show that organic matter has a variable effect on cement stabilization. Organic matter may have no effect on cement stabilization or organic matter can completely inhibit stabilization reactions. The variability is a result of the complex biochemical composition of organic materials. Glasser (1995) showed that organic compounds within waste sludge have detrimental effects on cementitious and pozzolanic reactions, which are important for stabilization. Organic molecules interfere with cementing by adsorbing onto the surface of anhydrous cement particles or by preventing calcium hydroxide crystallization (Young 1972, 1976).

In limited tests, Acosta et al. (2003) found that a high carbon fly ash was effective in stabilizing an organic clay (classifying as OH). The organic clay had an unstabilized California bearing ratio (CBR) of 0.3 and an unconfined compressive strength (q_u) of 32 kPa. After

stabilization with the high carbon fly ash, the CBR was 10 and the q_u increased to 100 kPa. Attempts to stabilize the soil with other fly ashes (all with carbon content < 6%) showed no appreciable stabilization. Although the reason why the high-carbon fly ash (HCFA) was more effective was not determined, higher organic content was the only apparent property differentiating the high carbon fly ash from the ashes that provided no stabilization.

2.3 Leaching of Metals from Fly Ash

There have been multiple approaches to describing the mechanisms of leaching of metals. Mudd et al. (2004) describe dissolution and desorption as the mechanisms by which metals are transferred into leachate. Kosson et al. (2002) define two leaching release mechanisms: equilibrium controlled and mass transfer rate controlled. Equilibrium controlled release is typical for cases of slow percolation through porous or granular materials. Mass transfer rate controlled release is typical of situations with rapid percolation (i.e. short contact time) relative to the mass transfer rate of the species being leached.

Many organic ligands tend to be present in fly ash leachate. Metal complexation with organic ligands is complicated, and speciation is not well understood (Allen 1993). Regardless of speciation, leaching of heavy metals from fly ash is primarily a function of pH (Theis and Wirth 1977). As the pH of the pore water increases, the amount of metals leaching into solution decreases. This is because the solubility of most metal complexes decreases with increasing pH. For most fly ash applications, the pH tends to be high, so the leaching of metals from fly ash may be solubility controlled (Murarka et al. 1991).

In contrast to Murarka et al. (1991), Bin Shafique et al. (2002) found metal leaching from fly-ash-stabilized soils to be adsorption controlled. The adsorption-desorption process is also significantly affected by solution pH. pH affects the surface potential of the adsorbent, which

consequently causes a change in competition between protons and metal ions for sorption sites (Sauve et al. 2000).

There have been several reports on how pH affects metals leaching from fly ash. Kim et al. (2003) performed column leach tests on Class F fly ash. They found that the elements investigated (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, and Zn) were generally insoluble or slightly soluble when deionized water was used as the leachant, but the same species tended to be more soluble when acid (pH 2.9 or pH1.2) was used as the leachant solution. They concluded that metal leaching from fly ash was limited under normal environmental conditions. Fleming et al. (1996) performed column leach tests on fly ash using 0.5 N acetic acid as the leachant solution. The pH was controlled using 0.1 M sodium hydroxide. They found that leachate concentrations of Cd, Cr, Zn, Hg, and Ag increased as the leachant solution pH decreased from 6.8 to 3.0.

Bin Shafique et al. (2002) performed a series of water leach tests and column leach tests on soil-fly ash mixtures. They found that metal leaching from soil-fly ash mixtures was lower than from bulk fly ash alone, and recommend that a systematic evaluation be used for each specific soil-fly ash mix application to realistically evaluate metal leaching potential. Additional discussion of Bin Shafique et al. (2002) is provided in subsequent sections.

2.4 leaching patterns

Two distinct leaching patterns have been observed during column leach tests on fly ash: "first flush" (or "early response") and "lagged response" (or "delayed response"). Examples of the two leaching patterns are shown in Fig. 1. The first flush response is characterized by high initial concentrations followed by decreasing concentrations with increasing pore volumes of



Pore Volumes of Flow

Fig. 1. Typical metal leaching patterns observed during column leach tests.

flow. The delayed response is characterized by low initial concentrations that steadily increase before reaching a "lagged" peak and decreasing.

Creek and Shackelford (1992) observed both leaching patterns during column leach tests on fly ash alone, fly ash mixed with sand, and fly ash/cement/bentonite mixtures. Ba, Ca, and Sr showed what the authors called "delayed response" leaching behavior. Al, B, Cd, Cr, Cu, Fe, Mn, Mo, Pb and Zn exhibited "early" leaching. Creek and Shackelford (1992) concluded that leaching behavior is related to the charge density of the metal being leached, and that the equilibrium chemistry of the leaching fluid plays a significant role in the rate at which metals are leached.

Edil et al. (1992) observed "first-flush" and "lagged-flush" leaching patterns in column leach tests conducted on fly ash alone, and fly ash/sand mixtures. Edil et al. (1992) concluded that the leaching behavior is due to changes in solubility with changes in pH and alkalinity.

Bin Shafique et al. (2002) performed column leach tests on soil-fly ash mixtures. Two of the fly ashes (Dewey and King) used by Bin Shafique et al. (2002) were used in the present study. Bin Shafique et al. (2002) exclusively observed first flush leaching behavior, and the leaching pattern agreed with the analytical solution of the advection-dispersion equation with adsorption controlled release. Bin Shafique et al. (2002) concluded that the metal leaching from soil-fly ash mixtures was adsorption controlled.

2.5 Fly Ash Reuse Criteria in Wisconsin

Section NR 538 of the Wisconsin Administrative Code describes regulations for re-use of fly ash and other industrial byproducts in Wisconsin. Byproducts are categorized as 1, 2, 3, 4, or 5 based on concentrations determined from an ASTM D 3987 water leach test and total elemental analysis. Twelve 'beneficial uses' for industrial byproducts are defined, with the acceptable uses for a material defined based on its categorization. Materials falling in Category 1 typically leach at the lowest concentrations and have the broadest range of acceptable reuse applications, whereas materials falling Category 5 leach at the highest concentrations and are the most restricted. Using fly ash to stabilize soft soil for roadways falls under Beneficial Use 5, which requires that the fly ash fall in Categories 1-4. Species of concern for Category 4 byproducts are cadmium (Cd), chromium (Cr), selenium (Se), silver (Ag), and sulfate. Regulatory limits for Category 4 byproducts based on NR 538 are summarized in Table 2.

Section NR 140 of the Wisconsin Administrative Code describes regulations for groundwater quality. This standard is relevant for comparing metals leaching from column leach tests to the levels considered acceptable in the field. The regulatory limits for Cd, Cr, Se, and Ag as defined by NR 140 are shown in Table 2.
Table 2.	Regulatory limits for cadmium, chromium, selenium, and
	silver as defined by Sections 538 and 140 of Wisconsin
	Administrative Code.

Element	Maximum Concentration (μg/L)					
Liement	NR 538	NR 140				
Cadmium	25	5				
Chromium	500	100				
Selenium	250	50				
Silver	250	50				

3. MATERIALS

3.1 Fly Ash

Three fly ashes were used in this study: Dewey, King, and Presque Isle. These fly ashes were provided by Alliant Energy (Dewey), Xcel Energy (King), and We Energies (Presque Isle). The fly ashes were selected because of their relatively high carbon content, as will be shown subsequently. Dewey and King fly ashes were used in previous studies by Bin Shafique et al. (2002) and Acosta et al. (2003). However, the Dewey and King ashes used in this study are from different batches of ash than those used by Bin Shafique et al. (2003). Information regarding the sources of the fly ashes is summarized in Table 3. Dewey and King fly ashes are produced from the combustion of sub-bituminous coal, and Presque Isle fly ash is from a plant burning bituminous coal. Petroleum coke is added to the coal during combustion at the plants producing Dewey and King fly ashes.

Particle size distribution curves for the fly ashes are shown in Fig. 2. All of the fly ashes contained more than 60% fines (passing 0.075 mm sieve). King and Presque Isle have similar and narrow gradations, whereas Dewey is more well-graded. Physical and chemical properties of the fly ashes are summarized in Table 4 along with the criteria for Class C and Class F ashes in ASTM C 618. A summary of the chemical composition of the fly ashes, along with typical compositions of typical Class C and Class F fly ash is in Table 5. None of the fly ashes used in this study meet the Class C or Class F criteria. All three ashes exceed the loss on ignition (LOI) requirement (an index of organic carbon content), and both the Dewey and King fly ashes have insufficient trioxide content (SiO₂ + Al₂O₃ + Fe₂O₃). In addition, the fineness of the Presque Isle ash exceeds the maximum for Class C and F, and the pozzolanic activity at 7 d of the Presque Isle ash does not meet the minimum for Class C and F. King fly ash is the closest to a typical Class C fly ash of the ashes included in this study.

Table 3.Coal source, boiler type, and fly ash collection and storage
information for the power plants producing Dewey, King, and Presque
Isle fly ashes.

Properties	Dewey	King	Presque Isle
Company	Alliant Energy	Xcel Energy	WE Energy
Location	Cassville, WI	Bayport, MN	Marquette, MI
	Sub-Bituminous	Sub-Bituminous	Bituminous
Type of Coal and Source	80% Montana Coal with Colorado or Petroleum Coke	20% Montana Powder River Basin Coal, 72% Wyoming Powder River Basin Coal, 8% Petroleum Coke	100% Colorado Bituminous
Collection Method	Electrostatic	Electrostatic	Fabric Filter
Storage Type	Dry Silo	Dry Silo	Dry Silo
Type of Boiler Cyclone		Cyclone	Front Wall/Tangential



Fig. 2. Particle size distribution curves for Dewey, King, and Presque Isle fly ashes.

Chamical Paguiroments	ASTM Rec	ASTM Requirements		King	Presque	
Chemical Requirements	Class F	Class C	Dewey	King	Isle	
$SiO_2 + Al_2O_3 + Fe_2O_3, min$ (%)	70	50	17.6	45.0	57.1	
SO ₃ , max (%)	5	5	-	-	-	
Moisture Content, max (%)	3	3	1.5	0.1	11.0	
Loss on Ignition, max (%)	6	6	42	12	34	

Table 4.	Properties of Dewey, King, and Presque Isle fly ashes with ASTM C 618
	chemical and physical criteria for Class C and Class F fly ash.

Physical Poquiromonts	ASTM Requirements		Dowov	King	Presque	
Filysical Requirements	Class F	Class C	Dewey	Killy	Isle	
Fineness, max (%)	34	34	12.7	10.4	39.2	
Strength Activity @ 7 Days, min (%)	75	75	82.7	77.7	48.5	
Strength Activity @ 28 Days, min (%)	75	75	-	-	-	
Water Requirement, max (%)	115	105	-	-	-	
Autoclave Expansion, max (%)	0.8	0.8	-	-	-	
Density Variation, max (%)	5	5	-	-	-	
Variation of % Retained on 45-um filter, max (%)	5	5	-	-	-	

	Percent of Composition							
Chemical Species	Typical Class C ¹	Typical Class F ¹	Dewey ²	King²	Presque Isle ²			
CaO	24	9	9.2	25.8	3.2			
SiO ₂	40	55	8.0	24.0	35.6			
Al ₂ O ₃	17	26	7.0	15.0	18.0			
Fe ₂ O ₃	6	7	2.6	6.0	3.5			
MgO	5	2	2.4	5.3	1.0			
SO ₃	3	1	-	-	-			

Table 5.Chemical composition of the fly ashes in this study along with the composition
of typical Class C and Class F fly ash.

¹ From FWHA (2003), ² Whole rock geochemical analysis performed by ALS Chemex, Sparks, NV.

3.2 Soils

Three organic soils were selected for use in the study: Lawson organic clay, Markey peat, and Theresa organic clay. These soils were selected to represent typical organic soils found during highway construction in Wisconsin, i.e., peat and organic clay. The soils are from southern and central Wisconsin, as shown in Fig. 3. Samples of each soil were collected from shallow test pits approximately 1.2 m deep and were stored in airtight buckets to preserve the natural water content.

Index tests were conducted on each soil for classification purposes. The index properties and the index test methods are summarized in Table 6. A standard Proctor compaction test (ASTM D 698) was also performed on each soil. Optimum water content and maximum dry unit weight are summarized in Table 6. Unconfined compression tests were also conducted on specimens of each soil compacted at the natural water content and dry unit weight. Methods described in ASTM D 5102 were followed. The unconfined compressive strengths are summarized in Table 6.

The Lawson and Theresa soils classify as organic clays in the Unified Soil Classification System (USCS) (OL-OH for Lawson, OL for Theresa). The Lawson soil is more plastic (PI = 19 vs. 8) and considerably finer than the Theresa soil (Fig. 4). Markey soil is a black sandy organic soil that is nearly non-plastic and classifies as a peat (Pt) in the USCS. Markey soil is coarser (Fig. 4) and more organic (see LOI in Table 6) than the Lawson or Theresa soils. All three soils have near neutral pH (6.3-7.1), although the Markey soil is the more acidic (pH 6.3).

All three soils are very soft in their natural condition (Table 6), having unconfined compressive strengths less than 60 kPa. These low strengths make each of these soils poor subgrades for highway construction.



Fig. 3. Locations where soils were sampled.

				Ge	eneral Pro	perties				e,	Soil Class	ification	
Sample ID	LOI (%)	рН	Liquid Limit (LL)	Plasticity Index (Pl)	Specific Gravity	Natural Water Content	Optimum Water Content	Max Dry Unit Weight	Unconfined Compressive Strength	US			USDA
			()	. ,		(%) (%) (kN/m°) (kPa)	(кра)	Group			OODA		
	ASTM D 2974	ASTM D 4972	ASTM D 4318	ASTM D 4318	ASTM D 854	ASTM D 2216	ASTM D 698	ASTM D 698	ASTM D 5120	Symbol	Name		
Lawson Soil	5	6.9	50	19	2.58	28	28	13.3	57	OL-OH	Organic Clay	A-7-5 (23)	Silty Clay
Markey Soil	27	6.3	53	1	2.23	57	46	10.3	15	Pt	Sandy Peat	A-8(0)	Sandy Loam
Theresa Soil	6	7.1	31	8	2.57	20	21	15.2	36	OL	Sandy Organic Clay	A-4(5)	Silty Clay

Table 6. Index properties, compaction characteristics, and classifications of Lawson, Markey, and Theresa soils.



Fig. 4. Particle size distribution curves for Lawson, Markey, and Theresa soils.

The Theresa organic clay was intended to be the same soil (Theresa silt loam) used by Bin Shafique et al. (2002) and Acosta et al. (2002). However, the index tests showed that the soils are not the same (Table 7). Theresa organic clay has a lower LOI and lower natural moisture content than Theresa silt loam. The Theresa silt loam (PI = 19) was much more plastic than the Theresa organic clay (PI = 8). Theresa organic clay also has a higher specific gravity, likely due to higher sand content and lower organic matter content.

		Gen	eral Prope	USCS Classification			
Sample ID	LOI (%)	Liquid Limit (LL)	Plasticity Index (Pl)	Natural Water Content (%)	Specific Gravity	Group Symbol	Group Name
Theresa Organic Clay	6	31	8	20	2.57	OL	sandy organic clay
Theresa Silt Loam	10	61	19	35	2.24	ОН	high plasticity organic clay

Table 7. Index properties and classification of Theresa organic clay and Theresa silt loam.

4. METHODS

4.1 Water leach TESTS

Water leach tests (WLTs) were performed on fly ash alone, soil alone, and soil-fly ash mixtures having various fly ash contents, following the procedures described in ASTM D 3987. A summary of the materials that were tested is in Table 8. The soil-fly ash mixtures were prepared by mixing air-dried soil with the specified percent fly ash (by weight). Deionized water was added using a spray bottle so that the mixture had a water content 2% dry of standard Proctor optimum water content. The mixtures were sealed in plastic bags and allowed to cure in a moisture-controlled environment for 7 d prior to testing.

The WLTs were conducted using 70 g of solid material mixed with 1400 ml of ASTM Type II water in 2 L HDPE bottles. The bottles were rotated continuously for 18 hours at 29 revolutions per minute. After rotation, the solution was allowed to settle for 5 min and the supernatant was collected, filtered, and the pH was recorded. Samples of the supernatant were then preserved with nitric acid to pH < 2. All samples were analyzed for Cd, Cr, Se, and Ag using inductively coupled plasma optical emission spectrometery (ICP-OES).

4.2 Column Tests

The column leach test (CLT) procedure used in this study was similar to that described by Bin Shafique et al. (2002). Soils were air-dried prior to sample preparation. For mixtures containing fly ash, 30% fly ash (by weight) was hand mixed with the dry soil. The dry soil-fly ash mixture (or soil alone) was wetted by spraying with deionized water to reach the desired moisture content. This procedure was used to ensure

Soil	Fly Ash	Fly Ash Content (%)
		20
	Dewey	30
		40
		20
Lawson	King	30
		40
		20
	PI	30
		40
		20
	Dewey	30
		40
		20
Markey	King	30
		40
		20
	PI	30
		40
	Dowov	20
	Dewey	30
		40
Theresa	King	20
Theresa	King	40
		20
	PI	30
		40
Lawson		0
Markev	None	0
Theresa		0
	Dewey	100
None	King	100
	PI	100

Table 8. Summary of fly ash and soil mixtures prepared for water leach tests.

uniform mixing of fly ash within each specimen. Specimens for the CLTs were prepared in a compaction mold (101.6 mm diameter by 116.4 mm tall) using standard Proctor compactive energy. The molding water content was 2% dry of standard Proctor optimum water content so that the hydraulic conductivity would be high enough to provide adequate flow in a reasonable amount of time. After compaction, the specimens were sealed in plastic and cured for 7 days prior to testing.

The CLTs were conducted using flexible wall permeameters in an up-flow mode. The effective confining pressure was 15 kPa and the hydraulic gradient was between 7 and 10. The influent solution (0.1 M LiBr) was exposed to the atmosphere to reach an equilibrium pH of 6. Effluent from each column was collected in sealed Teflon bladders. Leachate was removed from the bladders after approximately 30~60 mL of flow had accumulated (0.1 pore volumes). The leachate volume and pH were recorded and samples of the leachate were filtered and preserved with nitric acid to pH < 2. All samples were analyzed for Cd, Cr, Se, and Ag using ICP-OES.

A summary of the specimens used in column leach testing (and their respective hydraulic conductivities) is included in Table 9. Tests were performed on soils alone and soil stabilized with 30% fly ash (by weight). CLTs were also conducted on specimens of clean sand mixed with 30% fly ash. These tests were conducted to simulate a fly ash mixture where sorption of the soil solids would be negligible.

4.3 chemical ANALYSIS

The procedures described in Bin Shafique et al. (2002) were followed for sample handling, preservation, and analysis (including quality control measures). Samples from both the CLTs and WLTs were filtered through a 0.45- μ m membrane filter and then acidified to pH <2 using high purity nitric acid. The samples were stored in a temperature controlled cold room at 4°C prior to analysis. Lab blank samples were

Table 9.Summary of water content, dry density, and hydraulic conductivity for all column
leach test specimens.

Soil	Fly Ash	% Fly Ash	γ _d (kN/m³)	w (%)	K _s (cm/sec)
	Dewey	30	14.4	26	6.0x10 ⁻⁷
Lawson	King	30	14.9	26	8.3x10 ⁻⁸
	Presque Isle	30	15.1	26	9.1x10 ⁻⁸
	Dewey	30	10.3	44	1.8x10 ⁻⁶
Markey	King	30	10.3	44	2.7x10 ⁻³
	Presque Isle	30	10.4	44	1.2x10 ⁻⁶
	Dewey	30	15.1	19	2.1x10 ⁻⁵
Theresa	King	30	15.3	19	1.7x10 ⁻⁵
	Presque Isle	30	15.5	19	3.1x10 ⁻⁴
	Dewey	30	18.2	11	5.0x10 ⁻⁴
Sand	King	30	17.9	8	2.1x10 ⁻⁵
	Presque Isle	30	18.2	9	3.5x10 ⁻⁴
Lawson		0	13.4	26	5.7x10 ⁻⁷
Markey	None	0	10.3	44	1.3x10 ⁻⁶
Theresa		0	15.3	19	1.1x10 ⁻⁶

collected and treated with the same protocol as the samples of column leach test effluent and batch test supernatant.

All samples were analyzed using ICP-OES at either CT Laboratories in Baraboo, WI or at the water chemistry laboratory at the University of Wisconsin-Madison (UW). CT laboratories used a Thermo Jarrell Ash ICAP 61E Trace Analyzer for ICP analysis. The UW laboratory was equipped with a Perkin Elmer Optima 4300 DV ICP-OES with an AS 90 Plus autosampler. Quality control measures used during ICP-OES analysis included calibration blanks every 10 to 20 analyses and calibration verification every 10 analyses. A reagent blank was tested every 20 samples and a spiked sample was analyzed every 10 samples. The limits of detection for the ICP analysis are in Table 10.

Table 10. Limit (Bar	ts of detection for ICP-OES pe aboo, WI), and at the University c	erformed at CT Laboratories of Wisconsin-Madison.
Element	CT Laboratories	UW-Madison
	Detection Limit (µg/L)	Detection Limit (µg/L)
Cd	0.7	0.2
Cr	1.7	1.0
Se	4.0	10
Ag	0.8	2.5

5. RESULTS

5.1 WATER LEACH TESTS

Thirty-three water leach tests (ASTM D 3987) were conducted on soils alone, soil-fly ash mixtures, and fly ashes alone. A summary of the mixtures that were tested is in Table 8. The soil-fly ash mixtures were prepared with fly ash contents of 20%, 30%, and 40%. The three fly ash contents for the mixtures were selected based upon unconfined compressive strength testing, which is described in Tastan (2005). Leachate from the water leach tests (WLTs) was analyzed for Cd, Cr, Se, and Ag as required by the Category 4 standards defined in NR 538.

5.1.1 Water Leach Tests on Fly Ashes Alone

Cd, Cr, Se, and Ag concentrations and leachate pH for all WLTs performed are NR 538 defines beneficial reuse applications for industrial shown in Table 11. byproducts in part based on WLTs performed on the byproduct alone. According to the NR 538 criteria, the Dewey, King, and Presque Isle fly ashes meet the Category 4 WLT requirements and can be used in confined geotechnical fill applications. Cd was not detected in the WLT on King fly ash, and Cd in the leachate from the WLTs on Dewey and Presque Isle fly ashes was more than 50 times lower than the requirement for Category 4 byproducts defined in NR 538 (Table 2). Cr concentrations between 12-60 μ g/L were found in the WLTs on the fly ashes, which are 8 to 38 times lower than the Category 4 requirement in NR 538. Se concentrations in the leachate from the WLTs on Dewey and King fly ashes were at least 7 times lower than the NR 538 requirement for Category 4 byproducts, and the Se concentration from the WLT on Presque Isle was still 34% lower than the NR 538 requirement for Category 4 byproducts. The Aq concentrations observed in the leachate from the WLTs on Dewey, King, and Presque

Soil	Fly Ash	Fly Ash Content (%)	Leachate pH	Metal Concentration (µg/L)			
3011				Cd	Cr	Se	Ag
Lawson	Dewey	20	9.9	0.8	2.8	30.6	ND
		30	10.0	ND	1.4	ND	ND
		40	10.2	ND	4.8	ND	ND
	King	20	11.3	ND	1.8	ND	ND
		30	11.0	0.9	7.3	11.5	ND
		40	11.2	ND	5.3	ND	ND
	PI	20	9.2	1.0	1.2	38.7	ND
		30	9.5	1.1	1.9	44.4	ND
		40	9.4	ND	1.2	ND	ND
	Dewey	20	8.2	ND	ND	20.8	ND
		30	8.6	ND	ND	26.5	ND
		40	8.6	ND	ND	ND	ND
	King	20	9.6	ND	1.1	ND	ND
Markey		30	10.0	0.4	27.9	21.9	ND
_		40	10.5	ND	3.9	ND	ND
	PI	20	8.5	ND	ND	18.4	ND
		30	9.2	ND	ND	30.4	ND
		40	8.9	ND	ND	12.0	ND
	Dewey	20	9.4	ND	ND	ND	ND
		30	10.2	ND	7.0	ND	ND
		40	9.7	ND	1.5	ND	ND
	King	20	11.3	ND	9.4	ND	ND
Theresa		30	11.6	0.3	50.4	23.7	ND
		40	11.4	ND	14.8	ND	ND
	PI	20	9.7	ND	ND	ND	ND
		30	10.1	ND	4.1	12.4	2.7
		40	9.9	ND	1.2	ND	ND
Lawson	None	0	8.0	ND	ND	ND	ND
Markey		0	8.2	ND	ND	ND	ND
Theresa		0	9.1	0.3	ND	17.6	ND
None	Dewey	100	10.7	0.4	12.8	22.8	6.6
	King	100	11.4	ND	59.9	31.5	3.6
	PI	100	11.9	0.5	16.5	165	ND
NR 538 Category 4		100	-	25	500	250	250

Table 11.	pH and concentrations of Cd, Cr, Se, and Ag from water leach tests on soils, fly
	ashes, and soil-fly ash mixtures.

ND: Not Detected.

Detection limits: 0.2 $\mu g/L$ for Cd, 1.0 $\mu g/L$ for Cr, 10 $\mu g/L$ for Se, and 2.5 $\mu g/L$ for Ag.

Isle fly ashes were at least 35 times lower than the 250 μ g/L requirement for Category 4 byproducts (NR 538).

None of the fly ashes consistently leached metals at higher concentrations compared to the other fly ashes. Dewey fly ash leached the highest concentration of Ag. King fly ash leached the most Cr, and Presque Isle leached the most Cd, and Se.

5.1.2 Water Leach Tests on Soils Alone

WLTs were conducted on the soils to define concentrations of Cd, Cr, Se, and Ag that would leach from the soils without any addition of fly ash. Results of these WLTs are summarized in Table 11.

Leachate from the WLTs on the soils alone contained lower concentrations of Cd, Cr, Se, and Ag compared with leachate from WLTs on the fly ashes alone. The only exception was the concentration of Cd in the leachate from the WLT on Theresa soil (0.3 μ g/L), which exceeded the concentration of Cd in the leachate from the WLT on King fly ash (below the detection limit of 0.2 μ g/L). Leachate from the WLTs on Lawson soil and Markey soil was below the detection limits for Cd, Cr, Se, and Ag. The leachate from the WLT on Theresa soil alone contained Cr and Ag below the detection limits, but contained 17.6 μ g/L of Se and 0.3 μ g/L of Cd. Both the Cd and Se concentrations found in the leachate from the WLT on Theresa soil alone were more than 14 times lower than the NR 538 requirements for Category 4 byproducts. However, the Se concentration is greater than the 10 μ g/L requirement for NR 538 Category 1 byproducts. If Theresa soil were an industrial byproduct, the Wisconsin DNR would need to approve the material before it could be used in unconfined geotechnical fill.

5.1.3 Water Leach Tests on Soil-Fly Ash Mixtures

WLTs were also performed on soil-fly ash mixtures to assess leaching that would occur in the actual application (i.e., a mixture). Results of these WLTs are also summarized in Table 11.

Cd concentrations were below detection limits (<0.2 μ g/L) in the leachate from the WLTs on 21 of the 27 mixtures. For the mixtures in which Cd was detected in the leachate, the Cd concentrations were still at least 20 times lower than the Category 4 limit of 25 μ g/L. Cr concentrations were below the detection limit (<1.0 μ g/L) in the leachate from 8 of the 27 WLTs on soil-fly ash mixtures. The WLT on Theresa soil mixed with 30% King fly ash had the highest total Cr concentration at 50.4 μ g/L, which was still more than 9 times lower than Category 4 requirements (500 μ g/L). The Cr concentrations found in the leachate from the WLTs on soil-fly ash mixtures were all lower than the concentrations from the WLTs on the respective fly ashes.

Se concentrations were above the detection limits in the leachate from 12 of the 27 WLTs on the soil-fly ash mixtures. The highest Se concentration observed in the leachate from the WLTs on soil-fly ash mixtures came from the mixture of Lawson soil and 30% Presque Isle fly ash (44.4 μ g/L). This concentration is still 5.7 times lower than the NR 538 requirement for Category 4 byproducts. Ag was only above the detection limit (<2.5 μ g/L) in the leachate from one of the WLTs on soil-fly ash mixtures, Theresa soil mixed with 30% Presque Isle fly ash. Silver was not detected in the leachate from WLTs on Theresa soil alone or Presque Isle fly ash alone.

The Cd, Cr, Se, and Ag concentrations in the leachate from WLTs on the soil-fly ash mixtures tended to be higher than the concentrations from the WLTs on soils alone and lower than in the leachate from the WLTs on fly ashes alone. The data were analyzed to find out if the lower concentrations found in the leachate from the WLTs on soil-fly ash mixtures were the result of dilution compared to the WLTs on fly ash alone. Diluted concentrations were calculated based on the concentrations from the WLTs on the soil alone and the fly ash alone weighted according to their respective proportions in the mixture. Graphs of observed concentrations vs. diluted concentrations are in Fig. 5. There is not trend in these graphs. The observed concentrations are as likely to be higher than the diluted concentrations as they are likely to be lower than the diluted concentrations.

Bin Shafique et al. (2002) compared the concentrations observed in the leachate from WLTs on soils, fly ashes, and soil-fly ash mixtures to "normalized" concentrations. The normalized concentrations were computed as the difference between the concentration from the WLT on the soil-fly ash mixture and the concentration from the soil alone, divided by the concentration from the WLT on the fly ash alone. Bin Shafique et al. (2002) found that the normalized concentration increased with increasing fly ash content, but the rate of increase diminished as the fly ash content increased. They concluded that the relationship between normalized concentration and fly ash content was not linear because the pH of leachate from the WLTs on fly ashes and soilfly ash mixtures increases with increasing fly ash content, affecting the partitioning of metals in the leachate. The normalized concentrations for the current study are not presented because the normalized concentrations are either zero or undefined (i.e. concentration from WLT on fly ash alone equals zero) for 70% of the cases (33 of 108).

5.1.4 Relationship Between pH and Metal Leaching in WLTs

The relationship between leachate pH and fly ash content from the WLTs is shown in Fig. 6. The leachate pH is higher for the soil-fly ash mixtures compared to the soils alone, but is relatively insensitive to the fly ash content (Markey soil mixed with King fly ash being an exception, showing increased pH at increased fly ash content).



Fig. 5. Comparison of WLT leachate concentrations and diluted concentrations of (a) Cd, (b) Cr, (c) Se, and (d) Ag.



Fig. 6. Leachate pH from water leach tests on soil-fly ash mixtures containing (a) Dewey fly ash, (b) King Fly ash, and (c) Presque Isle fly ash.

The pH of WLT leachate from mixtures prepared with Markey soil was always lower than mixtures prepared with Theresa soil for any given fly ash type and fly ash content, with Lawson generally falling in the middle. Markey soil also had a lower paste pH (ASTM D 4318) than both Lawson soil and Theresa soil (pH 6.3 v. 6.9 and 7.1, respectively). Markey soil (LOI of 27%) has a higher organic content than Lawson soil (LOI of 5%) and Theresa soil (LOI of 6%), so the lower paste pH and WLT leachate pH for Markey soil may be due to larger quantities of organic acids present in the Markey soil.

pH of leachate from the WLTs on the fly ashes alone was highest for King fly ash and lowest for Dewey fly ash. Separate pH tests were also performed on fly ash-water pastes using a solid-solution ratio of 1:4. Presque Isle fly ash had the highest paste pH at 11.3, followed by King fly ash at 10.9, and Dewey fly ash with a paste pH of 9.9. Although Presque Isle had the highest paste pH, leachate from the King fly ash WLT had the highest pH. This was likely due to a higher buffering capacity of King fly ash, which had the highest CaO content (25.8%) compared to Presque Isle fly ash, which had the lowest CaO content (3.2%, Table 5). The WLT pH and paste pH for each fly ash were different because the two tests were performed at different solid-solution ratios (1:20 for the WLTs, 1:4 for the paste pH).

The relationship between metals concentrations and leachate pH from the WLTs is shown in Figs. 7 and 8. Concentrations below the detection limits were omitted from the graphs. The Cr concentration increases with increasing pH (Fig. 7b). No trends were observed in the plots of Cd, Se, and Ag versus pH, although most of the Ag concentrations were below the detection limits. Theis and Wirth (1977) found that desorption of Cd and Cr from fly ash into solution *decreased* with increasing pH. There are possible explanations for the conflicting observations between Theis and Wirth (1977) and the current study. The points in Fig. 7b with the highest concentration and



Fig. 7. Relationship between concentrations of (a) Cd and (b) Cr and leachate pH from water leach tests on mixtures containing Dewey, King, and Presque Isle fly ashes.



Fig. 8. Relationship between concentrations of (a) Se and (b) Ag and leachate pH from water leach tests on mixtures containing Dewey, King, and Presque Isle fly ashes.

highest pH are from the WLTs on King fly ash. The WLTs on Dewey fly ash and Presque Isle fly ash have lower Cr concentrations, and lower pH. The combination of the high Cr concentration and high pH may be a result of the properties of the King fly ash. The WLT on King fly ash alone produced leachate with the highest Cr concentration in the study, and King fly ash also had the highest CaO content, contributing to the high pH. Contrary to the results of Theis and Wirth (1977), Brookings (1988) produced Pourbaix (Eh-pH) diagrams for the Cr-O-H system that show Cr may form oxyanions (CrO_4^{-2}) at the pH present in the WLTs (pH 7-11). Although the Pourbaix diagrams are simplified compared to the conditions present in the WLTs, anionic Cr is more mobile than cationic Cr (Cr^{+3} , $CrOH^{+2}$, etc), and less likely to be adsorbed onto the soil or fly ash particles. Another possibility is that the SiO₂ in the fly ash may have dissolved at the higher pHs, and the metals that were encapsulated within the fly ash particles were released. Stumm and Morgan (1996) report that the solubility of SiO₂ increases above pH 9.

5.1.5 Relationship between Soil Properties and Metals Leaching in WLTs

The soils used in this study were selected to represent a range of organic soils found in Wisconsin. LOI and PI were identified as two soil properties with the potential to influence leaching of metals from soil-fly ash mixtures. LOI is a measure of the organic content of the soil. Organic carbon may retard metal mobility by providing sorption sites, but organic acids may increase metal mobility because many metals have increased solubility under acidic conditions. PI is a measure of the clay content and clay type, both of which affect the number of sorption sites.

The relationship between WLT concentration and LOI is shown in Fig. 9, and the relationship between WLT concentration and PI is in Fig. 10. While the concentrations from the WLTs on soils alone tended to be lower than the concentrations from the soil-fly



Fig. 9. Relationship between concentrations of (a) cadmium, (b) chromium, (c) selenium, and (d) silver from water leach test and soil loss on ignition.



Fig. 10. Relationship between concentrations of (a) cadmium, (b) chromium, (c) selenium, and (d) silver from water leach test and soil plasticity index.

ash mixtures (Table 11), there were no consistent trends between the WLT concentrations from soil-fly ash mixtures and soil LOI (Fig. 9) or PI (Fig. 10). The Se concentrations shown in Fig. 9 tended to be higher for CLTs on soils with lower LOI, but the data are too variable to develop a significant relationship between LOI and metals concentrations.

5.1.6 Comparison With Results From Bin Shafique et al. (2002)

Bin Shafique et al. (2002) performed WLTs on the Dewey and King fly ashes. A comparison of concentrations and pHs from Bin Shafique et al. (2002) and the current study is shown in Table 12. The Cr and Se concentrations reported by Bin Shafique et al. (2002) are between 1.3 and 4.6 times higher than those measured in the current study. The concentrations of Cd were less than 5 μ g/L for both studies, but those reported by Bin Shafique et al. (2002) were consistently higher. The Ag concentrations were within 20% for both studies. The variation between the concentrations found by Bin Shafique et al. (2002) and the current study are likely because the ashes tested were from different batches. However, even though there were variations between the leachate concentrations reported by Bin Shafique et al. (2002) and the Shafique et al. (2002) and those measured in the current study, the concentrations measured in both studies were below NR 538 regulatory limits for Category 4 byproducts.

5.2 COLUMN LEACH TESTS

Fifteen column leach tests were performed using 3 soils and 3 fly ashes, as summarized in Table 9. Column leach tests (CLTs) were performed on mixtures of soil and fly ash to provide a better representation of the flow-through condition existing in the field. CLTs were also conducted on soils alone (no fly ash added) to provide a baseline for comparison with the soil-fly ash mixtures. Fly ash-sand mixtures were also tested to

Table 12.pH and Cd, Cr, Se, Ag concentrations for leachate from WLTs performed by Bin
Shafique et al. (2002) and in the current study.

Leachate	Bin Shafique	et al. (2002)	Current Study		
Concentration	Dewey Fly Ash	King Fly Ash	Dewey Fly Ash	King Fly Ash	
Cadmium (µg/L)	3.2	1.7	0.4	ND	
Chromium (µg/L)	59.0	123.2	12.8	59.9	
Selenium (µg/L)	82.0	41.0	22.8	31.5	
Silver (µg/L)	6.2	4.5	6.6	3.6	
рН	10.5	11.5	10.7	11.4	

simulate soil-fly ash mixtures with minimal adsorption onto the soil solids. Effluent from the CLTs was analyzed for Cd, Cr, Se, and Ag, i.e., the same elements considered in the WLTs.

5.2.1 Elution Curves

Typical elution curves from two CLTs are shown in Fig. 11. Elution curves for all of the tests that were conducted are included in Appendix 6. The curves in Fig. 11 exhibit the two leaching patterns observed during the study: first-flush and lagged-response.

The first-flush pattern is shown in Fig. 11a for Cr leached from sand mixed with 30% King fly ash. The concentration decreases monotonically with increasing pore volumes of flow (PVF). Because approximately 0.1 pore volumes were required to perform the metals analysis, none of the samples exactly represent the initial first-flush effluent concentration (i.e. PVF=0). Tests that had the highest concentration in the first sample collected were considered to follow the first-flush leaching pattern. The first-flush leaching pattern was observed for 16 tests.

The "lagged response" pattern is shown in Fig. 11b for Se leachate from the Theresa soil-Presque Isle fly ash mixture. The Se concentration initially is below detection limits (<4.0 μ g/L), and then steadily increases to above 115 μ g/L. After reaching the peak concentration near 1.5 PVF, the concentration steadily drops, falling below the detection limit again after 5 PVF. Fifteen of the elution curves displayed the lagged response pattern.

Approximately half (29 of 60) of the elution curves did not fit the first-flush or lagged-response leaching patterns, because the concentrations were below detection limits for the entire test (12 tests), or because too few data points were above detection limits to characterize a leaching pattern (17 tests). These cases with inconclusive



Fig. 11. Typical patterns observed in elution curves from column leach tests: (a) first-flush, and (b) lagged response.

leaching patterns are considered to have minimal impact on groundwater, because for all analysis the detection limits were at least 5 times below USEPA MCLs.

The CLT data are summarized in Tables 13 and 14 in terms of peak concentration, pH at peak concentration, PVF to reach peak concentration, and type of leaching pattern. A box plot showing the PVF to the peak concentrations for Cd, Cr, Se, and Ag is shown in Fig. 12. Ag reached a peak concentration after 2.7 pore volumes of flow on average, and Cd (average 1.2 PVF), Cr (1.6 PVF) and Se (1.1 PVF) tended to reach peak concentrations within the first 2 pore volumes of flow.

Leaching patterns observed from the CLTs are summarized in Table 15 with respect to soil, fly ash, and element. Table 15 shows the number of times each pattern was observed for CLTs containing Markey soil, Lawson soil, Theresa soil, and sand. Each soil had approximately the same number of cases with first-flush leaching as lagged-response. CLTs containing Lawson soil had more cases (11) in which the elution pattern was inconclusive compared with the CLTs containing Markey soil (7), Theresa soil (6), and Sand (5). This indicates that there may be increased sorption of metals onto Lawson soil (which had the highest PI) compared to the other soils.

Table 15 also shows the number of times each leaching pattern was observed from CLTs containing Dewey fly ash, King fly ash, Presque Isle fly ash, and no fly ash (soils alone). The CLTs containing Dewey fly ash and the CLTs on the soils alone were equally likely to have first-flush or lagged-response leaching patterns. The CLTs containing King fly ash were more likely to show first-flush leaching (7 cases) compared to lagged-response (2 cases). None of the CLTs containing Presque Isle fly ash had first-flush leaching patterns for any of the metals studied. Presque Isle has the lowest CaO content and King has the highest CaO content, suggesting that leaching behavior may be influenced by the CaO content (i.e. first-flush leaching behavior is more likely from CLTs on fly ashes with higher CaO content). A second possible explanation of this
	10313.									
				Cd		Ag				
Soil	Fly Ash	Peak Conc (μg/L)	PVF to Peak	pH at Peak	Leaching Pattern	Peak Conc (μg/L)	PVF to Peak	pH at Peak	Leaching Pattern	
	None	0.42	0.2	8	FF	3.2	0.9	7.4	LAG	
	Dewey	ND	-	-	INC	2.4	0.1	7.7	INC	
Lawson	King	ND	-	-	INC	ND	-	-	INC	
	Presque Isle	0.85	1	7.7	INC	61.7	1.4	7.7	LAG	
	None	4	0.23	7	FF	1.7	3.2	8.2	INC	
	Dewey	0.66	1.4	8.3	INC	8.6	1.2	8.1	LAG	
Markey	King	1.7	0.5	8.1	FF	ND	-	-	INC	
	Presque Isle	ND	-	-	INC	2.3	3.5	7.5	INC	
	None	29.2	1.3	8.4	LAG	17.7	0.1	8.4	FF	
	Dewey	1.5	0.24	8.8	INC	7.1	4.4	7.6	LAG	
Theresa	King	0.41	4.3	7.1	INC	6.1	1.7	7.4	INC	
	Presque Isle	ND	-	-	INC	24	6.4	7.9	LAG	
	Dewey	ND	-	-	INC	22.6	6.5	10.3	LAG	
Sand	King	ND	-	-	INC	2.4	3.9	10.9	INC	
Cana	Presque Isle	ND	-	-	INC	3	1.2	7.8	INC	

Table 13. Peak effluent concentrations of Cd and Ag, pH at the peak concentration, and the number of pore volumes of flow to reach the peak concentration for column leach tests.

ND: Not Detected.

FF: First-flush leaching pattern.

LAG: Lagged-response leaching pattern.

INC: Inconclusive leaching pattern.

Detection limits: 0.4 μ g/L for Cd, and 0.8 μ g/L for Ag.

NR 140 limits: 5 μ g/L for Cd, and 50 μ g/L for Ag.

Table 14. Peak effluent concentrations of Cr and Se, pH at the peak concentration, and the number of pore volumes of flow to reach the peak concentration for column leach tests.

	10313.									
	Fly Ash			Cr		Se				
Soil		Peak Conc (μg/L)	PVF to Peak	pH at Peak	Leaching Pattern	Peak Conc (μg/L)	PVF to Peak	pH at Peak	Leaching Pattern	
	None	ND	-	-	INC	6.1	2	7.3	INC	
	Dewey	3.1	0.1	7.7	INC	6.1	0.3	7.8	INC	
Lawson	King	3.1	0.2	8.3	FF	734	0.3	6.5	LAG	
	Presque Isle	660	4.1	7.8	INC	213	4.1	7.8	INC	
	None	2.9	5.24	8.1	INC	67.2	4	8.1	LAG	
	Dewey	23.6	0.2	8.1	FF	162	0.1	7.9	FF	
Markey	King	3.2	0.5	8.1	FF	135	1.2	7.4	LAG	
	Presque Isle	ND	-	-	INC	140	0.4	8.3	LAG	
	None	3.1	7.4	8.2	INC	29.3	0.4	8.6	FF	
	Dewey	123	0.24	8.8	FF	81.1	0.53	8.9	LAG	
Theresa	King	470	0.4	7.5	FF	836	0.4	7.5	FF	
	Presque Isle	ND	-	-	INC	113	1	8.4	LAG	
	Dewey	295	0.3	10.6	FF	133	0.3	10.6	FF	
Sand	King	5590	0.4	11.1	FF	2760	0.4	11.1	FF	
Cana	Presque Isle	63	0.35	8	LAG	145	0.35	8	LAG	

ND: Not Detected.

FF: First-flush leaching pattern.

LAG: Lagged-response leaching pattern.

INC: Inconclusive leaching pattern.

Detection limits: 1.7 μ g/L for Cr, and 4.0 μ g/L for Se.

NR 140 limits: 100 μ g/L for Cr, and 50 μ g/L for Se.

Leaching		S	oil						
Pattern	Lawson	Markey	Theresa	Sand					
First-Flush	2	5	5	4					
Lagged- Response	3	4	5	3					
Inconclusive	11	7	6	5					
Loophing		Fly Ash							
Pattern	Dewey	King	Presque Isle	None					
First-Flush	5	7	0	4					
Lagged- Response	4	2	6	3					
Inconclusive	7	7	10	5					
Leaching		Eler	nent						
Pattern	Cd	Cr	Se	Ag					
First-Flush	3	7	5	1					
Lagged- Response	1	1	7	6					
Inconclusive	11	7	3	8					

Table 15.Number of occurrences of first-flush, lagged-response,
and inconclusive leaching patterns from CLTs based on
soil, fly ash, and element.



Fig. 12. Comparison of the number of pore volumes of flow to reach peak concentration in CLT effluent for Cd, Cr, Se, and Ag.

is that the metals in the Presque Isle fly ash may have been encapsulated, only to be released after dissolution of the SiO_2 (Presque Isle has the highest SiO_2 content of the ashes studied). However, no testing was conducted to investigate the surface chemistry or the total elemental composition of the materials studied, and the peak concentrations from the CLTs containing Presque Isle fly ash tended to occur near pH 8, and SiO_2 is relatively insoluble at pH <9 (Stumm and Morgan 1996).

A summary of the leaching patterns observed for Cd, Cr, Se, and Ag is in Table 15. Evaluation of the leaching patterns by element indicates that Cd is released at low levels, if at all. When Cd is released, the leaching tended to follow the first-flush pattern. Cr typically followed first-flush leaching, Ag typically showed lagged-response leaching, and Se was equally split between first-flush and lagged-response leaching patterns.

Cd was below the detection limits for all samples from 7 CLTs. For the CLTs in which Cd was detected in the effluent, Cd showed a first-flush leaching pattern in 3 tests, a lagged-response pattern in one CLT, and in 4 tests too few samples showed detectable Cd concentrations to reach a conclusion on the leaching pattern. No total elemental analysis was performed on the soils or fly ashes, but it is possible that leaching behavior of Cd is due to low Cd content in the materials studied rather than release mechanisms. Brookins (1988) provides a Pourbaix diagram for the Cd-C-S-O-H system. Although simplified compared to the actual condition, the diagram shows that Cd is likely to occur as CdCO₃, CdS, or Cd(OH)₂ for the pH ranges found in the CLTs. All of these forms are relatively immobile, providing a possible explanation for the low Cd concentrations.

Seven CLTs showed first-flush leaching patterns for Cr. One CLT showed a lagged-response for Cr, and 4 CLTs had too few data points above the detection limits to characterize the leaching pattern. The effluent was below the detection limits for all samples collected from 3 column leach tests. The high initial Cr concentration present for 7 CLTs may be attributed to the mobile anions that Cr forms in the +6 oxidation state.

Brookins (1988) provides Pourbaix diagrams for the Cr-O-H system that indicate that Cr is likely to exist as Cr_2O_3 , or CrO_4^{-2} for the pH conditions present in the CLTs. Negatively charged ions are not readily sorbed by negatively charged clay particles. No testing was conducted to identify the oxidation state of Cr or the Cr speciation in the leachate.

The leaching pattern for Se was evenly split between first-flush response (5 CLTs) and lagged-response (7 CLTs). Three CLTs had too few data points above the detection limits to classify the leaching pattern. Se can exist in several oxidation states in groundwater, and form complexes such as Se(s), HSe⁻, SeO₃⁻², HSeO₃⁻, and SeO₄⁻² in pH conditions found in the CLTs (Brookins 1988). The range of complexes from solid to oxyanions may explain the lack of a trend in leaching patterns for Se.

Ag was most likely to show lagged-response leaching. Ag showed a first-flush leaching pattern for one CLT. For two CLTs the Ag concentration was below the detection limit for the entire test. Six of the CLTs showed a lagged-response leaching pattern and 6 of the CLTs had too few data points above the detection limit to characterize the leaching pattern. Four of the CLTs with too few data points to characterize a leaching pattern had between 1-3 data points above the detection limit at 1.5-3 PVF. These CLTs appear to have had a lagged-response leaching pattern for Ag, but too few data points were collected to capture the entire profile. According to the Pourbaix diagram for the Ag-Cl-S-O-H system presented in Brookins (1988), Ag is likely to be present as Ag(s), Ag⁺, or AgCl₂⁻. Although the conditions present in the CLTs are more complex than those presented by Brookins (1988), Ag(s) and Ag⁺² are relatively immobile. The presence of these species would explain the consistent lagged-response leaching patterns.

The first-flush and lagged-response leaching patterns are similar to patterns reported by Creek and Shackelford (1992) and Edil et al. (1992) for tests on compacted fly ash. Bin-Shafique et al. (2002) also observed the first-flush pattern for leaching of Cd, Cr, Ag, and Se from soil-fly ash mixtures prepared with inorganic clays and sand. Creek and

Shackelford (1992) observed specific leaching patterns for specific elements from CLTs on fly ash alone. They concluded that the first-flush pattern was typical of elements with higher charge density (including Cd and Cr), and the lagged-response pattern was typical of elements with lower charge densities such as Ba, Ca, and Sr. The results of the current study fit with the conclusions of Creek and Shackelford (1992) for Cr, but differ for Cd. Creek and Shackelford (1992) did not present results for Ag or Se. Edil et al. (1992) observed first-flush and lagged-response leaching patterns from CLTs conducted on fly ash alone, and fly ash/sand mixtures. Edil et al. (1992) concluded that the leaching behavior is due to changes in solubility with changes in pH and alkalinity.

5.2.2 Comparison Between Peak CLT Concentrations and Regulatory Limits

The peak effluent concentration, the pH at peak concentration, the PVF to reach the peak concentration, and the leaching pattern for each CLT are shown in Tables 13 and 14 along with Wisconsin regulatory standards. The peak Cd concentrations are consistently below the groundwater quality requirements specified in Section NR 140 of Wisconsin Administrative Code and the Category 4 requirements of NR 538. The only CLT that produced leachate with Cd concentrations exceeding the NR 140 standard was the CLT on Theresa soil alone. The peak Cd concentration from the CLT on Theresa soil alone. The peak Cd concentration in the leachate dropped below the NR 140 requirements after 1.3 PVF.

The peak Cr concentration found in the leachate from 5 of the 15 CLTs exceeded the NR 140 limit of 100 μ g/L. Two of the CLTs had peak concentrations that exceeded the NR 538 Category 4 limit of 500 μ g/L. In 2 of the CLTs that had Cr concentrations exceeding the NR 140 limit, the peak concentration was the only sample above detection limits. The other 3 CLTs with Cr concentrations in the leachate above the NR 140 limit had

first-flush elution patterns, and all had effluent concentrations stabilize below the NR 140 limit within 3 PVF.

The peak Se concentration in leachate from 12 of 15 of the CLTs exceeded the NR 140 limit of 50 μ g/L. Only two CLTs had leachate that exceeded the NR 538 Category 4 limit of 250 μ g/L. The Se concentrations dropped below the NR 140 limit within 2 PVF for the leachate from 10 of the 15 CLTs.

The Wisconsin groundwater standard for Ag (50 μ g/L) was only exceeded in the leachate from one of the CLTs (Lawson soil mixed with 30% Presque Isle fly ash). The peak concentration in the leachate from the CLT on Lawson soil mixed with 30% Presque Isle fly ash was 61.7 μ g/L, which occurred after 1.4 PVF. This peak concentration was the only sample collected from the CLTs that exceeded the NR 140 limits. None of the leachate samples collected from the CLTs exceeded the Category 4 limits of NR 538.

5.2.3 Comparison of Results from CLTs on Soils alone and Soil-Fly Ash Mixtures

Comparison of the data in Tables 13 and 14 for soil-fly ash mixtures and soils alone shows that Cd concentrations from CLTs on soil-fly ash mixtures were lower than concentrations from soils alone (except for the CLT on Lawson soil mixed with 30% Presque Isle fly ash). In contrast, Cr concentrations from CLTs on mixtures of soil and fly ash were higher for all cases compared with soils alone (except Markey soil mixed with 30% King fly ash, and Theresa soil mixed with 30% Presque Isle fly ash). For example, the maximum Cr concentration in the leachate from the CLT on Lawson soil alone was below the detection limit of 1.7 μ g/L, compared with concentrations of 3.1 μ g/L for the mixture of Markey soil with 30% Dewey fly ash, 3.1 μ g/L for the mixture of Markey soil and 30% King fly ash, and 660 μ g/L for the mixture of Markey soil with 30% Presque Isle fly ash. Se concentrations in the leachate from CLTs on soil-fly ash mixtures were always higher than

from CLTs on soils alone. The peak Ag concentration in the leachate from 5 of the 9 CLTs on soil-fly ash mixtures was lower than the peak concentration observed from the CLTs on the soils alone.

There were few similarities between the elution curves for CLTs on soils alone and soil-fly ash mixtures. One exception are the Se elution curves from the CLTs on Theresa soil alone, sand mixed with 30% King fly ash, and Theresa soil mixed with 30% King fly ash shown in Fig. 13. Similar figures for the other combinations studied are included in Appendix 7. The elution patterns are similar for the CLTs on sand mixed with 30% King fly ash and Theresa mixed with 30% King fly ash. The Se concentrations from the CLT on Theresa soil mixed with 30% King fly ash are consistently lower than the Se concentrations from the CLT on sand mixed with 30% King fly ash. This suggests that Se release is reduced due to sorption onto the fine-grained particles of the Theresa soil compared to the sand. Additionally, the lower peak concentrations from the soil-fly ash mixtures compared to the sand-fly ash mixtures suggests that Cr release is also reduced due to sorption onto solids in the finer-textured soils. The one exception is the Cr concentration from the CLT on Lawson soil mixed with 30% Presque Isle fly ash (Cr = 660 μ g/L), which exceeded the concentrations from the CLT on sand mixed with Presque Isle fly ash (Cr = 63 μ g/L).

5.2.4 Comparison With Bin Shafique et al. (2002)

Two of the fly ashes used in the current study (Dewey and King) were also used by Bin Shafique et al. (2002). They also performed CLTs on sand mixed with 20% fly ash. A comparison is shown in Table 16 between the peak Cd, Cr, Se, and Ag



Fig. 13. Selenium elution curves from CLTs on Theresa soil, Theresa soil mixed with 30% King fly ash, and sand mixed with 30% King fly ash.

Table 16.Comparison of peak effluent concentrations from CLTs performed on sand-Dewey
and sand-King mixtures by Bin Shafique et al. (2002) and the current study.

	Peak Column Leach Test Effluent Concentration (µg/L)							
Metal	Bin Shafique	et al. (2002)	Current Study					
	Sand + 20% Dewey	Sand + 20% King	Sand + 30% Dewey	Sand + 30% King				
Cadmium	42	21	<0.4	<0.4				
Chromium	300	700	295	5590				
Selenium	300	180	133	2760				
Silver	75	42	22.6	2.4				

concentrations from CLTs on the sand-fly ash mixtures by Bin Shafique et al. (2002) and similar tests performed on sand mixed with 30% fly ash as part of the current study. The peak Cd, Cr, Se, and Ag concentrations from the CLT on sand mixed with 20% Dewey fly ash performed by Bin Shafique et al. (2002) are comparable or higher than the concentrations from the CLT on sand mixed with 30% Dewey fly ash from the current study. The peak Cd and Ag concentrations from the CLT on sand mixed with 20% King fly ash were higher than the concentrations from the CLT on sand mixed with 30% King fly ash. The CLT on sand mixed with 30% King fly ash produced leachate with higher Cr and Se concentrations. The leaching followed the first flush behavior in all cases. The CLTs on sand mixed with 30% Dewey fly ash and sand mixed with 30% King fly ash showed firstflush leaching patterns for Cr and Se and Cd was below the detection limits. The Ag profile from the CLT on sand mixed with 30% Dewey fly ash showed a lagged response, but too few samples were above the detection limit to characterize the leaching pattern from the CLT on sand mixed with 30% King fly ash. The reason for these differences is not known, but the most likely cause is that different batches of fly ash were used in this study than in Bin Shafique et al. (2002).

5.3 Comparison Between WLT and CLT CONCENTRATIONS

The relationship between peak concentrations from the CLTs and the concentrations from the WLTs is shown in Fig. 14. Points below the detection limits were omitted from the graphs. The concentrations found in the leachate from the CLTs are between 0.1 to 1000 times greater than the concentrations from the WLTs.

Bin Shafique et al. (2006) found that concentrations from WLTs on soil-fly ash mixtures could be multiplied by a scaling factor (50 for Cd and Ag, 10 for Cr and Se) to



Fig. 14. Comparison of peak effluent concentrations of (a) Cd and Ag, and (b) Cr and Se from the CLTs and the WLT concentrations.

conservatively estimate the initial effluent concentration for CLTs on mixtures of inorganic soils and fly ash that exhibited the first-flush elution pattern. However, the scaling factors found by Bin Shafique et al. (2002) did not provide a conservative estimate for all peak CLT concentrations in the current study of organic soils stabilized with high carbon fly ashes. The scaling factors were not conservative for estimating the peak CLT concentrations of Cd from one test, Cr for 4 tests, and Se for 2 tests. A scaling factor of 50 provides a conservative estimate of the peak Cd, Cr, Se, and Ag CLT concentrations for 23 of the 27 cases in the current study (23 cases had concentrations from the WLTs or CLTs below detection limits). A standard scaling factor of 50 is more appropriate for estimating maximum concentrations of Cd, Cr, Se and Ag from CLTs on organic soils mixed with high carbon fly ash compared with the scaling factors reported in Bin Shafique et al. (2002).

5.4 Implications for groundwater quality

CLT concentrations represent concentrations reaching groundwater only if the groundwater table is at the base of the pavement profile. In many roadways, the groundwater table will be deeper. Processes such as sorption, diffusion, dispersion, and dilution occurring in soils between the base of the pavement and the groundwater table will result in lower concentrations by the time the groundwater table is reached.

Bin Shafique et al. (2002) conducted a modeling study to simulate the leaching of contaminants from pavement layers constructed with byproducts and transport to the groundwater table using a variably saturated model of flow and transport. The model was validated using data from field lysimeter studies. Their findings indicate that the maximum relative concentration decreases with increasing depth to the groundwater table. In particular, the maximum concentration 1 m below the byproduct layer typically is 20% of the peak concentration at base of the byproduct layer and 10% of the peak concentration 5 m below the byproduct layer.

Estimated concentrations at the groundwater table obtained by applying these factors to the peak CLT concentrations are in Table 17, along with Wisconsin groundwater standards (NR 140). With the exception of the estimated Se concentrations from the CLTs on Lawson soil mixed with 30% King fly ash and Theresa soil mixed with 30% Presque Isle fly ash, and Cr concentration from the CLT on Lawson soil mixed with 30% Presque Isle fly ash, the estimated concentrations 1 m from the organic soil-high carbon fly ash mixtures are below Wisconsin groundwater standards.

			Cd			Cr		Se			Ag		
Soil	Fly Ash	Peak CLT	Est. Conc.	Est. Conc.	Peak CLT	Est. Conc.	Est. Conc.	Peak CLT	Est. Conc.	Est. Conc.	Peak CLT	Est. Conc.	Est. Conc.
	-	Conc.	at 1 m	at 5 m	Conc.	at 1 m	at 5 m	Conc.	at 1 m	at 5 m	Conc.	at 1 m	at 5 m
		(μg/L)	(µg/L)	(µg/L)	(mg/L)	(mg/L)	(mg/L)	(μg/L)	(µg/L)	(µg/L)	(μ g/L)	(µg/L)	(µg/L)
	Dewey	ND	-	-	3.1	0.6	0.3	6.1	1.2	0.6	2.4	0.5	0.2
Lawson	King	ND	-	-	3.1	0.6	0.3	734	146.8	73.4	ND	-	-
Lawson	Presque Isle	0.85	0.2	0.1	660	132	66	213	42.6	21.3	61.7	12.3	6.2
	Dewey	0.66	0.1	0.1	23.6	4.7	2.4	162	32.4	16.2	8.6	1.7	0.9
Markey	King	1.7	0.3	0.2	3.2	0.6	0.3	135	27	13.5	ND	-	-
Markey	Presque Isle	ND	-	-	ND	-	-	140	28	14	2.3	0.5	0.2
	Dewey	1.5	0.3	0.2	123	24.6	12.3	81.1	16.2	8.11	7.1	1.4	0.7
Theresa	King	0.41	0.1	0.0	470	94	47	836	167.2	83.6	6.1	1.2	0.6
meresa	Presque Isle	ND	-	-	ND	-	-	113	22.6	11.3	24	4.8	2.4
NR 1	40 Limits		5			100			50			50	

Table 17. Peak concentrations observed from CLTs and estimated concentrations after 1 m and 5 m of migration from a fly-ashstabilized soil layer based on Bin Shafique et al. (2002).

6. SUMMARY AND CONCLUSIONS

The objective of this study was to investigate leaching of Cd, Cr, Se, and Ag from soft organic soils stabilized with high carbon fly ashes. The investigation was composed of two groups of tests: water leach tests (WLTs) and column leach tests (CLTs). Tests were performed on three soils and three fly ashes. The soils represent typical organic clay and peat in Wisconsin. The three fly ashes are representative of high carbon fly ashes in Wisconsin, and have carbon contents greater than 6%.

The Cd, Cr, Se, and Ag concentrations in the leachate from the WLTs on the soilfly ash mixtures were higher than the concentrations found in the WLTs on the soils alone, but lower than the WLTs on fly ash alone. The lower concentrations in the leachate from the WLTs on soil-fly ash mixtures were not due to lower fly ash content (i.e. dilution), suggesting that metals release is reduced due to sorption onto fine-grained soil particles.

Leachate from the WLTs showed a trend of increasing Cr concentrations with increasing leachate pH. This trend is the opposite of the results reported by Theis and Wirth (1977), who found increased Cr desorption with decreasing leachate pH. The increasing Cr concentration with increasing pH suggests that Cr^{+6} is present, forming mobile oxyanions.

Comparison of concentrations from the WLTs and CLTs showed that the applying a scaling factor of 50 to the WLT concentrations generally provides a conservative estimate of the peak concentrations for the CLTs. This agrees with the scaling factor for Cd and Ag presented by Bin Shafique et al. (2006), but is 5 times higher than the scaling factor they reported for Cr and Se.

Two leaching patterns were observed in the effluent from the CLTs: first-flush, and lagged-response. The first-flush leaching pattern was observed for 16 tests, and 15 of the elution curves displayed the lagged-response pattern. Nearly half (29 of 60) of the cases had inconclusive leaching patterns because concentrations were consistently below the detection limits. These cases pose low risk to groundwater, because the detection limits of the analysis were at least 10 times lower than the USEPA MCLs. No relationship was found between leaching pattern and soil type (except Lawson soil tended to show inconclusive leaching patterns). However, trends were found between leaching patterns and both fly ash and element. The first-flush leaching behavior was more likely to occur from CLTs on fly ash with higher CaO content. Cr was likely to follow the first-flush leaching pattern, and Ag was likely to show lagged-response behavior. Cd was generally present at lower concentrations, showing inconclusive leaching patterns. The leaching patterns can be explained by the complexation as shown in Pourbaix diagrams from Brookins (1988). Further study is needed to better understand the conditions present in the CLTs, and identify the specific complexes present.

Comparison of concentrations from the CLTs on the soil-fly ash mixtures prepared with organic soils and those prepared with sand indicates that release of metals from soil-fly ash mixtures was reduced by adsorption onto the solids in the finertextured organic soils.

Leachate from CLTs on the soil-fly ash mixtures had Cr, Se, and Ag concentrations above Wisconsin groundwater standards. However, fly ash-stabilized soils are usually placed above the groundwater table. Bin Shafique et al. (2002) report as a rule of thumb that the maximum concentration 1 m below the byproduct layer will be 20% of the peak concentration observed in the pore fluid in the byproduct layer. Following this assumption, using high-carbon fly ash to stabilized organic soils more than 1 m above the water table should present a low risk of groundwater contamination.

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7. ACKNOWLEDGEMENTS

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ANALYTICAL METHODS SUMMARY

			1	MB concenti	ations mg/L	-			
	Ag	Ag	Cd	Cd	Cr	Cr	Se	Se	
Sample #	328.068	338.289	214.440	228.802	205.560	267.716	196.026	203.985	_
1	1.209	-0.494	-0.499	-0.047	-0.908	0.128	6.723	3.397	
2	0.936	-0.489	-0.534	-0.069	-0.956	-0.005	4.499	-1.261	
3	0.753	-1.269	-0.670	-0.171	-1.021	-0.238	6.917	-0.913	
4	0.772	-1.440	-0.759	-0.103	-1.143	0.178	4.945	3.621	
5	1.588	-1.901	-0.812	0.061	-1.305	0.428	8.717	-0.828	
6	1.885	0.009	-0.585	-0.202	-1.021	-0.652	6.048	-1.799	
7	0.537	-0.089	-0.551	-0.332	-0.894	-0.700	4.052	3.485	
8	0.224	-0.381	-0.658	-0.043	-1.017	-0.398	3.174	4.220	
9	0.528	-0.552	-0.690	-0.206	-1.019	-0.358	5.494	-0.848	
10	0.991	-0.136	-0.556	-0.199	-0.944	-0.697	4.981	-0.710	
11	0.285	0.123	-0.476	-0.068	-0.596	-0.636	4.065	3.325	
12	0.296	-0.182	-0.432	-0.119	-0.621	-0.544	5.221	6.530	
13	0.188	-0.812	-0.251	-0.009	-0.695	-0.084	3.589	3.192	
14	1.209	-0.494	-0.286	-0.047	-0.850	0.128	6.723	3.397	
15	0.936	-0.489	-0.336	-0.069	-0.781	-0.005	4.499	-1.261	
16	0.753	-1.269	-0.475	-0.171	-0.886	-0.238	6.917	-0.913	
17	0.772	-1.440	-0.375	-0.103	-0.882	0.178	4.945	3.621	
18	1.588	-1.901	-0.275	0.061	-1.122	0.428	8.717	-0.828	
19	1.885	0.009	-0.563	-0.202	-0.740	-0.652	6.048	-1.799	
20	0.537	-0.089	-0.561	-0.332	-0.774	-0.700	4.052	3.485	
	0.224	-0.381	-0.468	-0.043	-0.804	-0.398	3.174	4.220	-
Standard									
Deviation:	0.527	0.646	0.158	0.109	0.178	0.391	1.566	2.640	
Mean:	0.893	-0.664	-0.517	-0.119	-0.909	-0.222	5.516	1.356	
Calculated	2 17	1 07	0.04	0.24	0 27	0.05	10.21	0.20	ma/l
Calculated	2.47	1.27	-0.04	0.21	-0.37	0.95	10.21	9.28	mg/L
LOQ:	8.25	4.25	-0.14	0.69	-1.24	3.17	34.05	30.92	mg/L

Table A1.1 MCL Study from UW ICP analysis.

COLUMN LEACH TEST RESULTS

Bottom Ash Column Leach Test Results											
	5 4	Influent nH	Co	ncentration	n (g/L)						
ESTPVF	рп	innuent pr	Cd	Cr	Se	Ag					
0.0											
0.1	7.2	6.8									
0.2	7.3	6.8	ND	292	ND	ND					
0.2	7.5	6.8									
0.4	7.5	6.8	ND	625	ND	2.4					
0.4	7.6	6.8									
0.5	7.6	6.8	ND	684	7.6	1.6					
0.5	7.6	6.8									
0.6	7.7	6.8	ND	730	10.5	1					
0.7	7.7	6.8									
0.7	7.7	6.8	ND	961	17.2	1.4					
0.8	7.6	6.8									
0.9	7.6	6.8									
0.9	7.7	6.8	ND	863	14.9	1.5					
1.4	7.6	6.8	ND	365	ND	ND					
1.5	7.8	6.8									
1.6	8.0	6.8									
1.6	8.0	6.8	ND	324	ND	2.6					
2.2	8.1	6.8	ND	311	ND	2.4					
2.4	8.0	6.8	ND	232	ND	1.8					
2.7	8.3	6.9	ND	188	ND	2.5					
2.8	8.1	6.9									
3.1	8.4	6.9	ND	131	ND	2.4					
3.4	8.4	6.9									
3.6	8.4	6.9	ND	67.3	ND	0.87					
3.7	8.2	6.9	ND	45.7	ND	1.2					
4.0	8.3	6.9									
4.2	8.4	6.9	ND	7.2	ND	ND					
4.6	8.5	6.9									
5.1	8.5	6.9	ND	2.7	ND	2.5					
5.6	8.6	6.9									
6.0	8.2	6.9									
6.4	8.4	6.9									
6.9	8.5	6.7	ND	ND	ND	4.4					
7.3	8.7	6.6									
7.9	8.7	6.7	ND	3	ND	2.7					
8.3	8.8	6.7									
8.7	8.7	6.8	ND	2	ND	3.4					
9.2	8.3	6.8									
9.6	8.4	6.7	ND	2.8	ND	3.4					
10.2	8.5	6.7									
10.6	8.6	6.7	ND	2	ND	2.4					

 Table A2.1 pH, Cd, Cr, Se, and Ag concentrations from CLT on bottom ash.

 Bottom Ash Column Leach Test Results

11.4	8.6	6.7				
12.2	8.8	6.7	ND	1.7	ND	2
12.7	8.9	6.7	ND	0	ND	3.6
13.3	8.9	6.7				
Est DVE	nН	Influent nH	Con	centration	(g/L)	
	рп		Cd	Cr	Se	Ag
14.6	9.0	6.7	ND	1.9	ND	0.86
15.2	9.0	6.7	ND	2.8	ND	2.9
15.7	9.1	6.6				
16.5	9.1	6.6	ND	2.8	24.1	3.5
17.1	9.0	6.6				
17.8	8.8	6.8	ND	3.9	ND	1.5
18.6	8.8	6.8	ND	ND	ND	ND
19.2	8.8	6.8	ND	ND	ND	1.7
20.0	8.6	6.8	ND	2.1	ND	2.2
21.0	8.6	6.8	ND	3.2	ND	ND
22.0	8.6	6.8	ND	3.7	ND	1.6
22.9	8.5	6.8	10.3	5.3	ND	1.4
23.7	8.5	6.8	ND	2.1	ND	1.9
24.5	8.5	6.8	ND	ND	ND	2.2
25.1	8.4	7.0	ND	ND	ND	1.1
26.0	8.4	6.9	ND	ND	ND	2.1
26.9	8.4	6.9	ND	ND	ND	1.6
27.8	8.6	6.9	ND	ND	ND	0.9
28.2	9.0	6.9	ND	ND	ND	ND
28.5	8.6	6.9	ND	6.5	ND	1.3
28.6	8.4	6.9	ND	6.3	ND	1.8
28.6	8.6	6.9	ND	5.1	ND	0.92
28.9	9.2	6.9	ND	2.3	ND	1.3
29.7	9.3	6.9	ND	10.2	22	2.5

Fly	Fly Ash Column Leach Test Results											
		Concentra	ation (mg/L)									
PVF	Cd	Cr	Se	Ag								
0.27338	3.76	60.24	32.38	5.84								
0.7605	4.63	62.93	30.07	5.35								
1.24	2.99	42.64	30.41	5.39								
1.8593	2.81	42.23	24.62	3.95								
2.5902	1.37	17.23	15.74	3.61								
3.3084	1.3	15.13	10.17	3.54								
4.0036	2.08	14.45	8.09	1.8								
4.9034	1.07	7.23	3.86	1.86								
6.0311	0.37	14.26	2.76	0.5								
7.2444	0.39	3.21	2.62	0.4								
8.3886	0.73	3.45	0.96	0.33								
9.5244	0.34	2.95	0.73	0.61								
10.719	0.63	0.28	0.57	0.28								
11.887		0.32		0.32								

Table A2.2 Cd, Cr, Se, and Ag concentrations from CLT on fly ash.

Foundry Sand Column Leach Test Results												
Ect DVE	54	C	oncentrati	on (g/L)								
ESLEVE	рп	Cd	Cr	Se	Ag							
0.14	8.4	32.9	ND	ND	3.1							
0.21	8.5	1.2	ND	ND	1.7							
0.32	8.5	1.2	ND	ND	4.4							
0.39	8.5	1.4	ND	ND	1.7							
0.59	8.4	ND	ND	ND	ND							
0.79	8.4	ND	ND	ND	2							
1.03	8.4	ND	ND	ND	4.2							
1.11	8.4	ND	ND	ND	2.7							
1.25	8.5	ND	ND	ND	6.1							
1.35	8.6	ND	ND	ND	ND							
1.41	8.7	ND	ND	ND	ND							
1.58	8.1	9.2	ND	ND	1.2							
1.58	8.5	ND	ND	ND	6.7							

 Table A2.3 pH, Cd, Cr, Se, and Ag concentrations from CLT on foundry sand.

Foundry Slag Column Leach Test Results											
Ect D\/E	ъЦ	Influent nH	Co	ncentration	(g/L)						
	рп		Cd	Cr	Se	Ag					
0.0											
0.0	7.1	6.84									
0.2	7.1	6.84	ND	1790	ND	ND					
0.3	7.4	6.84									
0.3	7.3	6.84	ND	3740	ND	ND					
0.4	7.3	6.84									
0.5	7.3	6.84	ND	5460	ND	ND					
0.5	7.3	6.84									
0.6	7.4	6.84	ND	6530	ND	ND					
0.7	7.5	6.84									
0.8	7.5	6.84	ND	5830	ND	ND					
0.9	7.5	6.84									
0.9	7.5	6.84	ND	4690	ND	ND					
1.4	8.6	6.84	ND	3220	ND	2.4					
1.5	8.5	6.84									
1.5	8.7	6.84	ND	2250	ND	2					
1.6	8.9	6.84	ND	2050	ND	1.6					
2.3	9.2	6.84									
2.4	9.3	6.84	ND	1520	ND	ND					
2.8	9.4	6.89									
2.9	9.4	6.89	ND	1060	ND	ND					
3.2	9.5	6.87									
3.6	9.6	6.88	ND	640	ND	ND					
3.8	9.5	6.9									
3.9	9.2	6.89	ND	525	ND	ND					
4.1	9.5	6.91	ND	553	ND	ND					
4.4	9.6	6.93									
4.8	9.6	6.93	ND	482	ND	ND					
5.3	9.6	6.9	ND	246	ND	ND					
5.8	9.7	6.85	ND	165	ND	ND					
6.2	9.3	6.93									
6.7	9.4	6.92	ND	161	ND	ND					
7.2	9.6	6.68									
7.6	9.7	6.63	ND	118	ND	1.3					
8.2	9.6	6.67									
8.6	9.7	6.67	ND	113	ND	ND					
9.1	9.7	6.79									
9.6	9.7	6.78	ND	130	ND	ND					
10.0	9.7	6.72									
10.5	9.7	6.7	ND	91.1	ND	ND					
11.0	9.8	6.68									
11.8	9.8	6.67	ND	93	ND	ND					

 Table A2.4 pH, Cd, Cr, Se, and Ag concentrations from CLT on foundry slag.

 Foundry Slag Column Leach Test Results

12.6	9.8	6.7	ND	85.7	ND	ND
13.1	9.8	6.67				
13.8	9.8	6.66	ND	55.7	ND	ND
14.4	9.8	6.66	ND	52.6	ND	ND
	лЦ		Con	centration (g/L)	
ESLEVE	рп	initident pr	Cd	Cr	Se	Ag
15.7	9.8	6.67	ND	71.6	ND	ND
16.3	9.8	6.64	ND	77.7	ND	ND
17.0	9.9	6.61				
17.6	9.7	6.64	ND	38.3	ND	ND
18.4	9.6	6.83	ND	90	ND	ND
19.2	9.7	6.83				
19.8	9.7	6.83	ND	31.3	ND	ND
20.7	9.7	6.83	ND	45	ND	ND
21.7	9.5	6.83	ND	57.2	ND	ND
22.7	9.4	6.83	ND	52.2	ND	ND
23.6	9.6	6.83	ND	70.7	ND	ND
24.2	9.6	6.83				
25.0	9.6	6.83				
25.6	9.6	6.95	ND	37.9	ND	ND
26.5	9.5	6.88	ND	37.6	ND	ND
27.5	9.5	6.9	ND	46.1	ND	ND
28.5	9.4	6.9	ND	37.5	ND	ND
28.7	8.6	6.94	ND	17.1	ND	16.8
29.0	8.8	6.94	ND	95	ND	ND
29.1	8.5	6.94	ND	89.9	ND	ND
29.1	8.5	6.94	ND	91.5	ND	ND
29.6	9.0	6.87	ND	29.1	ND	ND
30.3	9.4	6.87	ND	177	ND	ND



Fig. A2.1 pH versus PVF for CLTs on foundry slag, foundry sand, and bottom ash.

WATER LEACH TEST RESULTS

Table A3.1pH, Cd, Cr, Se, Ag, Fe, and Pb concentrations from WLTs on
foundry sand, foundry slag, bottom ash, fly ash alone, and fly-
ash-stabilized soil.

Material	WLT pH and Concentration (g/L)						
	Cd	Cr	Se	Ag	Fe	Pb	рН
Foundry Sand	0.3	<1.0	<10	<2.5	430	8	9.0
Foundry Slag	0.2	<1.0	<10	<2.5	48.3	12	10.7
Bottom Ash	<0.2	1.1	32.5	<2.5	-	-	10.3
Fly-Ash-Stabilized Soil	0.6	46	16.2	1.8	-	-	11.0
Fly Ash Alone	0.7	95	26	2.2	-	-	11.8

MONITORING WELLS












APPENDIX 5

RESULTS OF WATER LEACH TESTS FROM HCFA PROJECT



Fig. A5.1. Cadmium concentrations from water leach tests on mixtures containing (a) Dewey fly ash, (b) King fly ash, and (c) Presque Isle fly ash.



Fig. A5.2. Chromium concentrations from water leach tests on mixtures containing (a) Dewey fly ash, (b) King fly ash, and (c) Presque Isle fly ash.



Fig. A5.3. Selenium concentrations from water leach tests on mixtures containing (a) Dewey fly ash, (b) King fly ash, and (c) Presque Isle fly ash.



Fig. A5.4. Silver concentrations from water leach tests on mixtures containing (a) Dewey fly ash, (b) King fly ash, and (c) Presque Isle fly ash.

APPENDIX 6

RESULTS OF COLUMN LEACH TESTS FROM HCFA PROJECT



Fig. A6.1. Effluent pH from column leach tests on Dewey, King, and Presque Isle fly ashes mixed with sand.



Fig. A6.2. Effluent pH from column leach tests on soil-fly ash mixtures containing Lawson soil.



Fig. A6.3. Effluent pH from column leach tests on soil-fly ash mixtures containing Markey soil.



Fig. A6.4. Effluent pH from column leach tests on soil-fly ash mixtures containing Theresa soil.



Fig. A6.4. Cadmium and chromium elution curves from column leach test on sand and 30% Dewey fly ash.



Fig. A6.5. Selenium and silver elution curves from column leach test on sand and 30% Dewey fly ash.



Fig. A6.6. Cadmium and chromium elution curves from column leach test on sand and 30% King fly ash.



Fig. A6.7. Selenium and silver elution curves from column leach test on sand and 30% King fly ash.



Fig. A6.8. Cadmium and chromium elution curves from column leach test on sand and 30% Presque Isle fly ash.



Fig. A6.9. Selenium and silver elution curve from column leach test on sand and 30% Presque Isle fly ash.



Fig. A6. 10. Cadmium and chromium elution curves from column leach test on Lawson soil.



Fig. A6.11. Selenium and silver elution curves from column leach test on Lawson soil.



Fig. A6.12. Cadmium and chromium elution curves from column leach test on Markey soil.



Fig. A6.13. Selenium and silver elution curves from column leach test on Markey soil.



Fig. A6.14. Cadmium and chromium elution curves from column leach test on Theresa soil.



Fig. A6.15. Cadmium and chromium elution curves from column leach test on Theresa soil.



Fig. A6.16. Cadmium and chromium elution curves from column leach test on Lawson soil and 30% Dewey fly ash.



Fig. A6.17. Selenium and silver elution curves from column leach test on Lawson soil and 30% Dewey fly ash.



Fig. A6.18. Cadmium and chromium elution curves from column leach test on Lawson soil and 30% King fly ash.



Fig. A6.19. Selenium and silver elution curves from column leach test on Lawson soil and 30% King fly ash.



Fig. A6.20. Cadmium and chromium elution curves from column leach test on Lawson soil and 30% Presque Isle fly ash.



Fig. A6.21. Selenium and silver elution curves from column leach test on Lawson soil and 30% Presque Isle fly ash.



Fig. A6.22. Cadmium and chromium elution curves from column leach test on Markey soil and 30% Dewey fly ash.



Fig. A6.23. Selenium and silver elution curves from column leach test on Markey soil and 30% Dewey fly ash.



Fig. A6.24. Cadmium and chromium elution curves from column leach test on Markey soil and 30% King fly ash.


Fig. A6.25. Selenium and silver elution curves from column leach test on Markey soil and 30% King fly ash.



Fig. A6.26. Cadmium and chromium elution curves from column leach test on Markey soil and 30% Presque Isle fly ash.



Fig. A6.27. Selenium and silver elution curves from column leach test on Markey soil and 30% Presque Isle fly ash.



Fig. A6.28. Cadmium and chromium elution curves from column leach test on Theresa soil and 30% Dewey fly ash.



Fig. A6.29. Selenium and silver elution curves from column leach test on Theresa soil and 30% Dewey fly ash.



Fig. A6.30. Cadmium and chromium elution curves from column leach test on Theresa soil and 30% King fly ash.



Fig. A6.31. Selenium and silver elution curves from column leach test on Theresa soil and 30% King fly ash.



Fig. A6.32. Cadmium and chromium elution curves from column leach test on Theresa soil and 30% Presque Isle fly ash.



Fig. A6.33. Selenium and silver elution curves from column leach test on Theresa soil and 30% Presque Isle fly ash.

APPENDIX 7

COMPARISON OF ELUTION CURVES FROM COLUMN LEACH TESTS ON SOILS ALONE, SOIL-FLY ASH MIXTURES, AND SAND FLY ASH MIXTURES



Fig. A7.1 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Lawson soil alone, Lawson mixed with 30% Dewey fly ash, and sand mixed with 30% Dewey fly ash.



Fig. A7.2 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Lawson soil alone, Lawson mixed with 30% King fly ash, and sand mixed with 30% King fly ash.



Fig. A7.3 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Lawson soil alone, Lawson mixed with 30% Presque Isle fly ash, and sand mixed with 30% Presque Isle fly ash.



Fig. A7.4 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Markey soil alone, Markey mixed with 30% Dewey fly ash, and sand mixed with 30% Dewey fly ash.



Fig. A7.5 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Markey soil alone, Markey mixed with 30% King fly ash, and sand mixed with 30% King fly ash.



Fig. A7.6 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Markey soil alone, Markey mixed with 30% Presque Isle fly ash, and sand mixed with 30% Presque Isle fly ash.



Fig. A7.8 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Theresa soil alone, Theresa mixed with 30% Dewey fly ash, and sand mixed with 30% Dewey fly ash.



Fig. A7.8 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Theresa soil alone, Theresa mixed with 30% King fly ash, and sand mixed with 30% King fly ash.



Fig. A7.9 Comparison of elution curves for (a) Cd, (b) Cr, (c) Se, and (d) Ag from CLTs on Theresa soil alone, Theresa mixed with 30% Presque Isle fly ash, and sand mixed with 30% Presque Isle fly ash.