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Final Report

**CONSTRUCTED WETLANDS FOR THE
REMEDICATION OF BLAST FURNACE
SLAG LEACHATES**

**M. Katherine Banks
A. Paul Schwab
James E. Alleman
James G. Hunter
Jason C. Hickey**

December 2006

Indiana
Department
of Transportation

Purdue
University

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INDOT Research

TECHNICAL *Summary*

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December 2006
Final Report

Constructed Wetlands for the Remediation of Blast Furnace Slag Leachates

Introduction

Recycling of industrial by-products and waste materials is popular among manufacturing and construction industries. This type of material reuse also has become accepted practice for transportation agencies since these materials are attractive based on cost compared to conventional aggregates. However, research has indicated that the chemical reactivity of these materials may result in negative environmental impact.

Air-cooled blast furnace slag (BFS) is a by-product of iron and steel production. This stone-like material is often used as support media for highway construction. Specific uses include concrete and asphalt aggregates, highway shoulder berms, driveway and parking lot fills, and as railroad grade ballast. There has been evidence that leachate with characteristics harmful to the surrounding ecosystem may be generated from this slag. Leaching issues are particularly problematic with unweathered slag. These problems include increases in pH, oxygen depletion, release of metals, sulfur, precipitation of drain clogging tufa, as well as occurrence of color and odor nuisances.

A slag leachate problem was observed in Northwest Indiana several years ago. Slag material

was used for an embankment located under I-65 near Hobart, Indiana. Approximately fourteen inches of slag was used in the construction of the sub-base under the highway pavement and slag surrounded the box culvert within the embankment. Groundwater in contact with the slag-produced leachate with a greenish/yellow color and hydrogen sulfide odor at a pH of 12. Indiana Department of Environmental Management (IDEM) classified this site as hazardous due elevated pH measurements.

In this research project, the use of engineered constructed wetlands was assessed to mitigate the impacts of the slag leachate. Constructed wetlands treatment is a low-cost, low maintenance process and is often used for the removal of contaminants from domestic and industrial wastewater. A field scale subsurface constructed wetland was designed to treat the slag leachate in northwest Indiana. If this constructed wetland approach is shown to be successful for remediation of slag leachate, then INDOT may have an alternative for addressing the problem statewide.

Findings

The constructed wetland was effective in reducing a number of the leachate constituents that impacted the adjacent surface water quality, including pH, TDS, salinity, and sulfate. The system was most effective under low flow conditions and extended retention times between surges of leachate into the wetland. The zero flow restriction of the system was met and resulted in

elevated concentrations of salts and metals in the sediments. Treatment of the slag leachate could possibly be enhanced through the use of a flow-through system that utilizes different options: reciprocating flow regime, alternating organic substrate, and process segmentation to utilize both aerobic and anaerobic processes.

Implementation

This report will be distributed to the INDOT staff responsible for environmental impact and

mitigation. The principal investigators will be available for presentations upon request.

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**CONSTRUCTED WETLANDS FOR THE REMEDIATION OF
BLAST FURNACE SLAG LEACHATES**

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16. Abstract A study was conducted at a site adjacent to I-65 site near Hobart, IN. The pilot scale study was designed to evaluate the use of a subsurface constructed wetland to treat leachate from the slag-based embankment. The constructed wetland proved to be effective in reducing a number of the leachate constituents that impact surface water quality, including pH, TDS, salinity, and sulfate. The system worked best under low flow conditions and extended retention times between surges of leachate into the wetland. The zero flow restriction of the system was met and resulted in elevated concentrations of salts and metals in the sediments. Treatment of the slag leachate could be enhanced through the use of a flow-through system that utilizes different options: reciprocating flow regime, alternating organic substrate, and process segmentation to utilize both aerobic and anaerobic processes. A better understanding of the speciation of target pollutants also would be beneficial in determining the fate and availability of the compounds. Additional analyses of substrate and precipitation products after treatment in conjunction with the modeling of chemical equilibria would be useful to determine if reaction rates are optimized.					
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TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABBREVIATIONS & NOMENCLATURE	x
CHAPTER 1. INTRODUCTION	1
1.1. Purpose.....	1
1.2. Objectives	3
CHAPTER 2. Background.....	4
2.1. Air-Cooled Blast Furnace Slag	4
2.2. Slag Leachate Formation	7
2.3. Environmental/Toxicological Affects of Slag Leachate.....	10
2.4. Constructed Wetlands	12
2.5. Proposed Treatment of BFS Leachate	23
2.6. Geochemical Modeling Results	25
2.7. Wetland Design.....	26
CHAPTER 3. CHARACTERISTICS OF SLAG LEACHATE PRODUCED UNDER REDUCED AND OXIDIZED CONDITIONS.....	35
3.1. Introduction.....	35
3.2. Materials and Methods.....	38
3.3. Results and Discussion	40
3.3.1. Chemical Processes Responsible for Leachate Characteristics	40
3.3.2. Effect of Oxidation/Reduction on Leachate Characteristics.....	42
3.4. Conclusions.....	43

CHAPTER 4. FIELD ASSESSMENT OF A CONSTRUCTED WETLAND USED FOR SLAG LEACHATE REMEDIATION	53
4.1. Introduction.....	53
4.2. Background of Field Study	55
4.2.1. Site Description.....	56
4.2.2. Chemical Characteristics of BFS Leachate.....	57
4.2.3. Constructed Wetlands Design and Construction	58
4.2.4. Selection of Plants.....	59
4.3. Materials and Methods.....	62
4.4. Results and Discussion	65
4.4.1. Site Hydrology	65
4.4.2. Water Quality Measurements.....	66
4.5. Conclusions.....	71
CHAPTER 5. CONCLUSIONS AND FUTURE RESEARCH	137
5.1. Conclusions.....	137
5.2. Future Research	141
REFERENCES	143
APPENDICES	
Appendix A Shaker Study: Setup and Observations	154
Appendix B I-80/94 Observations and Wetland Trench / Plant Species Survivability Study	158
Appendix C I-65 Field Site: Emergent Leachate Observations, Pre-Construction 2001-2002.....	163
Appendix D I-65 Field Site: Setup, Construction, and Observations	169

LIST OF TABLES

Table	Page
Table 2.1 Constituents of Blast Furnace Slag.....	29
Table 2.2 Effect of Aeration on Sulfur Compounds in Leachate	30
Table 2.3 Sulfate (SO_4^{2-}) and Total Soluble Sulfate as a Function of pH in a System with Sulfate, Calcite, and Gypsum.	31
Table 3.1 Representative Blast Furnace Slag Composition.....	45
Table 3.2 Chemical Characteristics of Leachate Generated at the Northwest Indiana Study Site.	46
Table 3.3 Trace Elements in Water After 21 Days of Exposure to Slag.	47
Table 4.1 INDOT Analysis of Leachate Adjacent to Bike Path in Robinson Park (October 2001).....	73
Table 4.2 Analysis of Leachate of BFS Leachate Sampled from the Weir Box (May 2003 –May 2005).....	74
Table 4.3 Alternate/Additional Species Based on the Adaptive Modes and Tolerance to Elevated pH.....	75
Table 4.4 Plant Provided by J.F. New Nursery Used at I-80/94 Under Drains Site.....	76

LIST OF FIGURES

Figure	Page
Figure 2.1 Blast Furnace Slag Sample from Levy Company (Gary, IN)	32
Figure 2.2 Transformation Pathways for Physical and Chemical Reactions of Slag Leachate	33
Figure 2.3 Remediation Approach for Constructed Subsurface Wetland.....	34
Figure 3.1 Slag Leachate Generated at the Study Site.....	48
Figure 3.2 pH Changes Under Oxidized (A) Conditions and Reduced (B) Conditions.	49
Figure 3.3 Sulfate Changes Under Oxidized (A) and Reduced (B) Conditions.	50
Figure 3.4 Chromatogram for Laboratory Generated Leachate Produced Under Oxidized Conditions for 42 Days.....	51
Figure 3.5 Chromatogram for Laboratory Generated Leachate Produced Under Reduced Conditions for 34 Days.	52
Figure 4.1 I-65 Field Site Located 2.4 km North of Exit 255 in Hobart, IN.	77
Figure 4.2 Bike Path Leading to Concrete Box Culvert.....	78
Figure 4.3 Design of the Constructed Wetland.....	79
Figure 4.4 Layers of Gravel Media as a Function of Depth	80
Figure 4.5 Planting and Sampling Layout for the Wetland	81
Figure 4.6 Average Flow (gallons per day)	82
Figure 4.7 Max Flow (gallons per day)	83

Figure	Page
Figure 4.8 Cumulative Inflow Volume (May 2003 –Jan 2005).....	84
Figure 4.9 Precipitation Daily Average Crown Point & Lowell and Monthly Northwest Indiana.	85
Figure 4.10 Groundwater Table Levels (ft) at Selected Wells Local to the I-65 Wetland Site in Hobart, IN.	86
Figure 4.11 Typical Embankment.....	87
Figure 4.12 Groundwater and Embankment Interaction Schematic.....	87
Figure 4.13 Response During the Rhodamine Dye Tracer Test.	88
Figure 4.14 Temperature Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	89
Figure 4.15 Temperature Variation as Function of Time and Positions in Field	90
Figure 4.16 Temperature Distribution in Planted and Main Sections	91
Figure 4.17 pH Variation for Maximum, Average, and Minimum Value as Function of Time in Field	92
Figure 4.18 pH Variation as Function of Time and Positions in Field.....	93
Figure 4.19 pH Distribution in Planted and Main Sections	94
Figure 4.20 Oxidation Reduction Potential Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	95
Figure 4.21 Oxidation Reduction Potential Variation as Function of Time and Positions in Field.....	96
Figure 4.22 Oxidation Reduction Potential Distribution in Planted and Main Sections.....	97
Figure 4.23 Total Dissolved Solid Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	98
Figure 4.24 Total Dissolved Solid Variation as Function of Time and Positions in Field.....	99

Figure	Page
Figure 4.25 Total Dissolved Solid Distribution in Planted and Main Sections	100
Figure 4.26 Salinity Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	101
Figure 4.27 Salinity Variation as Function of Time and Positions in Field	102
Figure 4.28 Salinity Distribution in Planted and Main Sections	103
Figure 4.29 Sulfate Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	104
Figure 4.30 Sulfate Variation as Function of Time and Positions in Field.....	105
Figure 4.31 Sulfate Distribution in Planted and Main Sections.....	106
Figure 4.32 Sulfur Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	107
Figure 4.33 Sulfur Variation as Function of Time and Positions in Field	108
Figure 4.34 Sulfur Distribution in Planted and Main Sections.....	109
Figure 4.35 Aluminum Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	110
Figure 4.36 Aluminum Variation as Function of Time and Positions in Field	111
Figure 4.37 Aluminum Distribution in Planted and Main Sections.....	112
Figure 4.38 Barium Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	113
Figure 4.39 Barium Variation as Function of Time and Positions in Field	114
Figure 4.40 Barium Distribution in Planted and Main Sections.....	115
Figure 4.41 Calcium Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	116
Figure 4.42 Calcium Variation as Function of Time and Positions in Field	117
Figure 4.43 Calcium Distribution in Planted and Main Sections	118

Figure	Page
Figure 4.44 Iron Variation for Maximum, Average, and Minimum Value as Function of Time in Field	119
Figure 4.45 Iron Variation as Function of Time and Positions in Field	120
Figure 4.46 Iron Distribution in Planted and Main Sections	121
Figure 4.47 Magnesium Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	122
Figure 4.48 Magnesium Variation as Function of Time and Positions in Field	123
Figure 4.49 Magnesium Distribution in Planted and Main Sections	124
Figure 4.50 Manganese Variation for Maximum, Average, and Minimum Value as Function of Time in Field.....	125
Figure 4.51 Manganese Variation as Function of Time and Positions in Field.....	126
Figure 4.52 Manganese Distribution in Planted and Main Sections.....	127
Figure 4.53 Zinc Variation for Maximum, Average, and Minimum Value as Function of Time in Field	128
Figure 4.54 Zinc Variation as Function of Time and Positions in Field.....	129
Figure 4.55 Zinc Distribution in Planted and Main Sections.....	130
Figure 4.56 Arsenic Variation for Maximum, Average, and Minimum Value as Function of Time in Field	131
Figure 4.57 Arsenic Variation as Function of Time and Positions in Field for 2003	132
Figure 4.58 Arsenic Distribution in Planted and Main Sections for 2003.....	133
Figure 4.59 Lead Variation for Maximum, Average, and Minimum Value as Function of Time in Field for 2003	134
Figure 4.60 Lead Variation as Function of Time and Positions in Field for 2003	135
Figure 4.61 Lead Distribution in Planted and Main Sections for 2003	136

ABBREVIATIONS & NOMENCLATURE

AAS	atomic absorption spectrophotometry
ANOVA	analysis of variance
BDL	below detectable limit
BFS	blast furnace slag
CEC	cation exchange capacity
COD	chemical oxygen demand
DO	dissolved oxygen
Eh	Symbol for standard oxidation-reduction potential (in millivolts)
EPA	Environmental Protection Agency
FWS	free-water surface wetland
HRT	hydraulic retention (residence) time
IC	ion chromatography
ICP	inductively coupled plasma
INDEM	Indiana Department of Environmental Management
INDOT	Indiana Department of Transportation
LC ₅₀	Lethal Dose, 50% or median lethal dose to kill half of a tested population
mV	millivolts
pe	redox potential expressed in terms of $-\log$ of electron activity
pH	measure of the acidity of a solution in terms of activity of hydrogen (H^+)
ppt	parts per trillion (used for salinity)
NIST	National Institute of Standards and Technology
NSA	National Slag Association
ODOT	Ohio Department of Transportation
ORP	oxidation-reduction potential

RO	reverse osmosis
SRB	sulfate reducing bacteria
SS	subsurface wetland
TDS	total dissolved solids
USACE	United States Army Corps of Engineers
USDA	United States Department of Agriculture
USGS	United States Geological Survey
ZVI	zero valent iron (Fe^0)

Abbreviations for water-quality units (metric units):

Volumes of samples: liters (L) and milliliters (mL)

Chemical concentrations: grams per liter (g/L), milligrams per liter (mg/L), or
micrograms per liter ($\mu\text{g/L}$)

Conductivity: microsiemens per centimeter at 25 °C ($\mu\text{S/cm}$)

Redox potential of water is expressed in millivolts (mV)

CHAPTER 1. INTRODUCTION

1.1. Purpose

The recycling of industrial by-products and waste materials has many benefits and is currently popular among manufacturing and construction industries. This type of material reuse has become accepted practice for highway agencies; consequently, the market for waste aggregates for use in construction has increased. Because the potential performance benefits are positive, these materials also are attractive based on cost compared to conventional aggregates. However, it should be acknowledged that the chemical reactivity of these materials might result in negative environmental impacts.

Air-cooled blast furnace slag (BFS) is a by-product of iron production. This stone-like material is often used as support media for highway construction. Other principal uses for this slag are concrete and asphalt aggregates, highway shoulder berms, driveway and parking lot fills, and as railroad grade ballast. There has been published evidence that leachate with characteristics harmful to the surrounding ecosystem may be generated from this slag (Roadcap et al. 2005; USACE, 2002). Leaching issues are particularly problematic with unweathered slag. These problems include increases in pH, oxygen depletion, release of metals, sulfur, total dissolved solids (TDS), precipitation of drain clogging tufa, as well as occurrence of color and odor nuisances.

The production of slag leachate is a difficult issue for state agencies. The presence of the leachate indicates that the regulatory agencies allowed unweathered slag to be used in transportation and infrastructure projects. For example, this problem occurred in Baltimore, Maryland on I-695 with slag used as embankment fill. Discharge water had a pH of 12.5 to 13 with calcareous tufa precipitate. The Maryland State Highway Administration remediated this area at a cost in excess of \$1 million (Boyer, 1994). Slag leachate also appeared during airport runway construction in Cleveland, Ohio. The leachate discharge seriously impacted an adjacent river and the site was remediated at a cost of \$2.1 million (Rollenhagen, 2002). The problematic slag used in the airport project was also placed as support for an interstate highway interchange in Richfield, Ohio. Slag leachate was reported as a “nasty smelling, milky runoff” and contaminated a nearby creek, resulting in a \$35,000 fine levied by the Ohio Environmental Protection Agency (Akron Beacon Journal, 2003; Ohio EPA, 2003).

This research project was developed to address a similar situation in Northwest Indiana. Unsuitable slag material was used for an embankment located under I-65 near Hobart, Indiana. Approximately 35 cm of slag had been used in the construction of the sub-base under the highway pavement and slag surrounded the box culvert within the embankment. Groundwater in contact with the slag produced leachate with a greenish/yellow color and hydrogen sulfide odor at a pH of 12. Indiana Department of Environmental Management (IDEM) classified this site as hazardous because of high pH measurements, with concern for elevated metals (arsenic and lead) and sulfate concentrations.

1.2. Objectives

In this research project, the use of engineered constructed wetlands to mitigate the impacts of the elevated pH, sulfate, and dissolved solids of BFS leachate, was assessed. Constructed wetlands are considered to be a low-cost, low maintenance treatment alternative often used for the removal of contaminants from non-point source pollution, acid mine drainage, and domestic and industrial wastewater. This report includes results from: 1) a field scale subsurface constructed wetland that was designed to treat the slag leachate in Northwest Indiana, 2) laboratory studies conducted to evaluate the leachability of the slag material. Supplemental greenhouse and column experiments were performed to evaluate the efficiency of media and plant combinations and results are reported in Hunter, 2006 (PhD Dissertation).

CHAPTER 2. BACKGROUND

2.1. Air-Cooled Blast Furnace Slag

BFS is a by-product of iron production (Figure 2.1). BFS is defined as the “non-metallic product consisting essentially of silicates and alumino-silicates of calcium and other bases that is developed in the molten condition simultaneously with iron in a blast furnace” (NSA, 2003). Nearly 13 million tons are produced each year by the steel industry in the United States, with many recycled commercial uses (Proctor et al., 2000). The reuse of slag byproducts has a long history. As early as 350 B.C., Aristotle was prescribing slag to heal wounds (Kalyonku, 2003). In the 1500s, the Germans used this material to cast cannon balls (NSA, 2003). The predominant modern application for air-cooled blast furnace slag aggregate is support media for construction and transportation structures (e.g., road bed, fill material). Other uses for slag include cement, concrete aggregates, glass, soil amendments in agriculture and treatment/filter media.

Blast furnace slag is generated when iron ore (usually hematite - Fe_2O_3 , magnetite - Fe_3O_4 , limonite - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or siderite - FeCO_3 , in a silica - SiO_2 matrix), coke (heat purified coal), fluxing stone (calcitic, or dolomitic limestone), and hot oxygen are combined and allowed to react in a stratified high temperature furnace or blast furnace (Brain, 2003). Within a blast furnace, iron oxides in the ore are reduced by carbon monoxide to metallic iron and carbon dioxide gas:

The heated oxygen forces the coke to burn:

Carbon dioxide (CO₂) further reacts with the coke to produce carbon monoxide (CO):

CO then reacts with the ore to form ferrous oxide (FeO)- the steps vary depending on the mineral undergoing the reaction (France, 2003). Finally, FeO reacts with CO to form metallic iron:

However, because the above reaction is driven by high heat and the reaction occurs between impure solids, a fluxing agent (limestone) is used to simultaneously assist in heat transfer and increase the fluidity of the liquid constituents. The fluxing stones combine with silica, aluminum, and other impurities in the ore to form slag, which floats on the surface of, and can be separated from, the molten iron (USACE, 2002). In this process, limestone (as calcite, CaCO_{3(s)}) is first decomposed:

This is followed by the reaction:

Metal impurities are typically oxidized and partition into the molten slag. A representative BFS composition as simple oxides by weight is shown in Table 2.1, but will vary based on the type of iron or steel being produced, as well as the quality of the ore used (NSA, 1988).

Slag is primarily composed of silica, aluminum, magnesium, sulfur, iron, manganese, and calcium with other trace elements. These constituents usually exist as an isomorphic mixture with the following general formula $\text{Ca}_2(\text{MgFeAl})(\text{SiAl})_2\text{O}_7$ (NSA, 2003).

The formation of blast furnace slag tends to be glassy or will crystallize into a number of minerals. The relatively slow cooling rate of slag lends itself to the formation of a solid crystalline blend. Mineralogically, this represents the calcium aluminosilicate mellilite group with akermanite ($2\text{CaO} \circ \text{MgO} \circ 2\text{SiO}_2$) and gehlenite ($2\text{CaO} \circ \text{Al}_2\text{O}_3 \circ \text{SiO}_2$). Some of the other mineralogical phases that are commonly observed include wollastonite ($\text{CaO} \circ \text{SiO}_2$), dicalcium silicate ($2\text{CaO} \circ \text{SiO}_2$), dicalciumferrite ($2\text{CaO} \circ \text{Fe}_2\text{O}_3$), merwinite ($3\text{CaO} \circ \text{MgO} \circ 2\text{SiO}_2$), anorthite ($\text{CaO} \circ \text{Al}_2\text{O}_3 \circ 2\text{SiO}_2$), and moticellite ($\text{CaO} \circ \text{MgO} \circ \text{SiO}_2$) all with various metallic substitutions (Inoue, 1994; Gupta et al., 1992; Lewis, 1982).

Mellilites represent about 65% of the slag by volume. However, prior to crystallization, some constituents are concentrated outside of the crystal structure and exist as an interstitial, iron-rich silicate glass with a low degree of polymerization - mainly monomers and dimmers enclosing oxide ((Ca, Mg, Fe, Mn)O (lime)), and sulfide (as CaS (oldhamite), FeS (pyrrhotite), MnS (alabanite), and MgS (niningerite)) crystals-

representing approximately 20% of the slag by volume (Ott, 2000; Cao, 1989; Vom Ende et al., 1965).

The material contains vesicles or unconnected voids due to the method of production. As compared to natural aggregates, BFS typically has slightly lower particle and bulk density, higher water absorption, unique particle shape, rougher texture and lower wet strength (QCL Group, 1999). Slag's bulk specific gravity ranges from 2- 2.5 and the bulk density ranges 1120-1360 (kg/m³) Absorption of water by slag ranges from 1- 5% by volume and slag solubility in water ranges from 0.1- 0.5% by mass (Segall, 1970). The color of the slag is dark grey to white and is normally processed in a crushing and screening plant to isolate products of particular size and grade (Figure 2.1).

2.2. Slag Leachate Formation

For this investigation, application of blast furnace slag for transportation support structures (i.e., fill for roads and embankments) is the focus. Trace constituents and impurities trapped as oxides in the slag calciumalumino-silicate glassy matrix are of particular concern. The resulting leachate properties appear to be associated with the presence of stagnant or slow moving water that has inundated slag used as fill material (NCDPPEA, 2002). Consequently, the infiltration of water through this soluble matrix produces leachate that releases calcium and manganese oxides which increases pH to as high as 12.5 (Ziemkiewicz, 1998).

The stagnant water in contact with BFS also generally exhibits high concentrations of calcium and total sulfur. Although blast furnace slag typically contains

a small component of elemental sulfur (1 to 2 percent), the leachate has a hydrogen sulfide odor and sulfate concentrations increases with oxidation (NCDPPEA, 2002). In certain situations, the leachate from blast furnace slag may be discolored (characteristic yellow/green color). When this leachate is exposed to oxygen, sulfides react with oxygen to form a white precipitant, colloidal (yellow) elemental sulfur, and produces calcium thiosulfate, which is a clear solution (Yassini, 1996).

The leachate contains sulfur (from CaS, calcium sulfide), available calcium, aluminum, and magnesium, hardness and pH will increase from the free lime content (CaO), and trace concentrations of metals. As the leachate becomes aerated over time, the sulfur in the solution oxidizes and the CaO reacts with CO₂ to become CaCO₃, causing pH to decrease to values ranging from 7.5 to 8.5. The National Slag Association (NSA) states that the typical chemical progression is as follows:

Calcium sulfide (CaS) + water (H₂O) (green liquid) → hydrogen sulfide (sulfur odor) (H₂S) + calcium sulfate (CaSO₄) → calcium carbonate (CaCO₃) (white) (NSA, 2003)

Table 2.2 shows the sulfur species of BFS leached by water and how these compounds are affected by aeration. Column leaching studies have shown that alkalinity concentrations remain high (about 2000 mg/l) for extended periods, depending on the thickness of the slag layer (Ziemkiewicz, 1998). After a period of time, the leachate is reduced as the finer particles are dissolved. Eventually, concentrations reach a stable level (about 100 mg/l). This is an important issue because even if slag is exposed to the

outdoor environment for years, this material can still generate high levels of alkalinity and pH.

Presented below is a hypothetical series of events that could account for the physical and chemical observations of leachate generated by water contacting a buried slag emplacement such as the type used as transportation support structures. Many mineralogical phases and dissolved species are believed to be present, however, only those thought to be responsible for the physiochemical observations are examined here.

First, groundwater in contact with the slag hydrates freshly exposed or residual free lime, rapidly producing alkalinity. This alkaline environment further enables the interstitial glass to be dissolved, contributing to the elevated pH and releasing most of the major metallic components of the leachate, in addition to sulfur. In this reductive environment where oxygen potential is low, sulfur in solution from the dissolution of oldhamite (CaS) and managense sulfide (MnS), tends to stay in the sulfide form (S^{2-}). Soluble iron from the dissolution of iron inclusion, as a “wafer” of unstable potassium-iron-sulfide which leads to “iron decay” in BFS, will be in the reduced form (Fe^{+2}), with other possible alkali-manganese sulfides and trace elements (Vom Ende et al., 1965). These phases, when present in “unweathered” BFS, can readily dissolve into leachate.

As the groundwater emerges and is exposed to the atmosphere, leachate will go through a complex series of pseudo-stable phases as evaporation concentrates dissolved constituents and equilibrium with the atmosphere occurs. Exposure to elevated carbon dioxide, either from atmosphere, or due to microbially active zones, will buffer the pH of the leachate. Saturation and/or evaporation encourage the precipitation of calcium carbonate (CaCO_3), a white solid commonly referred to as tufa. Also, as the pH drops,

sulfide volatilizes, yielding the rotten egg odor attributed to H_2S . Calcium bisulfite ($\text{Ca}(\text{HSO}_3)_2$) may also play a role in the smell and coloration (Yzenas, 2003). Further oxidation of sulfur results in the formation of sulfate (SO_4^{2-}), which can react with calcium to form gypsum

White precipitates, resulting from free lime in slag, can combine with water to produce calcium hydroxide ($\text{Ca}(\text{OH})_2$). The exposure of calcium hydroxide to atmospheric carbon dioxide results in calcite (CaCO_3) precipitation. This white, powdery precipitate is also called tufa. Tufa occurs in nature, is usually found in water bodies, and can clog soil and drains. The tufa formation can potentially clog drainage structures. Unweathered slag can exhibit an extreme level of chemical reactivity that is moderated after a short period of weathering. After this initial decline however, changes in reactivity are slow. Even after decades of weathering in bank storage, disturbed slags can remain highly reactive (Griffiths, 2002; USACE, 2002). Aging of blast furnace slag can delay the formation of yellow leachate under poor drainage conditions but does not appear to be a preventative measure, because the discolored leachate can still form if stagnant water is left in contact with the slag for an extended period (NCDPPEA, 2002). The leachate from stabilized slag can remain alkaline and can undergo mineralization, containing various quantities of calcium, magnesium, sulfate, fluoride and potassium (USACE, 2002).

2.3. Environmental/Toxicological Affects of Slag Leachate

The effect of slag leachate on aquatic habitats is important to evaluate given the concern about potential environmental impact. With the trace metals present in fresh

slag, there is concern that these metals may be released by leaching. An aquatic habitat may be degraded if toxic levels of metals or nutrients are released in large quantities from fresh slag. Slag saturated in a confined anoxic environment creates aesthetic considerations such as generation of odoriferous (rotten egg) hydrogen sulfide gas, precipitation of iron mono-sulfide, and altered water color (Yassini, 1996). In addition, increase in pH, possible release of heavy metals, and elevated sulfate concentrations, may not comply with federal and state water quality standards and can be potentially toxic to aquatic ecosystems.

These reactions may result in degradation of the aquatic environment, which may negatively impact the habitat of plants and animals (Roadcap et al. 2005; USACE, 2002). The potential for these effects will be governed by variables that impact potential ecological degradation: position and amount of slag used; physical and chemical characteristics of the slag; age and weathering of slag; engineering design of the support structure; and time that the slag has been in contact with groundwater, rainfall and runoff.

Specifically, slag placement in or near an aquatic environment could have the following effects on water quality; 1) elevation of pH, 2) release of sulfides, 3) increase in salinity (conductivity), 4) increase in hardness, 5) increase in chloride and sulfate levels (Muston et al., 1991). The U.S. Army Corps of Engineers has published results of extensive long-term studies of slag and slag leachate (Bayless et al., 1998). One interesting observation is that after decades of slag use in transportation projects, some slag banks remain sparsely vegetated or entirely unvegetated.

Fresh slag leachate samples, though tested negative for most priority pollutants, produced significant mortalities in 96-hour static bioassays (USACE, 2002). The

leachate from a 4:1 river water slag wash resulted in the death of all aquatic organisms tested; minnows, midge larvae and daphnia. The LC_{50} for fish and *Daphnia* was in the range of 13 to 36 percent of the original 4:1 elution concentration (USACE, 2002). Further examination suggests that the caustic alkalinity of the leachate was sufficient to account for the observed mortality to aquatic organisms. The pH of the 4:1 elution immediately increased the pH to 11.2 and after 450 minutes, reached a pH of 11.9 (USACE, 2002).

2.4. Constructed Wetlands

Wetlands have many values and functions. One of the most important functions of a wetland system is its ability to retain, transform, or degrade pollutants. Wetlands are among the most highly productive ecosystems on earth, exhibiting high levels of photosynthesis, transpiration, and other functions (Williams, 2002). Wetlands can act as sinks for many pollutants, and constructed wetlands have been used to treat domestic wastewater, mine drainage, non-point source pollution, stormwater drainage and landfill leachate (Mitsch and Gosselink, 2000). More specifically, wetlands may also function as effective sinks for sulfur (Hammer, 1989). In this research project, the potential use of constructed wetlands for high sulfate/sulfide, pH, and heavy metals was evaluated. Constructed wetlands can be defined as a man-made media of saturated substrates, emergent and submergent vegetation, animal life, and water (Hammer, 1989).

Most constructed wetlands have five principal components; 1) substrates with various rates of hydraulic conductivity, 2) plants adapted to water-saturated anaerobic substrates, 3) a water column (water flowing in or above the surface of the substrate), 4)

invertebrates and vertebrates, and 5) an aerobic and anaerobic microbial population (Hammer, 1989).

The use of constructed wetlands is low-cost, with minimal operation and maintenance requirements compared to conventional wastewater treatment facilities. Constructed wetlands are used for the remediation of heavy metals, nutrients and pesticides from non-point source pollution, acid mine drainage, and domestic and industrial wastewaters. Constructed wetland systems are frequently used for treatment of high volume, dilute wastewaters, such as landfill leachate and acid mine drainage (Dierks, 2001). In constructed wetlands, pollutants are removed from waste streams by plant uptake, chemical precipitation, ion exchange and adsorption onto clay, organic and inorganic compounds (Manios et al., 2003). Wetlands also have the ability to buffer pH by microbial activity.

Wetlands can be utilized for their distinctive biological and physicochemical processes to remove low levels of contamination from large volumes of water (Debusk et al., 1996). There are three general types of wetlands that can be used to treat pollution and wastewater: natural wetlands, free-water surface wetlands and subsurface flow wetlands. Natural wetland systems are existing wetlands where wastewater, by design, is introduced. These areas are effective for wastewater treatment because they support a large and diverse population of bacteria which grow on submerged roots and stems of aquatic plants. These areas are also conducive to sedimentation of solids. With the Clean Water Act enforced by the U.S. EPA, the general public's and government's view of the importance of wetlands was enhanced, and the use of natural wetlands to treat wastewater became prohibited. Only recently has sufficient research concerning the

safety and use of these systems for pollution control been published (Mitsch and Gosselink, 2000).

The alternative to using natural wetlands for treatment is the use of constructed wetlands. Constructed wetlands offer a compromise between preservation of existing natural systems and utilization of the distinctive biological and physicochemical processes of wetlands to remove low levels of contamination from large volumes of water (Debusk et al., 1996). The two types of constructed wetlands are free-water surface (FWS) and subsurface wetlands (SS). FWS wetlands have shallow water depths and usually support a variety of emergent, submergent, and floating species of wetlands plants. These systems typically have low velocity flows and long, narrow channels to minimize short circuiting (EPA, 2000). SS wetlands usually use some type of gravel or sand media, with emergent plants that have extensive root systems.

FWS wetlands are termed “aerobic wetlands”, and are typically used in the treatment of acidic mine water, with removal occurring due to oxidation, hydrolysis, and sedimentation (Batty and Younger, 2002). For example, aerobic wetlands are being used to treat low residual iron concentrations (<0.5 mg/L) (Batty and Younger, 2002). In contrast, compost wetlands are SS wetlands when organic matter is added to the system to encourage bacterial sulfate reduction processes typical for treating wastewaters and drainage with heavy metal concentrations.

Certain plant/substrate combinations appear to be more efficient in constructed wetlands treatment systems. Three commonly used wetland plants, cattail, bulrush, and reed, tend to create and/or maintain single species stands by inhibiting other plants. Substrates (various soils, sands, or gravel) provide physical support for plants;

considerable reactive surface area for complexing ions, anions, and other compounds; and attachment surfaces for microbial populations (Hammer, 1989). Limestone and organic carbon additions (i.e. peat, compost, etc) are used to facilitate treatment, particularly with high sulfate acid mine drainage.

The major removal mechanisms that initiate reduced contaminant concentrations are sedimentation, microbial activity, redox reactions, chemical precipitation and plant uptake (adsorption). Contaminants such as metals are not "degraded", but rather accumulate in sediments and biomass of the constructed wetland (Debusk et al., 1996).

A key removal mechanism is adsorption of heavy metals in and around the root zone of the macrophytes. For instance, a substantial concentration of the metals, especially Cu, Pb and Cd were retained in the first segment of a constructed wetland, i.e., in the root zone section (vegetated submerged bed wetland filter). An overall removal efficiency of 92.3% Cd, 89.4% Cu and 87.8% Pb for the vegetated submerged bed wetland was reported (Obarska-Pempkowiak and Klimkowska, 1999). Uptake or translocation of metals, particularly iron, is possible. Plant root absorption of heavy metals can occur by either passive (nonmetabolic) or active (metabolic) uptake. Non-metabolic uptake moves ions from the soil solution into the outer root structures (endodermis). This movement results in the formation of plaques of iron, lead and other metals onto the root (Scholz et al., 2002). Plaques of iron and manganese oxyhydroxides often form on waterlogged roots, and co-precipitation of other metals in these plaques may explain the elevated concentrations found in roots (Vesk and Allaway, 1997). Immobilization of metals by co-precipitation in the iron oxyhydroxide plaque layer on root surfaces has been demonstrated for several wetland plants (Ye et al., 1997).

Sorption in the root zone is the main mechanism of heavy metal removal from wastewater, while accumulation in the plant biomass plays a minor role. For example, biomass metals concentrations outside of the root zone were 1.0% Cd, 3.4% Pb, and 1.9% Cu (Obarska-Pempkowiak, 2001). Manios et al. (2003) reported that leaves and stems reach a saturation point at high metal concentration, but the roots removed considerably larger amounts of metals, without reaching a saturation state (Manios et al., 2003).

Although wetland plants play a direct role in phytoremediation, their interaction with sediment microbes can play an equal or greater role. Rhizosphere and sediment microbial activity directly affects contaminant uptake by wetland plants (Williams, 2002). In addition to areas around plant roots and rhizome surfaces, microbial transformation and sorption in soil are largely responsible for removal of pollutants. Metals accumulate predominantly within the litter zone and the rhizomes of the macrophytes (Scholz et al., 2002; Obarska-Pempkowiak, 2001). When a metal is introduced into a wetland system, the bulk of the metal is immobilized by the media and rhizomes through complexation or chelation, with only a small percentage of the metal remaining in the aqueous phase (Lim et al., 2003; Hawkins et al., 1997). Wetland biofilms (Scholz and Xu, 2002) enhance metal accumulation that removes lead and copper. Scholes et al. (1999) investigated the ability of microorganisms to accumulate heavy metals; they report that bacteria, fungi and actinomycetes are efficient biosorbents of metals.

Treatment of wastewaters also can be facilitated by clays, humic materials (peats), aluminum, iron, and/or calcium. Metals entering wetlands react with the negatively

charged surface of clay particles, precipitate as inorganic compounds (including metal oxides, hydroxides, and carbonates), bind to humic materials, and are adsorbed. One of the components of wetlands that may adsorb metals is peat. The most abundant and effective surface-active components that contribute to metal adsorption are complex humic and fulvic acids. Ion exchange and complex exchange are probably the main mechanisms for heavy metal adsorption onto peat (Dierks, 2001). Manios et al. (2003) reported that the presence of organic matter (peat) in the wetland resulted in a mixture with high cation exchange capacity (CEC). This high CEC supplied by the organic substrate enhanced removal of large amounts of heavy metals. Debusk et al. (1996) concluded that based on microcosm results, plant metal accumulation was of secondary importance compared with sediment activity.

A primary mechanism responsible for the removal and retention of iron, manganese, and sulfate in constructed wetlands receiving acidic mine drainage included the formation of metal oxides and sulfides within organic matter and sediments (Tarutis and Unz, 1995). These reactions are also affected by addition of organic matter to the system, namely spent mushroom compost, hay, manure, wood chips and calcite (EPA, 2000).

Natural wetlands are effective sinks and transformers of sulfur (Figure 2.3). A subsurface wetland may create anaerobic conditions needed to facilitate bacterial treatment of sulfur. Sulfur transformations are dominated by biologically mediated processes. A significant removal pathway for sulfate is by reduction to hydrogen sulfide by anaerobic bacteria (*Desulfovibrio*) (Eastlick, 1999). This process requires suitable organic substrate, which is oxidized with sulfur as the electron acceptor.

Chemoautotrophic and photosynthetic bacteria also oxidize hydrogen sulfide to sulfur and sulfites under aerobic conditions (Eastlick, 1999; Mitsch and Gosselink, 2000). Hydrogen sulfide can further react to form insoluble sulfides with metal ions (Eastlick, 1999).

Primary mechanisms responsible for the removal and retention of iron, manganese, and sulfate in constructed wetlands receiving acidic mine drainage include the formation of metal oxides and sulfides within organic matter and sediments (Tarutis and Unz, 1995). These reactions are also enhanced by addition of organic matter to the CW system, namely spent mushroom compost, hay, manure, wood chips and calcite (EPA, 2000). This organic matter allows for production of H_2S by sulfur reducing bacteria and thus produces immobile metal sulfides.

The remediation of BFS slag leachates in this research was conducted by subsurface wetlands. Subsurface wetland systems have been successful for treatment of high sulfate, acid mine drainage. These systems use sulfate-reducing bacteria (SRB) to reduce sulfate to sulfide. Long-term S retention/removal depends on anaerobic, strongly reduced conditions to enhance sulfate reduction, storage in organic forms, and volatilization as H_2S or other organic S gases (Hammer, 1989). Wetlands constructed to remove/store S should be designed to promote these processes and avoid hydrologic release mechanisms associated with oxidized substrates.

Many systems have been constructed using compost to establish an anaerobic environment and provide a source of organic carbon (Eger and Wagner, 2003). SRB need two nutrients to survive: sulfate, which is present in slag leachate, and organic carbon. Complex organics present in the substrate are microbiologically degraded to

simpler organics, and are utilized by SRB (Eger and Wagner, 2003). Although wetland plants are sometimes present, many systems have been constructed without plants. Decaying wetland plants may provide carbon to the wetland, but many systems have not used plants because of the potential for plants to oxygenate the substrate and thus inhibit the sulfate reduction process (Jacob and Otte, 2003).

The oxidation of organic compounds, where CH_2O represents a small chain organic compound, contributes to sulfate reduction and the precipitation of metal sulfides as shown in the following equations, where Me^{2+} are divalent metal cations (Bjorn et al., 1996; Drury, 2000):

The reactions and products are dependent upon redox conditions, pH, and available sources of sulfate, carbon, and elemental concentrations. These reactions are responsible for the neutralization of pH and reduction of sulfate and metals in solution (Drury 2000).

In order for substantial sulfate reduction to occur, the following conditions must be take place: 1) absence of dissolved oxygen, 2) source of sulfate, 3) source of organic carbon, 3) presence of sulfate-reducing bacteria, 5) method to physically retain metal sulfide precipitates, and 6) pH above 5 (Dvork et al. 1992).

The reduction of sulfate leads to a variety of volatile sulfur compounds including hydrogen sulfide (H_2S), methylmercaptan (MeSH), dimethyl sulfide (DMS), dimethyl

disulfide (DMDS), carbonyl sulfide (COS), and carbon disulphide (CS₂). A portion of these biogenic sulfur gases are emitted to the atmosphere.

The treatment efficiency for constructed wetlands is high. The average percentage reduction of lead, copper, biological oxygen demand and turbidity were greater than 96%, 87%, 60%, and 82%, respectively (Scholz and Xu, 2002). Lead and copper were removed efficiently by high-cost filters, which contained additional adsorption media. In contrast, low-cost sand and gravel filters showed an early breakthrough of metals (predominantly copper). However, all filters performed equally well in terms of copper and lead reduction after nine weeks of operation. Removal efficiencies were as follows in a wetland system: Zn, 72% for Cd, 69% for Pb, 66% for Cu, 34% for Ni and 81 % for Cr (Scholes et al., 1999). Loads during dry weather concentrations are typically low. However, during storm events, concentrations are elevated and the loading increased by a factor between 8 and 84. A significant role for the first part of the wetland system was noted for the vegetated submerged bed wetland filter in removal of heavy metals (69.6% Cd, 69.2% Cu and 64.3% Pb). The average removal efficiency of the elements in the wetland system was: 92.3% Cd, 89.4% Cu and 87.8% Pb (Obarska-Pempkowiak, 2001).

At several wetland sites, the macrophytes showed some bioaccumulation of Pb, Zn, Cu and Cd. Tissue concentrations are generally higher in the roots and rhizomes compared to the leaves and stems of the macrophytes. This is generally consistent with the results of the other studies on heavy metal uptake by macrophytes (Mungur et al., 1997; Batty and Younger, 2002; Debusk et al., 1996; Hawkins et al., 1997; Manios et al., 2003; Ye et al., 1997; and Lim et al., 2003).

A number of factors control the uptake and removal of contaminants from the water column in the wetland including: metal speciation of the sediment, plant growth form, pH, redox potential, sediment organic matter and iron content (Vesk and Allaway, 1997). Heavy metals such as Fe, Cu, Cd, Zn, Pb, Ni and Co can be removed by constructed wetland systems, though the metal removal efficiency seems to be influenced by the types of media and the wastewater to be treated (Lim et al., 2003; Batty and Younger, 2002; Scholes et al., 1999; Mungur et al., 1997; Williams, 2002; Debusk et al., 1996). Among the most important characteristics affecting metal speciation and partitioning are pH and oxidation-reduction potential (redox). For example, changes in pH and redox can alter the concentration and oxidation state of wetland constituents and can influence the mobility and bioavailability of metals and nutrients (Hawkins et al., 1997).

High concentrations entering the wetland system also play a pivotal role in the ability of the system to effectively treat the contaminant. Batty and Younger (2002) suggest that direct removal of Fe by wetland plants can occur at relatively low concentrations. *Phragmites* (reeds) exposed to water containing 1 mg/L Fe was capable of removing 100% of the supplied iron by means of uptake. The growth of *Phragmites* seedlings (in terms of root length, dry weight of roots, and, to a lesser extent, dry weight of shoots) was significantly inhibited where Fe was supplied at a concentration greater than 1 mg/L, and thus, removal efficiency decreased. This inhibition may occur because elevated concentrations of metals may result in metal toxicity, and the higher concentration may have impeded uptake of other nutrients by the plants, thus resulting in nutrient deficiency.

The amount of time that the wastewater is retained in the system also affects treatment efficiency. Wetlands remove more metals from slow flowing water due to establishment of equilibrium. Lead and cadmium retention could be increased by increasing hydraulic retention times (HRT) in wetlands. Typically, HRT in treatment wetlands operated for nutrient removal are 8-30 days. Small subsurface flow wetlands that received a metal-laden wastewater at a six-day HRT were found to remove 98% of Cd (Debusk et al., 1996). Water depth maintained within the wetland also was important since the depth of water can influence the extent of hydrosol reduction or oxidation. (Hawkins et al., 1997)

Important factors relating to the growth of the macrophytes in the wetland system include nutrient availability, metal uptake, translocation and storage by macrophytes, (Debusk et al., 1996). Plant selection is critical. The criteria for plant selection for use in a constructed wetland should be based on previous knowledge of plant characteristics, experience, and scientific literature. Selection criteria for the wetland vegetation include: (1) effect on hydrosol pH and redox, (2) compatibility with selected hydrosol, (3) compatibility with the local climate, (4) ability to withstand hydroperiod fluctuations and changes in hydraulic retention time, (5) resistance to herbivory, (6) cost and availability and (7) nonexotic species. (Hawkins et al., 1997). Also, including a mixture of plant species is advisable to maximize potential metal bioaccumulation (Scholes et al. 1999).

Hydrosol and media selection is another important factor affecting treatment. Selection of media should be based on: 1) appropriate chemical and physical characteristics (ex. organic carbon), 2) ability to adsorb metals while decreasing associated toxicity, 3) minimal background metal and organic contaminant

concentrations, 4) compatibility with selected wetland plant species, 5) availability of nutrients for growth of selected plant species, 6) location/availability, and 7) transportation costs (Hawkins et al., 1997).

2.5. Proposed Treatment of BFS Leachate

It is hypothesized that remediation will occur in two distinct, simultaneous stages. Biological pathways include uptake of constituents by plants, microbial assimilation of soluble constituents, generation of $\text{CO}_2(\text{gas})$ by plants and microorganisms, anaerobic reactions in the lower 25 cm of the wetland, and aerobic reactions in the upper 25 cm. Abiotic pathways include chemical oxidation, precipitation of metal sulfides in the anaerobic zone, and precipitation of sulfate as gypsum in the presence of limestone, and mild acidification due to peat baffles.

Limestone (calcium carbonate, CaCO_3) is an inexpensive, stable, safe and easy chemical substrate for use in a constructed wetland. Crushed limestone is less caustic than lime and would be difficult to overdose in a treatment system, so the application of limestone to the wetland requires minimal calibration. Availability is not an issue, and purchase, delivery, and handling costs are low. Limestone is initially chosen as the substrate of choice in this research to reduce sulfate.

The other substrate, peat, acts as a carbon source necessary for sulfate reduction. In the anaerobic zone of the subsurface wetland, sulfate-reducing bacteria utilize both organic carbon and sulfate as nutrients, producing hydrosulfide ions (HS^-) at pH values

above 7 and thus precipitation of metal sulfides occur. Peat is also acidic and will lower the pH of the leachate. Figure 2.3 illustrates the general approach of this study.

In all wetlands, the upper few centimeters are aerobic, and anaerobic conditions are predominant at depth. This reduced environment is induced by the consumption of oxygen by active microbial pools and the limited diffusion of oxygen to these zones. The redox potentials generated in these zones are low enough to enhance the reduction of sulfate to sulfide; sulfide concentrations in reduced environments often decrease due to the reaction with metals to form metal sulfide solid phases with low solubility.

In the upper zone of the wetland, plant and biological activities will oxidize sulfides to sulfate, and sulfate is subsequently assimilated by these organisms. In addition, the CO_2 (gas) produced by plants and microbes will react rapidly (mostly sodium and calcium hydroxides) to produce bicarbonates, potentially precipitate calcite (CaCO_3), and buffer the leachate pH. The wetlands are designed to operate even if the plants are inactive or absent. This will insure that during the initial months when plant and microbial activities are low and during winter months when plants are dormant, treatment will continue.

For this research, there are several key assumptions; 1) presence and reactivity of calcite (assured by including 10% limestone in the gravel), 2) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) will precipitate. When concentrations of sulfate (SO_4^{2-}) are above 2000 mg/L, a reaction occurs between the limestone and sulfate that produces a solid gypsum (calcium sulfate, CaSO_4) precipitate.

Fully functional wetlands have a high capacity for sulfate reduction. As long as organic carbon is available, these wetlands have the capacity to reduce sulfate to sulfide, which is subsequently precipitated as insoluble metal sulfides and evolved as sulfuric gases. Active wetlands regenerate their own carbon supply through plant detritus, and sulfate reduction is active throughout the winter months (Allen et al., 2002; Fortin et al., 2000).

2.6. Geochemical Modeling Results

The U.S. EPA's MINTEQA2 was used as a geochemical model for this project. The original database was expanded as documented by Lindsay (1979) with additional constants from Smith and Martell. Initially in the investigation of the field site, a simple approach to the geochemical model was to assume that 2500 mg SO_4/L at pH 10 was equilibrated with calcite. If gypsum becomes supersaturated, it will precipitate. The model was directed to assume that the final pH was 8.0, 7.5, or 7.0. The results are shown in Table 2.3. From these results, it is readily apparent that strictly abiotic mechanisms can deplete sulfate below the required regulatory limit of 250 mg/L when the $\text{pH} \leq 7.5$.

The capacity of the cells to remove sulfate can be calculated by assuming an average SO_4^{2-} concentration of 2500 mg/L and 10% limestone by mass. Assuming an

average flow rate of 0.4 liters of leachate per minute, the cells would have the capacity to precipitate gypsum for 32 years.

2.7. Wetland Design

There are a number of considerations with the development and design of constructed wetlands. As with any engineered wetland, the goal is to mimic the functions of a natural wetland. The difficulties in recreating the complexity of natural wetlands must be recognized along with the opportunities to improve the efficiency of some wetland processes such as hydrology and maintaining plant population growth (Williams, 2002). Often, constructed wetlands have been designed without clear objectives or understanding, and utilization of the natural functions and values associated with the primary components of wetlands to accomplish specific purposes (Hawkins et al., 1997). The criteria for selecting wetland systems for treatment should include proper flow control and sufficient land since constructed wetlands tend to be land intensive (Mungur et al., 1997).

An understanding of long-term ecological succession is fundamental once the constructed wetland technology is established in the field. Seasons and weather can be highly variable and cause a shift in plant species composition in wetlands, altering phytoremediation characteristics. Seasonal changes in transpiration rates can change contaminant uptake rates, plume flow regulation by wetland plants, and the performance of treatment (Williams, 2002). When plants shut down seasonally, so does the potential for phytoremediation. Wetland systems of both *Typha latifolia* (cattails) and *Phragmites australis* show seasonal variations in metal concentrations. Both *Typha* and *Phragmites*

tend to contain highest concentrations in summer, followed by spring and winter, with lowest concentrations measured in plants collected in autumn (Scholes et al., 1999).

Another important consideration is the hyperaccumulation of constituents in the biomass of wetland plants (shoots and leaves) within the CW system. If bioaccumulation reaches levels that are toxic to the food chain, then the contaminated biomass must be removed appropriately. If plants accumulate high levels of metals and the litter of the plants degrades, the metal is re-released to the wetland system. Constructed wetland biomass may have to be harvested or otherwise stabilized to prevent further movement of contaminants to aquatic systems (Williams, 2002). Timely harvesting techniques must be utilized to prevent loss of metals-enriched plant biomass if high concentrations in the biomass reach problematic levels. Food chain implications of metals accumulation have not been adequately addressed. There is a clear risk of ingestion, especially by sediment feeding organisms. The accumulation of nonessential metals was studied for crayfish in a wetland environment contaminated with metals and hydrocarbons. The biomass concentrations reflected the concentrations of metals in the sediment (Anderson et al., 1997).

Contaminants also may inhibit microbial growth at specific concentrations. Microbial studies have shown that elevated contaminant concentrations limit the growth and size of microbial communities in and around the root zone (Scholz et al., 2002; Scholz and Xu, 2002; Williams, 2002). The dissolved fraction of metals within the litter zone led to a reduction in bioactivity (ciliated protozoa and zooplankton) (Scholz et al., 2002). The reduction of these bioindicators reflected the accumulation of toxic metals

within sediments and the food chain. This has a negative environmental impact on wildlife associated with wetlands (Scholz et al., 2002).

Metal concentrations also may affect the removal efficiency of other pollutants. Often constructed wetlands are used to treat more than one type of contaminant. Lim et al. (2003) concluded that nitrogen removal may deteriorate progressively with increasing metal loading. The relative effect of the heavy metals was found to increase in the order of Zn, Pb, Cd. The metals seem to exhibit an inhibitory effect on nitrogen uptake by cattails as indicated by lower nitrogen uptake rates compared to rates recorded in wetland systems treating domestic wastewater only (Lim et al. 2003). This may be due to formation of metallic oxyhydroxide plaque layers in the root zone (Ye et al. 1997).

The study of the media and substrate for use in a passive treatment system, such as a natural media biofilter or constructed wetland, is explored in the dissertation by Hunter, 2006. The wetland design used in this research is described in Chapter 4. Based on the literature presented in this section and stated assumptions, it is anticipated the wetland system will successfully remediate slag leachate.

Table 2.1 Constituents of Blast Furnace Slag (Lee 1974; USACE 2002)

<u>ELEMENT</u>	<u>PERCENT Wt.</u>
Lime	36-45% as CaO
Silica	33-42% as SiO ₂
Aluminum	10-16% as Al ₂ O ₃
Magnesium	3-12% as MgO
Sulfur	1- 3% as S
Iron	0.3-3% as FeO or Fe ₂ O ₃
Manganese	0.2-1.5% as MnO

Table 2.2 Effect of Aeration on Sulfur Compounds in Leachate (Beeghly, 1972)

	mg/l	Effect of Aeration (Time)
Total Sulfur as S	350-400	Decrease
Sulfates, SO_4^{-2}	50-300	Increase
Sulfite, SO_3^{-2}	10-20	Increase
Thiosulfate, $\text{S}_2\text{O}_3^{-2}$	10-30	Increase
Sulfide, S^{-2}	50-100	Decrease
Polysulfides, SS^{-2}	10-50	Increase

Table 2.3 Sulfate (SO_4^{2-}) and Total Soluble Sulfate as a Function of pH in a System with Sulfate, Calcite, and Gypsum.

Final pH	SO_4^{2-} (mg/L)	Total sulfate (mg/L)	% SO_4 precipitated
8.0	691	768	70
7.5	68	147	94
7.0	7	86	97

Figure 0.1 Blast Furnace Slag Sample from Levy Company (Gary, IN)

Figure 0.2 Transformation Pathways for Physical and Chemical Reactions of Slag Leachate

Figure 2.3 Remediation Approach for Constructed Subsurface Wetland.

CHAPTER 3. CHARACTERISTICS OF SLAG LEACHATE PRODUCED UNDER REDUCED AND OXIDIZED CONDITIONS

3.1. Introduction

Reuse of the slag products has gained popularity (NSA, 1998), but the application must be carefully chosen based on slag characteristics (Gunay et al., 2004; Emery, 2002). The environmental consequences of leachate from slag materials are of concern (Chou et al., 2002; INDOT, 2002; Odeigah et al., 1997). Although slag can form a stable Fe-Mn-Ca silicate material, it is not chemically inert and can significantly impact leachate conductivity and pH (Rastovcan et al, 2000). The elevated lime content of slag will generate highly alkaline solutions when in contact with water, as shown in Equation 4.1. In the presence of $\text{CO}_{2(g)}$, the latter reaction becomes somewhat buffered by the saturation of pore water with, and subsequent precipitation of CaCO_3 (Equation 4.4). Lime, $\text{CaO}_{(\text{lime})}$, initially reacts with water to generate calcium and hydroxide ions and a solution with pH 11 to 13:

Simple hydration of lime generates $\text{Ca}(\text{OH})_{2(s)}$

which in turn dissolves to generate a solution with pH 9 to 10:

As carbon dioxide reacts with these solutions, calcite precipitates and the pH decrease to $\text{pH} \leq 8.5$:

With exception of the use of slag to mitigate acid mine drainage (Drizo et al., 2002; Brubaker and Wilderman, 2001; Yan et al., 2000; Fallman, 2000), an alkaline leachate is generally considered undesirable (Fallman, 2000; Mann, 1997). To alleviate this problem, slag is often stored uncovered outdoors to remove the free (unhydrated) lime through the complete reaction with $\text{CO}_{2(\text{g})}$ (Equation 4.4). After six to nine months of weathering, the free lime content stabilizes at approximately 4% by mass (Thomas, 1979).

Other slag weathering processes are not well understood. The presence of dicalcium silicate indicates that as slag is hydrated, the potential exists to undergo moderate cementation:

In addition, other hydroxyl-poor minerals formed in the low moisture, high temperature environment of the blast furnace, when exposed to the atmosphere, should weather much like primary silicates (Equation 4.6) (Dimitrova, 2000). Weathering of the crystalline structure is both physically and kinetically limited.

The interstitial glass is perhaps the portion of the slag most susceptible to weathering, though this fraction probably represents the least available surface area. In

the initial stages of weathering (pH 7 to 9), hydrolysis reactions begin to attack the weakly polymerized structure, exchanging metal cations such as sodium and calcium with hydrogen ions (USDOT, 2003). As the pH rises (pH 9 and above), the structure is dissolved through removal of the siloxane linkages (Equation 4.7) (Cao, 1989). Dissolution of the interstitial glass is likely the most significant contributor to the presence of dissolved iron, sulfur and silica species. Weathering of three tons of slag can release one ton of SiO_2 (Ceccato, 2002).

Slag often is not aged evenly because of placement in piles with limited exposure to water and $\text{CO}_{2(aq)}$ in the inner portions. Exposure patterns are important in determining weathering reaction pathways, rates and products because these processes control the dissolved constituent concentrations and oxidation-reduction (redox) potential.

As mentioned earlier, slag leachate may have serious environmental consequences (Piatak, 2004). However, there is no representative slag leachate because this type of runoff has variable composition and concentrations due the specific impurities in the ores. Some of the most frequently encountered contaminants, without respect to concentration, include aluminum, arsenic, barium, cadmium, calcium, chloride, chromium, lead, magnesium, manganese, potassium, sodium, sulfur, and zinc (Leuven and Willems, 2004; Shen and Forssberg, 2003; Proctor et al., 2000; Meadowcraft et al., 1996).

The slag reuse application under investigation in this paper is the utilization of weathered slag in highway construction (Rohde et al., 2003; Mahur et al., 1999).

Although there is concern that quartz dissolution by hyperalkaline drainage may result in instability in the structures built on slag material (Bayless and Schultz, 2003), published work addressing the potential environmental impact of slag leachate is limited. In the case investigated here, during construction of Interstate 65 in Northwest Indiana, approximately 60,000 metric tons of slag were used for support of the highway and associated structures. Two years after construction, a green leachate with high pH and a strong sulfur odor began to emerge from an embankment supporting a culvert adjacent to a bike path and lake in a community park.

The primary objective of this experimental study was to identify the chemical processes responsible for leachate production and characteristics at the study site. In addition, the specific effects of oxidizing and reducing conditions on pH and sulfate concentrations in slag leachate were assessed in a laboratory study.

3.2. Materials and Methods

Because slag leachate may be produced under both oxidized and reduced conditions, two batch shaker studies were conducted. Unweathered slag aggregates, provided by the Levy Company (Gary, Indiana), were broken to expose reactive surfaces. Approximately 40 g of this material (excluding fines) were placed in a 250 mL Erlenmeyer flask with 80 g of distilled-deionized water (resistivity of $16 \text{ megaohm cm}^{-1}$, pH 6.33) and capped. While this slag:water ratio (1:2 by mass) is not totally representative of field conditions (1:0.34 based on mass), it was a convenient starting point.

This procedure was repeated thirteen times to produce a total of fourteen flasks. The flasks were then shaken continuously for a specified time. The shaker oscillated at 154 cycles per minute. The light cycle in the room was approximately 12 hours light and 12 hours dark. After the specified time, a flask was removed and the pH recorded for each flask. The simulated leachate was removed from each flask, filtered and analyzed for sulfate by ion chromatography.

To create a reduced environment, the headspace of each flask was purged with argon gas. Sacrifice of the flasks under reduced conditions occurred at days 1, 3, 7, 10, 15, 21 and 34. For the oxidized flasks, the headspace was purged with ambient air. Sacrifice of the flasks under oxidized conditions occurred at days 1, 3, 7, 31, 42 and 85 of the study.

The pH in the simulated leachate was measured using a Ross combination pH electrode which had been calibrated with pH 4 and 7 buffers. Sulfate was analyzed by ion chromatograph (Dionex ED50 Detector with PeakNet 6.4 Software). A sodium carbonate/bicarbonate (2.7 mM Na_2CO_3 /0.3 mM NaHCO_3) eluent with an applied current of 22 mA (ASRS Ultra 4mm Suppressor), resulting in a background conductivity of 14 μS , was used. Samples were diluted 1:10 and an injection volume of 25 μL was used (AS12A Anion Column and AG12A Guard Column).

3.3. Results and Discussion

3.3.1. Chemical Processes Responsible for Leachate Characteristics

Leachate produced at the field site under investigation was at pH 11 to 13, with a green, yellow, or milky-white appearance, and a sulfate concentration of greater than 2000 mg/L with a strong sulfur odor (Figure 4.1, Tables 4.2 and 4.3). As mentioned previously, the physical and chemical reactions responsible for this type of leachate generation are complicated. One hypothesis is that groundwater (or rainwater leaching from the overlying highway) reacts with the slag and hydrates freshly exposed or residual free lime. Alkalinity is rapidly produced, further enabling the interstitial glass to dissolve, resulting in an elevated pH and the release of the major metallic components and sulfur. In this reductive environment, sulfur in solution from the dissolution of oldhamite remains in the sulfide form (S^{2-}). Soluble iron will remain in the reduced form as well ($Fe^{2+}_{(aq)}$).

As groundwater emerges and is exposed to the elevated carbon dioxide in the atmosphere, the leachate will be somewhat pH buffered (Equations 4.8 and 4.9).

Saturation and/or evaporation will encourage precipitation of calcium carbonate ($CaCO_3$), a white solid commonly referred to as tufa (Equation 4.4). In this situation, rate of

decline in pH is more rapid than oxidation. Therefore, sulfide is protonated as the pH drops (Equation 4.10) (Johnson et al., 2003; Beeghley, 1972).

Once exposed to oxygen, dissolved sulfide is oxidized to zero valent sulfur or to any of a series of polysulfides (Stoechr, 1975).

The polysulfide particles are colloidal in nature and will impart a yellow color to the leachate. Calcium bisulfite ($\text{Ca}(\text{HSO}_3)_2$) may also play a role in odor production and coloration.

Further oxidation of sulfur results in the formation of sulfate (SO_4^{2-}), which can react with calcium to form gypsum.

Though the sulfur content of slag is limited to prevent degradation by expansion from the formation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), it is possible for sulfate levels in slag leachate to reach 2000 mg/L and above.

Dissolved iron has been reported to undergo a series complex transformations when groundwater emerges from a reduced environment (Christiansen, 2003; Wilkin, 2001) and is oxidized to form any of several iron minerals. Of particular interest are the

iron phases known as green rust ($[\text{Fe}^{2+}_{(1-x)} \text{Fe}^{3+}_x (\text{OH})_2]^{x+} [x/n \text{A}^{n-} \cdot m \text{H}_2\text{O}]^{x-}$, where $x = \text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, $\text{A} = \text{SO}_4^{2-}$ (group two), CO_3^{2-} (group one), or another anion and m is variable) and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), all green to blue solids (Wilkin, 2003; Wilkin, 2002; Refail, 2001).

Slag-blended concrete (under high pH conditions during formation) has been observed to possess a transient green to blue color, most likely due to the presence of melanterite during curing (Sioulas, 2001). This, along with two other iron hydroxides ($\text{Fe}(\text{OH})_2$ (a green to blue solid) and $\text{Fe}(\text{OH})_3$, as well as FeCO_3 (siderite, a white solid), may be present as colloids during leachate emergence and equilibrium.

Eventually, the leachate will stabilize and/or is flushed away, with iron oxidizing and transforming to goethite (a stable yellow iron mineral under atmospheric conditions), and sulfur to dissolved sulfate or other sulfate minerals. Most of these processes are reversible. It is the unique environment of emergence where the transformation of reduced to oxidized species under high to moderate pH results in the production of a leachate with a hybrid chemistry.

3.3.2. Effect of Oxidation/Reduction on Leachate Characteristics

The results of the laboratory experiment are shown in Figures 4.2 and 4.3. Under both oxidized and reduced conditions, the pH declined gradually over the 2500 hours of the study. Dissolution of minerals in the slag by the highly alkaline solution typically consumes small quantities of the base in both reduced and oxidized conditions. Normally in aerated environments, $\text{CO}_{2(g)}$ reacts rapidly with the alkalinity and results in $\text{pH} < 8.5$. The continued elevated pH in the oxidized flasks is the artifact of the experimental

design: the flasks were not open but were flushed with ambient air periodically. This approach, in retrospect, provided plenty of oxygen (see below) but $\text{CO}_{2(g)}$ was clearly limiting. An unlimited supply of $\text{CO}_{2(g)}$ would have resulted in far greater decreases in pH.

The presence of oxygen in the oxidized flasks resulted in significant accumulation of sulfate, with 225 mg/L produced on the first day to 914 mg/L on day eighty five of the experiment. The net reaction between sulfate and elemental oxygen is shown in Equation 4.11. A typical ion chromatogram for a flask under oxidized conditions is shown in Figure 4.4.

Sulfate in the reduced system decreased slowly over time. Under reduced conditions, the reaction in Equation 4.12 would be expected to proceed from right to left: sulfate would be transformed to sulfide. Some unknown compounds were produced in the reduced flasks, as shown in the chromatogram (Figure 4.5). The peak emerging at 3 minutes may be a form of reduced sulfur and the primary anionic product in this system. The characteristic green color developed and remained in the leachate only in the reduced flasks. The color remained after filtering, was concentrated near the bottom of the flask, and appeared to flocculate under stagnant conditions. In addition, only the simulated leachate from the reduced flasks developed a sulfur odor.

3.4. Conclusions

Leachate from slag in highway foundations is formed by a combination of physical and chemical processes under fluctuating oxidized and reduced conditions. As confirmed by the laboratory investigation, only under reduced conditions is the green

color and odor observed in the slag leachate. While sulfate levels increased as expected under oxidizing conditions, concentrations were reduced in the absence of oxygen. In addition, slag to water ratios may play an important role in leachate formation.

Table 3.1 Representative Blast Furnace Slag Composition.

Constituent	Composition (%)
CaO	32 to 45
SiO ₂	32 to 42
Fe	0.1 to 1.5
FeO	0.07 to 1.2
Fe ₂ O ₃	0.02 to 0.45
MnO	0.2 to 1.0
MgO	5 to 15
Al ₂ O ₃	7 to 16
S (typically CaS)	1 to 3
Metallic Fe	<1

Table 3.2 Chemical Characteristics of Leachate Generated at the Northwest Indiana Study Site.

Property	Min	Max
pH	4.8	11.5
	----- (mg/L) -----	
Alkalinity	5	370
Al	0.16	8.3
As	0.0069	8.014
Ba	0.11	0.46
Ca	N/A	N/A
Cr	0.014	0.019
Pb	0.025	0.029
Se	0.01	0.15
SO ₄ ²⁻	660	2600

Table 3.3 Trace Elements in Water After 21 Days of Exposure to Slag.

Element	Leachate Concentration (mg/L)
Aluminum	1.11
Arsenic	0.11
Boron	9.19
Beryllium	0.05
Calcium	331.33
Cadmium	0.34
Chloride	35.05
Cobalt	00.01
Chromium	No Detection
Copper	0.15
Iron	0.82
Lithium	0.52
Magnesium	No Detection
Manganese	0.06
Molybdenum	0.011
Sodium	124.72
Nickel	0.0005
Sulfur	>2000
Selenium	No Detection
Silica	7.23
Zinc	0.16

Figure 3.1 Slag Leachate Generated at the Study Site.

A

B

Figure 3.2 pH Changes Under Oxidized (A) Conditions and Reduced (B) Conditions.

Figure 3.3 Sulfate Changes Under Oxidized (A) and Reduced (B) Conditions.

Figure 3.4 Chromatogram for Laboratory Generated Leachate Produced Under Oxidized Conditions for 42 Days.

Figure 3.5 Chromatogram for Laboratory Generated Leachate Produced Under Reduced Conditions for 34 Days.

CHAPTER 4. FIELD ASSESSMENT OF A CONSTRUCTED WETLAND USED FOR SLAG LEACHATE REMEDIATION

4.1. Introduction

The use of recycled materials for highway construction is an area that has gained increasing attention, and it is recognized that the reuse of industrial by-products and waste materials has many practical benefits, providing a stream of revenue for producers and provides the end user with durable, cost-effective materials. However, when these materials are used in the highway environment, a number of considerations have to be taken into account. Some of these materials, including blast furnace slag, steel slag, coal fly ash, waste glass, building rubble, rubber tires, are not always inert chemically, and their eventual placement in the environment compounded with nature's weathering effects, can lead to leachate that could affect aquatic and terrestrial environments (Ahmed 1993).

Blast furnace slag is a popular recycled material often used in the highway environment as fill material for transportation support structures. This by-product of the iron industry offers many benefits including use as a fill aggregate, road base, concrete aggregate, railroad ballast, glass manufacture, mineral wool, liming agent, treatment media, products (Solomon, 1995). However, the use of unweathered BFS as fill in an area prone to stagnant water and constant interaction with water, can lead to the impairment of water quality. The leaching of calcium, sulfur, and other impurities of problematic BFS may lead to objectionable color (green/yellow), odor (H_2S), and

precipitation (tufa), as well as increase the concentration of total dissolved solids (TDS), COD, and alkalinity (Gross and Cooper, 1968; Beeghley, 1972; Yassni, 1996; Roadcap et al., 2005). Other elements in the BFS matrix that often appear in the leachate include some of BFS's major components: aluminum, calcium, iron, manganese, magnesium, and silicon, as well as minor impurities such as arsenic, barium, boron, chromium, lead, phosphorus, potassium, sodium, sulfur, and titanium (Vom Ende et al., 1965; Bayless et al., 1998; Proctor et al., 2000; Roadcap et al., 2005).

Few studies have investigated mitigation of the problematic nature of slag leachate (Boyer, 1994; Roadcap et al., 2005). The occurrence of this problem is limited, but when it has occurred resulting in undesirable conditions, it has led to costly dilemmas for state agencies. For example, slag leachate occurred in Baltimore, Maryland on I-695 with slag used as embankment fill. Discharge water had a pH of 12.5 to 13 with calcareous tufa precipitate. The Maryland State Highway Administration remediated this area at a cost in excess of \$1,000,000 in 1994.

The purpose of this research is to demonstrate the use of a constructed wetland and its related support media/substrate as a viable option for remediation to reduce the problematic characteristics of BFS leachate. These systems utilize the physical and biological processes, together with geochemical precipitation and transformation, to achieve treatment. Treatment for constructed wetlands is often dependent upon operating conditions where the type of media, plants, and amendments used, as well as retention time and system depth may affect optimal treatment capacity.

In the pilot study investigated in this research, construction on I-65 in Northwest Indiana led to the use of approximately 60,000 metric tons of slag as support for the

highway and associated structures. Two years after construction, it was reported that a green/yellow leachate with high pH, tufa precipitate, and “rotten egg” odor began to emerge from an embankment supporting a culvert adjacent to a bike path and lake in a community park. There were also concerns with regard to concentration of arsenic, lead, and other metals found in the leachate at this site.

4.2. Background of Field Study

On October 18, 2001, Indiana Department of Environmental Management (IDEM) was notified regarding a greenish liquid with a rotten egg odor, discharging from a box culvert part of a newly installed bike path, which runs under Interstate 65 north of interchange 255. IDEM investigated the discharge and determined that the liquid and odor was leachate generated by the reaction of water and slag, which had been used for backfill around the box culvert. Slag is a by-product of the steel mill industry and is an exempt waste in Indiana, it is beneficially reused for structural fill material. Based on field observations and laboratory analyses, IDEM determined that the leachate was objectionable due to pH, color, metals, and sulfate. As an initial response, IDEM and INDOT applied peat to the leachate and INDOT constructed earthen containment areas to prevent the release of the leachate to the adjacent surface water. The culvert of interest is located in Hobart, Indiana under I-65 (see Figure 4.1). The constructed wetland was placed on the southeast corner of the culvert. Analysis showed that pH, sulfate, aluminum, arsenic, and lead exceeded IDEM surface-water quality standards. For this site, a constructed wetland was designed to retain (zero effluent) and treat leachate by

chemical and biological processes facilitated by the wetland plants, media, hydraulic depth, and microbes.

4.2.1. Site Description

At the I-65 site, a concrete box culvert serves as a tunnel for a bike path under Interstate 65 (Figure 4.2). The bike path was built on a former railroad grade, which runs east to west. The box culvert is approximately 3.7 meters wide, 3.4 meters high and 72.8 meters long, traveling under six lanes of traffic. On either end of the box culvert are concrete buttresses. The concrete buttresses on the east end have two rows of weep holes located approximately six-inches and three-feet above ground level, respectively. The floor of the box culvert is constructed of concrete and has a gentle slope from the middle to each end and is slightly crowned, sloping from the middle to each wall.

The road surface of I-65 is approximately 6.4 meters above the surface of the bike path. The sides of the interstate slope steeply down to ditches that run along each side of the interstate. The ditch, which runs along the east side of I-65 drains from the south to the north, is divided by the bike path. The south portion of this east ditch drains to the bike path, travels along the path for approximately 15.2 meters and through a drainage pipe under the path, which drains into Robinson Lake. The north portion of the east ditch drains toward the north away from the path to a low spot.

During the original construction of I-65, a bridge extended over the former railroad tracks. With the railroad tracks no longer in use, the bridge was removed during the renovation of I-65 from interchange 255 (61st Street) to interchange 259 (I-80/I-94).

The former railroad grade was converted to a bike path and a box culvert was installed surrounded by 'B' Borrow fill material (slag) to replace the bridge. A 36-cm layer of slag was also used as subbase under the interstate pavement.

The surrounding area has a flat topography with an average elevation of 200 meters above sea level. Adjacent to the box culvert to the northeast is a park and Robinson Lake. The lake is approximately 61 meters from the box culvert. Pasture land and small wooded areas are located adjacent to the box culvert toward the southeast and southwest. A residential area is located to the northwest.

The containment phase of corrective action consists of collection of all visible free liquids that have been impacted by the slag, removal of all contaminated debris (primarily peat), sealing of box culvert joints, and removal/restoration of 15.2 meters of the bike path at either end of the box culvert. The collection phase includes the installed weep holes, collection piping, and weir box for flow measurement.

4.2.2. Chemical Characteristics of BFS Leachate

BFS leachate generated at the I-65 site exhibits a high pH. The pH of the leachate collected on-site at the weir box typically is between 6 and 11, depending on the flow rate. Sulfate concentration at the weir box has been measured as high as 2100 mg/L (July, 2003). Table 4.1 shows the analysis of leachate collected at the I-65 site prior to treatment (October, 2002).

4.2.3. Constructed Wetlands Design and Construction

The complete remediation system for the I-65 Box Culvert Site includes a leachate collection system and zero-effluent constructed wetland. The construction of the wetland system involves removal of the existing peat bags and grading the wetland area; liner installation in wetland bed; application and layering of the gravel layers with peat bag (currently on-site) baffles; retention berm (with height of 0.6 meters); connection of the collection system to the wetland inlet; planting of wetland species; wetland outlet and drainage controls; and securing the site (fence).

The collection phase consisted of placing 3.8 cm diameter weep holes into the walls of the box culvert, approximately eight feet on center. Installation of piping into the weep holes connects to two trunk lines running along the inside walls of the box culvert. Schedule 80 polyvinyl chloride (PVC) piping was used for the weep hole piping and the trunk line piping. The trunk line piping was anchored to the wall and sloped from the east end of the box culvert to the west end. Heat tape and insulation was wrapped around above ground piping, to prevent freezing during cold temperatures. A protective guardrail was installed over the piping to protect it from vandalism. Full construction of the wetland structure and piping was completed by Walsh Construction Company (LaPorte, IN).

All piping led to a weir box to quantify flow and distribution into the subsurface wetland. The weir box contains a 22.5° V-notch weir for flow measurement. An Isco 4220 flow meter system was installed by Gripp Inc. (Indianapolis, IN). The flow meter measured influent flow, internal level, pH, and influent temperature.

The weir box was connected to a perforated 4" distribution pipe in the wetland. The wetland has a base width of 8.5 meters and is 30.5 meters long. At the 16.8 meters length, the width is reduced to 3.0 meters wide at the outlet. The wetland was excavated 61 cm deep and filled with 30.5 cm 3.8 – 7.6 cm washed gravel, with 10% of this layer was comprised of limestone. The top 30.5 cm layer of the wetland was designed to hold 1.0 – 2.5 cm. gravel. The wetland was designed with a 1% slope from the inlet and outlet.

Peat bag baffles are placed within the first half of the wetland. The purpose of the peat bag baffle is three-fold: 1) To extend the flow path of the leachate in the wetland, creating an extended travel time towards the outlet; 2) To provide a carbon source for sulfur reducing bacteria; and 3) To reduce pH using the organic acids in the material. The wetland was built to replace the previous improvised retention structure that included peat bag barriers, and provide treatment via a subsurface wetland design. The wetland cell was proposed to be zero-effluent in light of permitting concerns, anticipated low influent events, and the experimental nature of the proposed treatment.

4.2.4. Selection of Plants

Plants can play an integral part in the treatment processes in constructed wetlands. The submerged surface area provides structure for the accumulation of microorganisms that are largely responsible for biological treatment. The emergent leaves provide shading and act as wind blocks, while the deposits created by plant litter provides a carbon source for microorganisms and thermal insulation. The plants fix atmospheric carbon into organic structures that provide inputs of different carbon materials into the

water, in addition to those materials already present in the water. The plants also can utilize trace constituents from the water for growth. Consideration must be given to rooting depth, invasiveness to populate other sections of the system, and tolerances to ranges of pH, salinity, metals, and other stressors from impacted water.

4.2.4.1. Plant Growth at I-80/94 Underdrains

Wetland trenches were constructed during the summer of 2002 as a remediation trial and plant selection study along Interstate 80/94. This study was used as a qualitative investigation to determine which plants to use for the I-65 pilot study site. Under-weathered slag material was also used in the construction around the drains under I-80/94 and generated similar unsightly leachate with odor. The resulting reactions from the BFS leachate produced a black residual and rotten egg odor, thought to be from sulfate/sulfide reaction, as well as elevated pH and TDS observed in water samples (Appendix B).

The remedial action for I-80/94 was designed for planted wetland trenches. The wetland trench functioned as a narrow wetland cell to treat the slag leachate. Six drains under I-80/94 were used as points for remediation. Each of these drains had wetland cells 1.2 meters from the effluent pipe. The cells have a base width of 1.2 – 1.5 meters and were 6 meters long. The trench was excavated 45-cm deep and filled with 30 cm of 2.5-4 cm washed gravel, 10% of this layer was comprised of limestone. The top width of the cells was 1.5 – 1.8 meters, with a 15 cm top layer of pea gravel. The cell's influent and effluent slopes are 1:1 (Appendix B).

Plants selected for this study were to have the following characteristics: 1) Plants were to be noninvasive and not spread beyond planted borders. 2) Selected plants were tolerant to elevated pH. 3) Plants were to be tolerant to elevated salinity ranges. 4) Plants tolerated variable conditions such as shades and possible drought conditions. Tables 4.2 and 4.3 show the plants considered and plants used in the trial (Appendix B). From the study, only the *Scripus validus* (soft stem bulrushes) consistently grew in the leachate and established lush sections in each plant trench. *Typha angustifolia* (cattails) originally considered for planting at the I-65, were not planted for this trial due to possible invasive concerns, but these plants had naturally established themselves on I-80/94 and were considered for their persistence in this stressed area. *Phragmites spp.* (reeds) also became established in most wetland trenches and grew quite aggressively. Although *Phragmites* are often used in constructed wetlands projects, these plants are considered an invasive wetland plant species in Indiana and were not considered for this study. The *Phragmites* were harvested upon each visit.

4.2.4.2. Vegetation at I-65 Field Site

For this project *Typha angustifolia* (cattails), *Scripus validus* (soft stem bulrushes), and *Carex comosa* (sedges) were used because of root structure and tolerance to higher pH in water (Allison, 2002; Thunhorst, 1993). Cattails (*Typha angustifolia*) were planted in the first third of the wetland, followed by soft stem bulrushes (*Scirpus validus*) in the middle portion of the wetland, and lastly, bottlebrush sedges (*Carex comosa*) in the last third. Wetland plants were transplanted at 0.3 meter centers with

staggered rows throughout the length of the wetland cell. Figures 4.3 through 4.5 illustrate the design of the subsurface wetland.

4.3. Materials and Methods

For the field investigation, a series of appropriate sampling procedures were employed to ensure samples for dissolved constituents gathered from the field were representative and remained so until analysis. As mandated by INDOT, chemical species of initial concern to human health (pH, lead (Pb), arsenic (As)), as well as those seen as species related to hydrogen sulfide formation (sulfate and total sulfur) were monitored on a monthly basis. In addition, other metals were monitored including aluminum, barium, calcium, iron, magnesium, manganese, and zinc, as well as other water quality parameters such as total dissolved solids, oxidation reduction potential (ORP), and conductivity. As a result, two separate sampling procedures were developed.

Grab samples are collected for water quality constituents requiring analysis in a laboratory. During the last week of each month, grab samples were taken from the wetland sampling points (Figure 4.5). At each sampling well, water was evacuated through the slotted PVC pipe at about a 5 liter volume.

Water samples were taken at the influent, effluent, and at the 21 sampling wells within the wetland and analyzed for dissolved sulfate concentrations, metal concentrations, and total sulfur. Field pH, temperature, conductivity, dissolved oxygen (DO), oxidation-reduction potential (ORP), and total dissolved solids (TDS) were measured at the time of collection with an YSI 556 Multi Probe System. The sample was

field filtered through a 0.2 μm Millipore filter to remove any suspended organic matter colloids and bacteria. Two filtered water samples were taken at each sampling point: one taken for sulfate analysis and one 50-mL sample was collected, acidified to $\text{pH} < 2$ with 5 mL 10% HNO_3 , and used for elemental analyses.

Samples were bottled, and preserved on ice for transport back to the lab. Water quality analysis was performed at Purdue University Soils Lab. Sulfate was determined by ion chromatography (IC). Metals (lead and arsenic) were determined by atomic absorption spectrophotometry (AAS). Common impurities found within the slag matrix by Proctor et al. (2000) were used as the baseline for subsequent analysis of trace elements (including arsenic, aluminum, barium, boron, calcium, iron, magnesium, manganese, sulfur, and zinc) analyzed by inductively coupled plasma (ICP) method.

Samples taken for metals analysis were to be filtered through a 0.2 μm regenerated cellulose filter in the field. The purpose of immediate filtering while in the field was two fold. First, this would prevent carryover of artifacts from the sampling method such as target species associated with suspended organic matter. Secondly, the filtration would sterilize the sample to prevent microbially mediated transformations of target species.

Samples for metals were collected in plastic containers and acidified with nitric acid to pH less than 2. Plastic was used to discourage partitioning of these target species on to the container walls. Nitric acid (HNO_3) was utilized to ensure dissolved metals would remain in solution and prevent formation of any irreversibly insoluble compounds.

In the case of sulfate, samples were field filtered for the reasons discussed above. Conversely, no acidification took place. Furthermore, translucent, amber glass vials with

autosampler septa were used to prevent inclusion of air in the sample, as well as to limit the amount of light transferred into the sample as sulfur is very sensitive to redox transformations, both spontaneous and microbially mediated.

As a means to detect any possible contamination of samples, both procedures utilized sample duplication, as well as field and pump blank analysis. Field blanks from filtered water (resistivity $\sim 16 \text{ MegaOhm} \cdot \text{cm}^{-1}$, pH ~ 6.33) were taken to the field and put through the sampling procedure with exception to the pumping process.

Once collected, samples were put on ice and returned to the lab for analysis. Each analytical method further duplicated five random samples in an attempt to detect any inconsistency in the analytical processes. Samples for metals were analyzed by graphite furnace (Shimadzu AA 6800 with GFA EX7). For lead, a 10 mg/L magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) matrix modifier was used. For arsenic, a 10 mg/L nickelous nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) matrix modifier was used. Both procedures utilized manufacturer programmed (Wizaard 2.3 Software) vaporization cycles.

Samples for sulfate were analyzed by ion chromatograph (Dionex ED50 Detector with PeakNet 6.4 Software). A sodium carbonate / bicarbonate ($2.7 \text{ mM Na}_2\text{CO}_3 / 0.3 \text{ mM NaHCO}_3$) elluent with an applied current of 22mA (ASRS Ultra 4mm Suppressor), and resulting in a background conductivity of $14 \mu\text{S}$ was employed. Samples were diluted 1:10 and an injection volume was $25 \mu\text{L}$ was used (AS12A Anion Column and AG12A Guard Column). Analyses were run under ambient thermal conditions.

4.4. Results and Discussion

Construction of the wetland cell began in September of 2002 and concluded with the installation of the weir box and flow monitoring equipment in March of 2003. Planting of cattails, bulrushes and sedges was completed in May of 2003. The monitoring of the constructed wetland started in April of 2003 and concluded in May of 2005. Photographs of the construction, planting, and operation of the study are shown in Appendix D.

4.4.1. Site Hydrology

The inflow collected from the embankment to the wetland cell is shown in Figures 4.6, 4.7, and 4.8. These figures respectively show the max flow, average flow, and cumulative flow at the site. In Figure 4.9, a line is drawn to indicate that when the area experienced accumulated rainfall >7.5 cm for a month, most inflow events were recorded from the flow meter. Influent into the wetland can be associated with the monthly precipitation recorded for Northwest Indiana and the groundwater table recorded by USGS (Figure 4.10). The resulting precipitation, along with snowmelt events during the winter thaw, and high, fluctuating water table for the area, contributed to unfavorable ground conditions that are highly cautioned for slag placement (Boyer, 1994, Griffiths, 2002). Figures 4.11 and 4.12 are illustrations of slag placement supporting the I-65 embankment and how the BFS material may be exposed to the fluctuating groundwater and perched water tables within in the structure. The resulting interaction leads the emergence of leachate pools from the embankment.

During the planning phase of the field site, it was determined that the wetland would be act as a zero-flow containment cell. It was assumed that the zero-flow cell would handle the expected inflow and that a minimal amount of leachate (<1900 liters max. from cumulative yearly rainfall events) would be collected from the box culvert collection system that fed the constructed wetland. Figure 4.8 shows that the cumulative inflow to the wetland was in excess of 45,425 liters (12,000 gallons) at the beginning of 2005. The result was a small overflow and tufa precipitation was found at the edge of the outlet side of the wetland (See Appendix D).

In November of 2005, an attempt was made to determine the hydraulic retention time in the wetland cell. A rhodamine dye tracer test was conducted to determine the travel time of two pulses of dye released from the inlet and at the center the wetland. Only a slight response was measured after 7 days from the center of the wetland to the outlet (Figure 4.13). The travel time can best be described as variable, depending greatly on the inflow.

4.4.2. Water Quality Measurements

The following water quality measurements were recorded for the wetland site: pH, ORP, temperature, total dissolved solids (TDS), salinity, sulfate, total sulfur, calcium, target metals (Al, As, Ba, Fe, Mg, Mn, Pb, and Zn). Each constituent has three associated figures, (a) monthly average, minimum, and maximum values recorded in the wetland cell, (b) measurements that start from the inlet to cell's end for end month, (c)

measurements separated by planted sections and by sections before and after the retention berm.

4.4.2.1. Temperature

The temperature recorded within the wetland followed the expected trend during the January to July, with temperature increases with seasonal changes and decreases following the summer months. The temperatures show slight convergence towards the end of the containment cell. The section planted with cattails had the highest temperature, mostly likely as a result that this section had less biomass cover as compared to the emergent soft stem bulrushes. The more cover offers shade from sunlight to the wetland surface.

4.4.2.2. pH

The fluctuations in pH are due to influent events are the result of rainfall and flow from elevated groundwater table. Interestingly, pH through the wetland from the inlet to the cell's end, converge towards a neutral range between 6 and 8, as previously targeted for treatment. This buffering effect could be due to a variety of reasons. A prevalent effect may be carbonate buffering. This is related to a number of interrelated sources: the dissolution of limestone; atmospheric CO₂ diffusion; and the precipitation of calcite from slag leachate with the release of protons (Roadkap 2005, Lindsay 1979). CO₂ diffusion from the atmosphere and respiratory processes from plants and microorganisms, forms carbonate species of carbonic acid (H₂CO₃) and bicarbonate (HCO₃⁻). This buffering

effect lowers pH within the wetland. Other reasons for pH reduction of the leachate include the interaction with the acidic peat material, and dilution.

4.4.2.3. Oxidation Reduction Potential

Field measured ORP gives a qualitative sense of the redox conditions in the wetland system. The ORP measurements readings indicate that the wetland system appears to become more reduced over time. The average ORP values measured for the wetland from 2003 to 2005 were -307.0 mV, -358.4 mV, and -442.0 mV, respectively. This is in agreement with observations from other constructed wetland studies, where the wetland becomes more reduced due to maturity (Machemer *et al.*, 1993, O'Sullivan *et al.*, 2004). This maturity results from the turnover of substrate and biomass in the wetland. From vegetative growth, it is calculated that approximately two thirds of plants become fully decomposed contributing organic carbon for microbial reductive processes, thus maintaining a reduced, anaerobic environment (Mitsch and Gosselink, 2000, O'Sullivan *et al.*, 2004).

4.4.2.4. Total Dissolved Solids and Salinity

TDS and salinity are two similar measurements that measures dissolved salts (primarily calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) metals, cations, anions, and small amounts of organic matter in water. The measures can be used interchangeably, salinity is used to reference plants survivability and TDS is a commonly used water quality measure. Both of these values are shown in Figures 4.23-

and 4.28. TDS and salinity show very similar trends in 2003, as the values for each month converged to 2.27-2.98 g/L for TDS and 1.85-2.47 ppt for salinity. At row 5, the boundary measurement at the retention berm, concentrations reflect a slight increase for both measurements. Afterwards, some spill over and dilution over the retention berm occurs into the last third of the cell.

During 2004, TDS and salinity concentrations reflect the pulses of influent into the wetland recorded during the spring to mid summer months where precipitation was near or above 3 inches. TDS and salinity throughout the wetland was above 3 g/L and 3 ppt for those measurements, respectively. Throughout the months of late summer to fall months, when precipitation was below 7.5 cm, small to no pulses of influent were recorded. The resulting TDS and salinity values actually decrease in the wetland below 3g/L and 3 ppt for those measurements, respectively, under the low to no flow conditions.

In 2005, large pulses of influent were recorded for the wetland, and this is reflected in the increase in concentrations recorded during between March and May. Interestingly, a slight decreasing trend is seen with the TDS and salinity concentrations along the flow path through the dense bulrush and peat bag baffles sections prior to row 5. This may be evidence of mitigation of these concentrations due to the interaction with the organic substrate and rhizosphere, thus increasing adsorption and precipitation of dissolved constituents.

4.4.2.5. Sulfate, Total Sulfur

Similar to the trends encountered with TDS and salinity measurements, sulfate treatment and concentrations are functions of inflow events and retention time between those events. This would be expected because sulfate is one of the dissolved constituents that comprise TDS. The best treatment for sulfate was recorded during 2003, when the total flow at the time of the last sample collection was < 7500 liters. Sulfate within the wetland cell converged towards < 500 mg/L at the end of the cell, with increases at the end of the cell mostly due to salt buildup. Months that experienced rainfall and hydrologic conditions that would produce influent into the wetland, had higher sulfate and total sulfur values. Periods of low to no flow during drier months also resulted in decreased sulfate and total sulfur measurements. This is due in part to the increased time between low or zero influent pulses, allowing for further microbial sulfate reduction, along with precipitation of metal sulfides, sulfur minerals, and volatilization of sulfuric gases (O'Sullivan et al., 2004).

4.4.2.6. Primary and Trace Elements

Primary elements expected to be found in BFS leachate include Al, Ca, Fe, Mg, and Mn and selected trace element expected to be in solution that were analyzed include As, Ba, Pb, Zn (Roadcap et al., 2005). The results for the elements are shown in Figures 4.35 through 4.62.

There was an initial concern for As and Pb concentrations, particularly As, that recorded as high as 8.014 mg/L (Table 4.1) at the field site prior to the wetland's construction. Arsenic occurs naturally in groundwater in this area at concentrations from

1-50 $\mu\text{g/L}$ (Ryker, 2001). However, it should be noted that because of its chemistry, arsenic becomes more mobile under reduced conditions and elevated pH (Dixit and Hering 2003). High pH resulting from BFS leaching may allow more arsenic to become more available in groundwater in areas where arsenic naturally occurs. Subsequent analysis during 2003 and 2004 did not identify elevated As in weir box samples.

Some reduction due to flow path and retention can be seen with Al, As, Ca, Pb, Zn. These reductions in concentration of metals may occur because there was some accumulation in substrates (plants and/or peat). It is possible that adsorption to organic matter precedes other biological, chemical, and physical processes since cation exchange reactions resulted in a “sponge” effect typically seen in newly created wetlands (O’Sullivan et al., 2004). Other elements like Mg and Mn, tended to accumulate towards the end of the wetland cell, due to either release of these cations from peat and/or the dissolution of these cations from particulate matter and precipitates of BFS leachate.

4.5. Conclusions

The pilot study at the I-65 site in Hobart, IN, was conducted to evaluate the use of a subsurface constructed wetland to treat emerging leachate from the slag-based embankment. The use of the constructed wetland proved to be effective in reducing a number of constituents that impact water quality, including pH, TDS, salinity, sulfate, and some elemental constituents of BFS leachate. The system worked best under low flow conditions and extended retention times between pulses of leachate received into the wetland. The zero flow restriction of the system retained the leachate within wetland cell, probably resulting in elevated concentrations of salts and metals. Treatment of BFS

leachate could improve using a flow through system that utilizes various capable options: reciprocating flow regime, more or different organic substrate, and segmentation to utilize both aerobic and anaerobic processes. A better understanding of the speciation of target pollutants would also be beneficial in determining their fate and availability for retention or transformation.

Table 4.1 INDOT Analysis of Leachate Adjacent to Bike Path in Robinson Park (October 2001)

	Min	Max
pH	4.8	9.5
	(mg/L)	
Alkalinity	5	370
Al	0.16	8.3
As	0.0069	8.014
Ba	0.11	0.46
Ca	N/A	N/A
Cr	0.014	0.019
Pb	0.025	0.029
Se	0.01	0.15
SO₄⁻²	660	2600

Table 4.2 Analysis of Leachate of BFS Leachate Sampled from the Weir Box (May 2003 –May 2005)

Parameter	Unit	Average	Min	Max
pH		8.74	3.93	13.67
TDS	g/L	9.05	3.17	11.33
Total S	mg/L	1624.36	909.00	2600.00
sulfate	mg/L	903.42	418.82	2098.77
Sulfide*	mg/L	830.00		
Alkalinity*	mg/L	1500.00		
COD*	mg/L	5500.00		
Chloride*	mg/L	2500.00		
Fluoride*	mg/L	BDL		
Nitrate*	mg/L	BDL		
Nitrite*	mg/L	BDL		
Phosphorus*	mg/L	0.10		
Sodium*	mg/L	1500.00		
Potassium*	mg/L	2100.00		
Al	mg/L	1.71	0.18	6.27
As	mg/L	BDL	BDL	BDL
Ba	mg/L	0.49	0.00	1.17
Ca	mg/L	898.09	747.20	1105.20
Cr*	mg/L	BDL		
Fe	mg/L	1.23	0.00	6.10
Mg	mg/L	2.44	0.00	10.31
Mn	mg/L	0.09	0.00	0.51
Pb	mg/L	BDL	BDL	BDL
Se*	mg/L	0.37		
Si*	mg/L	5.50		
Zn	mg/L	0.94	0.00	3.40

* From sample collected November 2004, analyzed by Heritage Environmental Laboratory, Indianapolis, IN.

BDL –Below Detectable Limit

Table 4.3 Alternate/Additional Species Based on the Adaptive Modes and Tolerance to Elevated pH

Alternate/Additional Species suggested by J.F. New Nursery			
Genus	Species	Common Name	pH- range
Cephalanthus	occidentalis	Button bush	6.0-8.5
Comus	obliqua	Silky dogwood	5.5-8.5
Comus	stolonifera	Red osier dogwood	5.5-8.5
Distichliis	spicata	Spike grass	4.1-9.5
Juncus	remerians	Black needle rush	3.5-9.5
Juncus	torreyi	Torreys rush	Alkali tolerant
Scirpus	cypernus	Wool grass	5.0-8.0
Scirpus	validus	Soft stem bulrush	6.5-8.5
Spartina	pectinatus	Prairie cord grass	4.5-8.5
Typha	angustifolia	Narrow leaved cattail	8.5

Table 4.4 Plant Provided by J.F. New Nursery Used at I-80/94 Under Drains Site

Species provided by J.F. New Nursery			
Genus	Species	Common Name	Notes*
Eleocharis	palustris major	Great spike rush	Tolerates alkaline soils & fresh-brackish water
Scirpus	validus	Soft stem bulrush	pH preference 6.5-8.5, Salinity up to 5 ppt
Scripus	fluviatilis	River bulrush	Salinity less than 0.5 ppt
Silphium	perfoliatum	Cup plant	-
Carex	lurida	Lurids sedge	Salinity less than 0.5 ppt
Andropogon	sorardii	Big blue stem	Salinity less than 0.5 ppt
Spartina	pectinatus	Prairie cord grass	Salinity less than 3 ppt

* Thunhorst, G.A. (1993). Wetlands Planting Guide for the Northeastern United States. St. Michaels, Maryland. Environmental Concern Inc.

Figure 4.1 I-65 Field Site Located 2.4 km North of Exit 255 in Hobart, IN.

Figure 4.2 Bike Path Leading to Concrete Box Culvert. Leachate is shown accumulating adjacent to bike path.

Figure 4.3 Design of the Constructed Wetland. A 25 cm peat bag barrier was located in the middle of the wetland to retain water in the upper half of the cell.

Figure 4.4 Layers of Gravel Media as a Function of Depth. Mulch layer is optional for thermal cover and reduction of odors.

Figure 4.5 Planting and Sampling Layout for the Wetland. Sampling occurs are throughout the wetland and samples are taken between the peat bag baffles. There are 23 total sampling points.

Figure 4.6 Average Flow (gallons per day)

Figure 4.7 Max Flow (gallons per day)

Figure 4.8 Cumulative Inflow Volume (May 2003 –Jan 2005)

Figure 4.9 Precipitation Daily Average Crown Point & Lowell and Monthly Northwest Indiana. Dashed line indicates probable inflow events, above 7.5 cm (3 inches).

Figure 4.10 Groundwater Table Levels (ft) at Selected Wells Local to the I-65 Wetland Site in Hobart, IN. (Data obtained from USGS website)

Figure 0.11 Typical Embankment. BFS fill for the subbase.

Figure 4.12 Groundwater and Embankment Interaction Schematic. Adapted from Boyer 1994

Figure 4.13 Response During the Rhodamine Dye Tracer Test.

Figure 4.14 Temperature Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.15 Temperature Variation as Function of Time and Positions in Field

A) Temperature Distribution in Planted Sections

B) Temperature Distribution in Main Sections

Figure 4.16 Temperature Distribution in Planted and Main Sections

Figure 4.17 pH Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.18 pH Variation as Function of Time and Positions in Field

A) pH Distribution in Planted Sections

B) pH Distribution in Main Sections

2003

2004

2005

Figure 4.19 pH Distribution in Planted and Main Sections

Figure 4.20 Oxidation Reduction Potential Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.21 Oxidation Reduction Potential Variation as Function of Time and Positions in Field

A) Oxidation Reduction Potential Distribution in Planted Sections

B) Oxidation Reduction Potential Distribution in Main Sections

2003

2004

2005

Figure 4.22 Oxidation Reduction Potential Distribution in Planted and Main Sections

Figure 4.23 Total Dissolved Solid Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.24 Total Dissolved Solid Variation as Function of Time and Positions in Field

A) Total Dissolved Solid Distribution in Planted Sections

B) Total Dissolved Solid Distribution in Main Sections

Figure 4.25 Total Dissolved Solid Distribution in Planted and Main Sections

Figure 4.26 Salinity Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.27 Salinity Variation as Function of Time and Positions in Field

A) Salinity Distribution in Planted Sections

B) Salinity Distribution in Main Sections

Figure 4.28 Salinity Distribution in Planted and Main Sections

Figure 4.29 Sulfate Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.30 Sulfate Variation as Function of Time and Positions in Field

A) Sulfate Distribution in Planted Sections

B) Sulfate Distribution in Main Sections

Figure 4.31 Sulfate Distribution in Planted and Main Sections

Figure 4.32 Sulfur Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.33 Sulfur Variation as Function of Time and Positions in Field

A) Sulfur Distribution in Planted Sections

B) Sulfur Distribution in Main Sections

Figure 4.34 Sulfur Distribution in Planted and Main Sections

Figure 4.35 Aluminum Variation for Maximum, Average, and Minimum Value as Function of Time in Field

2004

2005

Figure 4.36 Aluminum Variation as Function of Time and Positions in Field

A) Aluminum Distribution in Planted Sections

B) Aluminum Distribution in Main Sections

Figure 4.37 Aluminum Distribution in Planted and Main Sections

Figure 4.38 Barium Variation for Maximum, Average, and Minimum Value as Function of Time in Field

2004

2005

Figure 4.39 Barium Variation as Function of Time and Positions in Field

A) Barium Distribution in Planted Sections

B) Barium Distribution in Main Sections

Figure 4.40 Barium Distribution in Planted and Main Sections

Figure 4.41 Calcium Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.42 Calcium Variation as Function of Time and Positions in Field

A) Calcium Distribution in Planted Sections

B) Calcium Distribution in Main Sections

Figure 4.43 Calcium Distribution in Planted and Main Sections

Figure 4.44 Iron Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.45 Iron Variation as Function of Time and Positions in Field

A) Iron Distribution in Planted Sections

B) Iron Distribution in Main Sections

Figure 4.46 Iron Distribution in Planted and Main Sections

Figure 4.47 Magnesium Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.48 Magnesium Variation as Function of Time and Positions in Field

A) Magnesium Distribution in Planted Sections

B) Magnesium Distribution in Main Sections

Figure 4.49 Magnesium Distribution in Planted and Main Sections

Figure 4.50 Manganese Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.51 Manganese Variation as Function of Time and Positions in Field

A) Manganese Distribution in Planted Sections

B) Manganese Distribution in Main Sections

Figure 4.52 Manganese Distribution in Planted and Main Sections

Figure 4.53 Zinc Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.54 Zinc Variation as Function of Time and Positions in Field

A) Zinc Distribution in Planted Sections

B) Zinc Distribution in Main Sections

Figure 4.55 Zinc Distribution in Planted and Main Sections

Figure 4.56 Arsenic Variation for Maximum, Average, and Minimum Value as Function of Time in Field

Figure 4.57 Arsenic Variation as Function of Time and Positions in Field for 2003

A) Arsenic Distribution in Planted Sections

B) Arsenic Distribution in Main Sections

Figure 4.58 Arsenic Distribution in Planted and Main Sections for 2003

Figure 4.59 Lead Variation for Maximum, Average, and Minimum Value as Function of Time in Field for 2003

Figure 4.60 Lead Variation as Function of Time and Positions in Field for 2003

A) Lead Distribution in Planted Sections

B) Lead Distribution in Main Sections

Figure 4.61 Lead Distribution in Planted and Main Sections for 2003

CHAPTER 5. CONCLUSIONS AND FUTURE RESEARCH

5.1. Conclusions

Blast furnace slag is the byproduct of the iron and steel production industry. BFS is a versatile and durable as a recycled product. However, a number of adverse occurrences have arisen when the material was used as fill for transportation and support structures. This has led to a high pH and noxious leachate, with green/yellow color residuals and white “tufa” like precipitation. The leachate emerges from the infiltration and inundation of water through the slag material under poor ground conditions. Unweathered slag can exhibit an extreme level of chemical reactivity that is moderated after a short period of weathering. It should be understood that leachate from BFS is variable, based solely on the content of reactive minerals of the emplaced material. Although the occurrence of water pollution are rare, when they do occur they are often costly, problematic, and can occur for years (Griffiths 2002; USACE 2002).

The dissolution and weathering of BFS's inherent impurities and trace constituents trapped as oxides and sulfides, leaches and degrades water quality. The odor nuisance is caused by elevated concentrations of sulfur compounds; particularly the reduction of sulfate to hydrogen sulfide under anaerobic conditions. Elevated pH, total dissolved solids, and metals originate from the dissolution of soluble minerals, particularly calcium minerals (such as CaO and CaS). With concerns for nearby water resources and possible contact with plants, animals, or humans; the effects of leachate

exposure can be quite acute if there is little done to contain, dilute, or treat the resulting leachate.

The use of constructed wetlands is recognized as having many values and functions. One of the most important functions of a wetland system is its ability to retain, transform, or degrade pollutants. Wetlands are highly productive and efficient ecosystems, exhibiting geochemical, biological, and physical functions that enhance remedial actions. These wetland systems often utilize special substrate and support media such as gravel, limestone, compost, and peat, to reduce pollutants and support the growth of wetland plants.

Therefore, the main focal points of this study were to identify conditions and mechanisms of BFS leaching by laboratory shaker study and investigate the development of a low-cost, low-maintenance passive treatment system, to reduce pH, sulfur compounds, metal pollutants, and other nuisances associated with BFS leachate. A pilot study at the I-65 site in Hobart, IN was conducted, from April 2003 to May 2005, with a subsurface constructed wetland/retention cell designed to treat emerging leachate from the slag-based embankment. To support the field study, column and greenhouse experiments were used to explore the use of selected substrates to mitigate associated water quality impacts of BFS leachate (Hunter , 2006).

Results indicate that leachate from the study site is formed through a series of complex chemical reactions under fluctuating oxidized and reduced conditions. The elevated pH of the emergent leachate will decrease with exposure to atmospheric CO₂. Decreases in pH can occur due to the buffering effect related to carbonate equilibria in

water. Resulting pH from these reactions can influence the solubility of other constituents of the leachate.

For the field investigation, operation and treatment efficiency were ultimately affected by quantity of influent leachate. Inflow collected from the embankment can be correlated to local precipitation and water table records. This shows that the fluctuating high groundwater and/or perched water table inundates the slag-filled embankment, results in the inflow events measured from the collection system. The wetland operated as a containment cell for the retention and treatment of leachate. The eventual buildup of constituents in the wetland from inflow events and irreducible quantities, led to overall yearly increases for various water quality measures.

There were a number of issues encountered during the investigation of the I-65 field site, which by reassessment, some recommendations and revisions to the study and design would be considered. First, a more thorough investigation of the local hydrology in and around the embankment, as well as a review of historical records would have provided a better estimation of the potential flow that was encountered from the embankment. Monitoring wells in and around the perimeter of the embankment where the slag was placed would provide a better idea of the extent of the leachate problem. Second, monitoring of the site through the use of autosamplers, at strategic locations in the wetland, would provide more frequent data captured for specific influent events, thus providing a better determination of the treatment efficiency. Lastly, redesign of the wetland cell could be expanded to include the following possible changes:

- 1) Increase the surface area of the wetland cell to extend hydraulic retention time
- 2) Reciprocating flow design through the wetland cell with outlet control

- 3) Possible treatment configuration could include sections: settling tank or pond → into mushroom compost cell with iron amendment to (anaerobic) reduce sulfur → into peat cell → into planted rock or sand filter cell (aerobic) to raise pH and precipitate and filter iron, manganese, and other trace elements → outflow and/or reciprocated flow to inlet or irrigate to planted area with selected plant species.

Consideration should also be given to site security. The initial fencing effort was breached by vandals; this led to a number of disruptions and damage to equipment, plants, and wetland cell structure.

In addition, the supplemental column and greenhouse studies show that reduction of sulfate, metals, total dissolved solids, and other inorganic constituents, can be achieved by the abiotic and biotic processes in commonly used media of engineered wetland system. These studies indicate that treatment systems utilizing organic media (such as peat and mushroom compost) were more effective for reducing pH, total dissolved solids (TDS), sulfate, and total sulfur. Mushroom compost, amended with zero valent iron (ZVI) and operated with a residence time of 14 days, was the most effective matrix for the removal of sulfate (67%) and total sulfur (72%) (Hunter, 2006). The greenhouse study shows the ability of macrophytes to lower pH, but they also transport small amounts of oxygen to the root zone, oxidizing sulfur species. The favorable results from these studies emphasize the distinct capabilities that a passive, natural media treatment system have, if properly utilized and constructed. These systems can be far more viable than other costly clean-up and reconstruction alternatives.

Implications from this research raise relevant concerns about the use of blast furnace slag and other recycled materials in the highway environment. BFS producers

should continue to work closely with regulating agencies, engineers, and construction entities who intend to utilize slag as a fill material, to ensure adequate protection to the environment and reduce occurrences of potential costly nuisances often associated with slag. Potential users of BFS should be cautioned against the placement of slag in areas where the material would be in contact with or be submerged in water, giving rise to the dissolution of constituents that may impact water quality. The slag industry should continue to improve methods for quenching slag and “weathering” of slag piles prior to their use.

Proper testing of materials prior to, during, and after installation should be employed to ensure that these materials are safe and reliable. State agencies have increased measures to regulate the use of slag, as BFS leachate may be deemed harmful and slag material unacceptable, if regulations are not met with regards to pH, sulfur, TDS, conductivity, color, toxicity, and other water quality and esthetic measures (INDOT 2001, ODOT 2002, Ohio Steel 2003).

5.2. Future Research

The particular leachate problem experienced at the I-65 site should be revisited with modifications to the treatment design scheme and continued monitoring leachate generation and treatment during long-term study. This would also give an estimation of how long the problematic leachate would be generated at the site. Additional analysis of substrates and precipitation products after treatment, in conjunction with, modeling

chemical equilibria would be useful to determine of reaction rates in water and substrate and potential treatment efficiencies.

Future research related to the use of constructed wetlands and other passive treatment options can be extended to other forms of leachate caused by recycled materials. These treatment systems would focus on the utilization of low cost and readily available natural media (biotic and abiotic), to treat waste streams and for pollutant abatement. Future work could also extend to related areas of wetland and redox processes, natural media treatment, phytoremediation, restoration ecology and engineering, and soil and groundwater remediation.

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APPENDICES

APPENDIX A. SHAKER STUDY: SETUP AND OBSERVATIONS

Figure A.1 Crushing Apparatus for Blast Furnace Slag

Figure A.2 Slag Submerged in DI Water Prior Shaker Test

Figure A.3 Slag Under Oxidized Conditions

Figure A.4 Slag Under Reduced Conditions

**APPENDIX B. I-80/94 OBSERVATIONS AND WETLAND TRENCH / PLANT
SPECIES SURVIVABILITY STUDY**

Figure B.1 BFS Leachate from Under Drains of I-80/94 Resulting in Water and Soil Discoloration. Odor, high pH, and increased TDS present at these sites.

Figure B.2 Wetland Trench Design Drawings

Figure B.3 Construction wetland trenches Summer 2002

Figure B.4 Planting of Wetland Trenches Summer 2002

Figure B.5 Planted Wetland Trenches Summer 2002

Figure B.6 I-80/94 James Hunter in Front of Bulrush. Invasive Phragmites top left. June 2003 in trench six. Next is trench five.

Figure B.7 I-80/94 Trenches 1 through 6. Bulrush only plant emergent and showing growth apparent in the dense clusters shown in 4, 5, and 6. September 2003

**APPENDIX C. I-65 FIELD SITE: EMERGENT LEACHATE OBSERVATIONS,
PRE-CONSTRUCTION 2001-2002**

Figure C.1: Leachate problem October 2001

Milky white “tufa” leachate after reaction
to atmosphere and insitu elements

Flow from cross pipe to side ditch

Figure C.2 I-65 Hobart, Lake County, 2000 Project, R-24330, Photo 10/23/01,

Figure C.3 Seepage along walls within the embankment

Leachate approximately 50 feet from wingwall

Leachate at the wingwall

Cross pipe headwall, outlet of pipe

Seepage of leachate from highway embankment

Figure C.4 Seepage along outside of embankment

Milky white leachate in side ditch

Toe of slope, highway embankment

Figure C.5 Leachate problem, to lake 2001

Figure C.6 May 2002 - Leachate inside embankment prior to construction

Figure C.6 September 2002 - During construction, blackened soil and emergent leachate present.

APPENDIX D. I-65 FIELD SITE: SETUP, CONSTRUCTION, AND OBSERVATIONS

Figure D.1 Sampling layout

Figure D.2 Inlet schematic

Figure D.3 Layout sectional view

Figure D.4 Inlet view

Figure D.5 Construction – Retention mound constructed

Figure D.6 Drilling of new weep holes to be connected to sloped drainage pipes into wetland

Figure D.7 Construction during 2002

Figure D.8 Planting of I-65 field site

Figure D.9 Flow meter, Isco 4220

Figure D.9 Flow meter, Isco 4220

Figure D.10 Planting and progression, east end, 2003

May 2004

March 2005

June 2005

Figure D.11 Progression, east end, 2004 -2005

March 2006

Figure D.12 Progression, east end, 2006

Figure D.13 West side progression 2003

March 2004

May 2004

June 2004

Figure D.14 West side progression, 2004

May 2005

Figure D.15 West side progression, 2005

Figure D.16 Cattails emergent in June of 2005

Figure D.17 Bulrush emergent in June of 2005

Figure D.18 Emergent bulrush section- May 2004

June 2005

June 2005

Figure D.19 Sedges did not establish successfully in wetland

Figure D.20 Leachate build up effluent end of cell March 2005

Figure D.21 March 2005 – East end of wetland, white “tufa” precipitation showing evidence of momentary overflow of wetland.

Figure D.22 Before and After Vandalism at Field Site

Figure D.23 Vandalism at I-65 Field Site

Figure D.24 Fence Installed

Figure D.25 Leachate Emerging at Weir Box

Figure D.26 March 2004 – Emergent Leachate Around Weir Box Due to High Ttable of Area

Figure D.27 March 2004 – Temporary Cover of Area With Peat

Figure D.28 Ice Developed Inside of Weir Box During Winter Months

August 2004

May 2005

Figure D.29 Views From Inside the Weir Box

Figure D.30 July 2003 - Emergent Leachate East of Box Culvert

Figure D.31 July 2003 - Emergent Leachate East of Box Culvert

Figure D.32 March 2004 - Emergent Leachate East of Box Culvert

Figure D.33 March 2004 - Emergent Leachate East of Box Culvert
Blackened soil, perhaps due waterlogged/anaerobic soil conditions and iron sulfide formation.

Figure D.34 March 2005 - Emergent Leachate East of Box Culvert

Figure D.35 July 2003 – Leachate Leaking Under Insulated Drainage Structure

Figure D.36 May 2003 - Leachate Leaking Under Insulated Drainage Structure.
Could be emerging from floor or walls.

Biker Using Bike Path May 2005

Bike Path - East Away From Wetland

November 2005 – View From I-65

Recreational Users of Lake Robinson

Farm property south of wetland site

Figure D.37 Landuse of Area Adjacent to the Constructed Wetland Cell