

## ABSTRACT

Title of Document: LEACHING OF METALS FROM HIGH  
CARBON FLY ASH MIXED SOILS

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Fly ash produced by power plants in the United States occasionally contains significant amounts of unburned carbon due to the use of low nitrogen-oxide and sulphur-oxide burners in recent years. This ash cannot be reused in concrete production due to its reactivity with air entrainment admixtures and is largely placed in landfills. Highway structures have high potential for large volume use of high carbon fly ashes (HCFAs). However, in such applications, even though mechanical properties of the fly ash-amended highway base layers and embankments are deemed satisfactory, one key issue that precludes highway embankments built with fly ash is the potential for groundwater impacts caused by metals in the fly ash.

This study was conducted to evaluate the leaching potential of metals from high carbon fly ash stabilized highway base layers and high carbon fly ash amended highway embankment structures. Three different laboratory tests: (1) batch water leach tests, (2) toxicity characteristics leaching procedure tests, (3) column leach test and two different numerical modeling analyses: (1) WiscLEACH, (2) MINTEQA2, were carried out. Analysis were conducted on eight fly ashes and two locally available sandy soil materials that are mainly used in highway base layer and highway embankment structures.

Laboratory test results indicated that an increase in fly ash content in the soil fly ash mixtures yielded an increase in leached metal concentrations except Zn metal. The pHs had significant and different impacts on the leaching of metals. The leaching of Cr, Zn, Al, As and Se were increasing with pH while leaching of Ba, B, Cu, Fe, Mn, Sb, V were decreasing.

Numerical model WiscLEACH was used to simulate the leaching behavior of leached metals from HCFA stabilized highway base layers and amended highway embankment structures. WiscLEACH predicted field metal concentrations were significantly lower than the metal concentrations obtained in laboratory leaching tests, and field concentrations decreased with time and distance due to dispersion in soil vadose zone. Numerical model MINTEQA2 predicted that leaching of metals were solubility controlled except As, Se and Sb metals. Speciation analyses indicated that leached metals were present at their less or non-toxic forms.

LEACHING OF METALS FROM HIGH CARBON FLY ASH MIXED SOILS.

By

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# TABLE OF CONTENTS

Acknowledgements.....	ii
Table of Contents.....	iii
List of Tables.....	v
List of Figures.....	vi
1 Introduction.....	1
2 Leaching of Trace Metals from High Carbon Fly Ash Stabilized Highway Base Layers.....	5
2.1 Introduction.....	5
2.2 Materials.....	6
2.3 methods.....	10
2.3.1 Batch Water Leach Tests (WLTs).....	10
2.3.2 Column Leach Tests.....	10
2.3.3 Chemical Analysis.....	11
2.4 Results.....	12
2.4.1 Batch Water Leach Tests.....	12
2.4.2 Column Leach Tests.....	20
2.5 Metal Leaching.....	22
2.6 Comparison of WLTs and CLTs.....	29
2.7 Conclusions.....	31
3 Experimental and Numerical Analysis of Metals Leaching from Fly-Ash Amended Highway Bases.....	33
3.1 Introduction.....	33
3.2 Materials.....	34
3.3 Methods.....	37
3.3.1 Batch Water Leach Test (WLT).....	37
3.3.2 Column Leach Tests.....	38
3.3.3 Chemical Analysis.....	40
3.3.4 Chemical Transport Modeling.....	41
3.3.5 Model Formulation in Vadose Zone.....	44
3.3.6 Model Formulation in Groundwater.....	47
3.4 results of water leach tests.....	48
3.5 results of column leach tests.....	56
3.6 Total Leached Amount of Metals from WLTs and CLTs.....	61
3.7 Numerical Modeling.....	65
3.8 Conclusions.....	75
4 Leaching of Trace Metals from HCFA-Amended Structural Fills.....	78
4.1 Introduction.....	78
4.2 Materials.....	79
4.3 Methods.....	84
4.4 Results.....	84

4.4.1	Water Leach Tests.....	84
4.4.2	Column Leach Tests .....	92
4.4.3	Results Toxicity Characteristic Leaching Procedure Tests .....	110
4.4.4	Comparison of the Leaching Test Results .....	116
4.5	Chemical Transport Modeling .....	121
4.5.1	Numerical Model .....	121
4.5.2	WiscLEACH Results .....	123
4.6	Conclusions.....	145
5	Geochemical Modeling.....	148
5.1	Introduction.....	148
5.2	Geochemical Analysis .....	149
5.2.1	Speciation Analysis.....	150
5.2.2	Analysis of Controlling Mechanisms .....	155
5.2.3	Speciation of Al .....	157
5.2.4	Speciation of As .....	160
5.2.5	Speciation of Cr .....	166
5.2.6	Speciation of Mn.....	172
5.2.7	Speciation of Se .....	174
5.2.8	Speciation of Cu.....	177
5.2.9	Speciation of Fe .....	179
5.2.10	Speciation of V: .....	179
5.2.11	Speciation of Sb.....	181
5.2.12	Speciation of Zn.....	184
5.2.13	Speciation of B.....	186
5.3	Conclusions.....	187
6	Conclusions and Recommendations .....	191
6.1	Conclusions.....	191
6.2	Recommendations for Future Studies.....	195
6.3	Recommendations for Future Studies.....	196
	Appendix A: Elution Curves for Metals for High Carbon Fly Ash Stabilized Base Layer .....	198
	Appendix B: Predicted Metal Concentrations in Vadose Zone and Ground Water for High Carbon Fly Ash Stabilized Base Layers .....	203
	Appendix C: MinteqA2 Geochemical Analysis of the Species of the Leached Metals.....	226
	References.....	243

## LIST OF TABLES

Table 2.1.	Index properties of the materials used in current study.....	7
Table 2.2.	Chemical compositions and total metal contents of the materials utilized.....	7
Table 2.3.	Legend and compositions of the mixtures.....	8
Table 2.4.	Stabilized pH and peak effluent concentrations in CLTs. Concentrations exceeding MCLs in <b>bold</b> .....	19
Table 3.1	Physical and chemical properties of the materials used in current study..	35
Table 3.2	Aqueous concentrations of metals from WLTs.....	54
Table 3.3	Peak effluent concentrations of Ba, B, Cu, and Zn for column leach tests and pH at peak concentrations. Concentrations exceeding MCLs in <b>bold</b> .	55
Table 3.4	Hydraulic conductivities and transport parameters for all materials.....	68
Table 3.5	Retardation factors of the soil mixtures for different metals.....	68
Table 4.1	Physical properties of the soil and fly ashes.....	82
Table 4.2	Chemical compositions of the fly ashes tested. Concentrations of major minerals were determined by X-ray fluorescence spectroscopy analysis. All concentrations are in percentage by weight.	82
Table 4.3.	Total metal content of the fly ashes and sandy soil material from the total elemental analysis results.....	83
Table 4.4	Legend and compositions of the mixtures.....	83
Table 4.5	Stabilized pH and effluent concentrations in WLTs. Concentrations exceeding EPA MCL are in <b>bold</b> .....	86
Table 4.6	Stabilized pH and peak effluent concentrations in CLTs. Concentrations exceeding EPA MCL are in <b>bold</b> .....	95
Table 4.7.	Effluent metal concentrations in TCLP tests. Concentrations exceeding EPA MCL are in <b>bold</b> .....	112
Table 4.8	Input site parameters for embankment and soil structures.....	124
Table 4.9	Hydraulic and transport parameters or pavement, embankment, soil aquifer structures to be used as an input in WiscLeach .....	124
Table 4.10	Input parameters for specific soil-fly ash mixtures analyzed in WiscLEACH. ....	142
Table 4.11	Predicted maximum metal concentrations in groundwater at 1, 10, 20, and 40 years for specimens prepared with 100% PSP and DP fly ashes. Concentrations exceeding MCLs in <b>bold</b> .	142
Table 5.1	Comparisons of Cr speciation laboratory test results to MINTEQA2 results.....	154



## LIST OF FIGURES

Figure 2.1. Effect of LKD content on pH of the soil mixtures. Note: 10 BS, 10 PS, 10 DP .....	13
Figure 2.2. Effect of fly ash content on WLT concentrations of a) chromium, b) iron, c) aluminum, d) vanadium, e) antimony, and f) manganese. Mixtures prepared with 10% and 20% fly ash are amended with 5% LKD. 0% and 100% fly ash content corresponds to URM only and fly ash only specimens, respectively.....	16
Figure 2.3 Effluent pH in CLTs conducted on mixtures prepared with a) Brandon Shores fly ash , b) Paul Smith fly ash, and c) Dickerson Precipitator fly ash. ....	21
Figure 2.4 CLT elution curves for a) chromium, b) iron, c) aluminum, d) vanadium, e) antimony, and f) manganese. ....	24
Figure 2.5 Comparison of peak effluent concentrations of six metals from the CLTs and the WLTs.....	30
Figure 3.1 Particle size distributions of unpaved road material (URM) and fly ashes. ....	36
Figure 3.2 Conceptual model in WiscLeach for predicting impacts to the vadose zone and groundwater from HCFA stabilized highway base layer, .....	43
Figure 3.3 Effect of fly ash content on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs. 0% and 100% fly ash content corresponds to URM only and fly ash only specimens, respectively. ....	50
Figure 3.4 Effect of lime kiln dust content on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs. 0% lime kiln dust content corresponds to fly ash only. ....	52
Figure 3.5 Effect of pH on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs. ....	53
Figure 3.6 CLT elution curves for a) boron, b) barium, c) copper, and d) zinc. ....	58
Figure 3.7 Relationship between leaching amounts and concentration of metals in fly ashes (WLTs).....	63
Figure 3.8 Relationship between leaching amounts and concentration of metals in fly ashes (CLTs).....	64
Figure 3.9 Predicted Zn concentrations in vadose zone and ground water. Note: 20 PS + 5LKD designate the specimens with 20% Paul Smith fly ash and 5% lime kiln dust by weight. ....	69
Figure 3.10 Predicted Cu concentrations in vadose zone and ground water Note: Note: 20 DP + 5LKD designate the specimens with 20% Dickerson Precipitator fly ash and 5% lime kiln dust by weight. ....	70
Figure 3.11 WiscLEACH-based concentrations of a) boron and b) zinc at different locations beneath the pavement. X and Z are the horizontal and vertical distances measured from the center alignment of fly ash stabilized layer.....	71
Figure 3.12 Effect of fly ash content on WiscLEACH-based concentrations of a) and b) boron, and c) and d) zinc. ....	72

Figure 3.13 Maximum concentrations at POC over a 100 year-period: a) effect of groundwater depth, b) effect of base layer thickness, c) effect of precipitation rate. POC is 20 m down gradient from pavement centerline. Groundwater table (GWT) is fixed at 6 m below ground surface for b) and c).....	74
Figure 4.1 Effect of fly ash content on pH of the soil mixtures a) Water leach tests, b) Column leach tests, c) TCLP tests. (Note: BS: Brandon Shores Fly Ash, PSP: Paul Smith Precipitator Fly ash, MT: Morgantown Fly ash, DP: Dickerson Precipitator Fly Ash, Co: Columbia Fly Ash).....	87
Figure 4.2 Concentrations of six metals in the effluent from WLTs(Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgan Town) .....	89
Figure 4.3 pH of the effluents from CLT on soil, fly ash and their mixtures. ....	96
Figure 4.4 Concentrations of six metals in the effluent from CLTs (Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgan Town) .....	97
Figure 4.5 Elution curves for Aluminum Metal. ....	104
Figure 4.6 Elution curves for Arsenic Metal.....	105
Figure 4.7 Elution Curves for Boron metal.....	106
Figure 4.8 Elution curves for chromium metal .....	107
Figure 4.9 Elution curve for Manganese metal. ....	108
Figure 4.10 Elution curves for selenium metal.....	109
Figure 4.11 Concentrations of six metals in the effluent from TCLPs (Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgantown); MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water.) .....	113
Figure 4.12. Comparison of peak effluent concentrations of six metals from the CLTs and the WLTs.....	118
Figure 4.13. Comparison of peak effluent concentrations of six metals from the CLTs and the TCLPs .....	119
Figure 4.14. Comparison of peak effluent concentrations of six metals from the WLTs and the TCLPs .....	120
Figure 4.15. Conceptual model for embankment structure.....	122
Figure 4.16.Predicted Cr concentrations in vadose zone and ground water (Note: 20 PSP designate the specimens with 20 % Paul Smith Precipitator fly ash.) ....	126
Figure 4.17.Predicted Cr concentrations in vadose zone and ground water (Note: 40 PSP designate the specimens with 40 % Paul Smith Precipitator fly ash.) ....	127
Figure 4.18Predicted Cr concentrations in vadose zone and ground water (Note: 20 DP designate the specimens with 20 % Dickerson Precipitator fly ash.) .....	128
Figure 4.19 Predicted Cr concentrations in vadose zone and ground water (Note: 40 DP designate the specimens with 40 % Dickerson Precipitator fly ash.) .....	129
Figure 4.20.Conceptual model of WiscLEACH for multiple layer fly ashes. Note: POC = Point of compliance .....	131

Figure 4.21. Predictions of As concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash. ....	132
Figure 4.22 Predictions of Cr concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash. ....	133
Figure 4.23 Predictions of Se concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash. ....	134
Figure 4.24 Predictions of Mn concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash. ....	135
Figure 4.25 Predictions of As concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash. ....	136
Figure 4.26. Predictions of Cr concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash. ....	137
Figure 4.27 Predictions of Se concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash. ....	138
Figure 4.28 Predictions of Mn concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash. ....	139
Figure 4.29 Maximum metal concentrations within 100 years at point of compliance for specimens prepared with 100% PSP. ....	143
Figure 4.30 Maximum metal concentrations within 100 years at point of compliance. for specimens prepared with 100% DP. ....	144
Figure 5.1 Log activity of $Al^{3+}$ vs. pH in leachates (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures. ....	159
Figure 5.2 Log activity of $AsO_4^{3-}$ vs. pH in leachates from fly ashes, soil-fly ash mixtures. (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes. ....	163
Figure 5.3 Log activity of $AsO_4^{3-}$ vs. $Al^{3+}$ in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes. ....	164
Figure 5.4 Log activity of $AsO_4^{3-}$ vs. $Mn^{2+}$ in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes. ....	165
Figure 5.5 Log activity of $Cr^{3+}$ and $Cr^{6+}$ in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures. ....	170
Figure 5.6 Log activity of (a) $CrO_4^{2-}$ vs. $Ba^{2+}$ , (b) $CrO_4^{2-}$ vs. $Ca^{2+}$ , (c) $CrO_4^{2-}$ vs. $Cu^{2+}$ , and (d) $CrO_4^{2-}$ vs. ettringite leachates from fly ashes and URM-fly ash-LKD mixtures. ....	171

Figure 5.7 Log activity of $Mn^{2+}$ vs. pH in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures.....	173
Figure 5.8 Log activity of $HSeO_3^-$ vs. pH in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes.....	176
Figure 5.9 Log activity of (a) $Cu^{2+}$ vs pH, (b) $Fe^{3+}$ vs pH, and (c) V(IV) vs. pH in leachates from fly ashes and soil-fly ash-LKD mixtures.....	178
Figure 5.10 Log activity of (a) $Sb(OH)_6^-$ vs. pH, (b) vs $Ca^{2+}$ , and (c) $Zn^{2+}$ vs pH in leachates from fly ashes and soil-fly ash-LKD mixtures.....	183

# 1 INTRODUCTION

According to American Coal Ash Association (ACAA), the 45% of the electricity consumed in the United States in 2009 were supplied from the power plants that burn coal. Approximately 92.8 million of tons of coal combustion byproducts (CCBs) are produced in the United States each year as a result of burning coal at the electric power plants (ACAA 2008). As of 2009, 78% of these CCBs are fly ashes, and 42.3 million tons of fly ash is landfilled. ACAA estimates that this landfilled or stockpiled amount will be increasing each year.

Fly ash production causes two main problems: impacts to the environment and occupying valuable landspace. The first one is particularly important as fly ashes may contain high concentrations of important trace elements such as arsenic, boron, chromium, copper, zinc, vanadium, and nickel among many others. Disposing large amounts of fly ashes into landfills can cause leaching of these heavy metals to the groundwater through the soil vadose zone and may threaten the aquatic life and environment as well as human health.

There have been significant efforts on reusing of fly ash materials in construction and decreasing the disposal rate of fly ash. Fly ash is siliceous or alumino-siliceous pozzolanic material that can form cementitious compounds in the presence of water. The physical, chemical and mineralogical properties of the fly ash are strongly dependent on the type of the coal burning, type of combustion process, type of pollution control facilities and handling (Bin-Shafique et al. 2006). Fly ash is classified into two classes, F and C, based on the chemical composition of the fly ash, and the C (self-cementitious)

type fly ashes are readily and F type ashes are commonly reused as concrete additive or in cement production. However, fly ashes produced by several power plants in the United States in the last 5 years occasionally contains significant amounts of unburned carbon (i.e., high loss on ignition) due to the increasingly common use of low nitrogen oxide ( $\text{NO}_x$ ) and sulphur oxide ( $\text{SO}_x$ ) burners. This ash, called high carbon fly ash (HCFA), has a carbon content of 12-25%, cannot be efficiently re-burnt by using current technology, and has no value as a concrete additive as the unburned carbon tends to adsorb the air entrainment admixtures that are added to the cement to prevent crack formation and propagation. These ashes are typically classified as off-spec fly ashes meaning that they do not meet the physical and chemical requirements criteria outlined in ASTM C618 and are landfilled at large percentages.

The fly ashes produced by several power plants in Maryland and elsewhere occasionally contains significant amounts of unburned carbon (i.e., high loss on ignition), and cannot be used in concrete production. On the other hand geotechnical applications pose great potential for beneficial reuse of the fly ashes. In the current study, the applications of reusing of fly ash in construction of highway base layers (Sections 2 and 3) and embankments (Section 4) will be discussed.

Several studies have been conducted on leaching behavior of metals from coal combustion by-products and mechanisms that control the release of these metals (Wang et al. 2006, Bin-Shafique et al. 2006, Chen et al. 2006, Goswami and Mahanta 2007, Gosh 2008, Vitkova et al. 2008, Srivastava et al. 2008, Deng et al. 2008, Dutta et al. 2009, Komonweeraket et al. 2010). However, there is lack of information on leaching of

these contaminants from high carbon fly ash mixtures. The environmental risks associated with fly ash stabilization may be reduced when HCFAs are used as a stabilizing agent (e.g., unburned carbon or activated carbon is often used for pollution control). The high organic carbon content of HCFA may act as a sorbent to the heavy metals in the fly ash, and reduce the amount of metals that are released into the environment. Because of enhanced adsorption of metals by the unburned carbon, metal concentrations are likely to decrease to much lower values than the ones experienced in previous field applications. The environmental benefits of the high carbon content may also result in a broader range of permissible reuse applications for fly ash.

The objective of the proposed study is to evaluate the leaching potential of borrow materials mixed with HCFAs relative to those stabilized with conventional additives (low carbon fly ashes), and to evaluate the potential groundwater and soil vadose zone impacts. The experimental program consisted of the following tasks:

- 1) Determining the concentrations of minor, major and trace elements and other chemical properties of interests, speciation in leachates from soil – fly ash mixtures, as well as fly ashes and soil alone.
- 2) Running batch (small-scale) water leaching tests for a quick estimate of the metal leaching behavior.
- 3) Running long term column leaching tests to study metal leaching behavior and controlling mechanisms of the trace metals from the mixtures, and fly ash.
- 4) Running TCLP tests to determine the leaching potential of these fly ashes and mixtures under acidic conditions.

- 5) Comparing the results of different test results and try to obtain a relationship between these two tests to estimate the metal concentrations quickly in the field.
- 6) Determining the groundwater impacts through a computer model.
- 7) Predicting the species of the trace metals and determining the leaching controlling mechanisms of these metals species with the help of geochemical modeling tool.

This study focused on the leaching characteristics and behavior of 10 metals (aluminum, arsenic, antimony, boron, chromium, copper, iron, manganese, selenium, vanadium and zinc) from laboratory-simulated HCFA stabilized base layer and embankment fill materials. This dissertation contains 6 main sections as follows: Sections 2 and 3 evaluate the leaching potential of fly ashes used as stabilizing agents in highway base layers stabilized soils. Section 4 contains results of leaching tests on soil-HCFA mixtures for potential use in embankment constructions. Section 5 is geochemical modeling analysis and discusses the speciation of leached metals and their leaching controlling mechanisms in the aqueous solutions. Section 6 provides a summary of findings and general conclusions obtained from the research study.



## 2 LEACHING OF TRACE METALS FROM HIGH CARBON FLY ASH STABILIZED HIGHWAY BASE LAYERS

### 2.1 INTRODUCTION

Using fly ash in highway applications is gaining importance due to its potential to solve the landfilling problems and provide good strengthen material. The most important problem in highway constructions is building the suitable base layer that can provide enough support to the asphalt layer. The two conventional methods to stabilize the base layer are removing the soft soil and replacing it with a stronger material, such as granular materials (gravel), or in situ stabilization of the soil via physical and chemical techniques. However, these conventional methods can be costly and time consuming, and alternative approaches such as fly ash amendment could be very practical and provide an economical solution for stabilization of the existing soil (Cetin et al. 2010). Leaching of the metals from HCFA-stabilized soil layers is, on the other hand, the main concern for construction applications (Bin Shafique et al. 2002, Sauer et al. 2005, Goswami and Mahanta 2007).

Limited information exists on the reuse of high carbon off-spec fly ash in construction of highway pavements. This is particularly important when high carbon fly ash is non-cementitious and calcium-rich activators are required to generate pozzolanic reactions. In order to evaluate the environmental suitability of high carbon fly ash-stabilized URMs for potential highway applications, a series of short term batch water and long term column leaching experiments were conducted to evaluate the leaching of six heavy metals (Al, Cr, Fe, Mn, Sb, V). Results were used to determine leaching patterns and relationships between concentrations from the two laboratory tests.

## 2.2 MATERIALS

An unpaved road material and three fly ashes were used in this study. The unpaved road material (URM) was utilized in soil–fly ash–lime kiln dust mixtures in all tests as well as a reference material in both column leach and water leach tests. The mixtures with their proper percentages of fly ashes and lime kiln dust were selected based on strength and moduli determined in an earlier study by Cetin et al. (2010). The URM was collected from a highway construction site in Caroline County, Maryland and was stored in airtight buckets to preserve its natural water content. Any debris and foreign materials in the soil were removed by hand and by sieving through a 19-mm sieve. The soil was classified as poorly graded sand with gravel (SP) according to the Unified Soil Classification System (USCS), and A-1-b according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System. URM was chosen as it satisfied the gradation as well as maximum dry unit weight requirements by the Maryland State Highway Administration. Physical properties of the unpaved road material are summarized in Table 2.1. The optimum moisture contents ( $w_{opt}$ ) and maximum dry unit weights ( $\gamma_{dmax}$ ) of the soil-fly ash- LKD mixtures prepared using the standard Proctor effort (ASTM D 698) ranged from of 9% to 13.4% and, from  $17 \text{ kN/m}^3$  to  $19.4 \text{ kN/m}^3$ , respectively (Table 2.3).

Table 2.1. Index properties of the materials used in current study

Soil/ Fly ash	$C_u$	$G_s$	$w_{opt}$ (%)	$\gamma_{dmax}$ (kN/m <sup>3</sup> )	LL (%)	PI (%)	Gravel Content(>4.75 mm) (%)	Fines Content (<75 $\mu$ m) (%)	Fineness (>45 $\mu$ m) (%)	Classification	
										USCS	AASHTO
URM	6.7	2.64	13.4	18.8	NP	NP	30	3	0	SP	A - 1 - b (0)
BS	0.43	2.17	—	—	NP	NP	—	80	60	ML	A - 2 - 4 (0)
PS	11	2.2	—	—	NP	NP	—	95	86	ML	A - 2 - 4 (0)
DP	3.6	2.37	—	—	NP	NP	—	85	77	ML	A - 2 - 4 (0)

Table 2.2. Chemical compositions and total metal contents of the materials utilized. The compositions and concentrations were determined by X-ray fluorescence spectroscopy analysis, and total elemental analysis, respectively.

Chemical Composition													
Soil/ Fly ash													
	pH	LOI (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	CaCO <sub>3</sub> (%)	Al (mg/L)	Cr (mg/L)	Fe (mg/L)	Mn (mg/L)	Sb (mg/L)	V (mg/L)
URM	6.5	2.4	NA	NA	NA	NA	NA	2400	15.5	6300	26.5	0.02	16.5
BS	9.6	13.4	45.1	23.1	3.16	7.8	NA	28600	65.7	34600	115	0.01	164
PS	7.55	10.7	50.8	26.9	5.5	0.7	NA	10000	24.3	10700	38.2	0.02	53.7
DP	8.8	20.5	34.9	24.4	12.6	3.2	NA	19200	47.1	12700	38.3	0.02	82.4
LKD	12.7	NA	10	NA	NA	60	30	NA	NA	NA	NA	NA	NA

Notes: URM: Unpaved road material, PS: Paul Smith fly ash, DP: Dickerson Precipitator fly ash, BS: Brandon Shores fly ash, LKD: Lime kiln dust, LOI: Loss on ignition.  $G_s$ : Specific gravity,  $C_u$ : Coefficient of uniformity,  $w_{opt}$ : Optimum water content,  $\gamma_{dmax}$ : Maximum dry unit weight, LL: Liquid limit, PI: Plasticity index NP: Nonplastic, NA: Not available

Table 2.3. Legend and compositions of the mixtures.

Specimen name	URM Content (%)	Fly Ash Content (%)	LKD Content (%)	Optimum Water Content, $w_{opt}$ (%)	Maximum Dry Unit Weight, $\gamma_{dmax}$ (kN/m <sup>3</sup> )
URM	100	0	0	13.4	18.8
10 BS + 2.5 LKD	90	10	2.5	10	19.2
10 BS + 5 LKD	90	10	5	9.5	19.2
20 BS + 5 LKD	80	20	5	13	17.4
10 PS + 2.5 LKD	90	10	2.5	9.0	18.8
10 PS + 5 LKD	90	10	5	10	18.8
20 PS + 5 LKD	80	20	5	13	17.0
10 DP + 2.5 LKD	90	10	2.5	9.0	19.1
10 DP + 5 LKD	90	10	5	10	19.4
20 DP + 5 LKD	80	20	5	12	18.0

Note: BS: Brandon Shores fly ash, PS: Paul Smith fly ash, DP: Dickerson Precipitator fly ash, LKD: Lime kiln dust, URM: Unpaved road material.

The fly ashes used in this study were obtained from three power plants in Maryland: Brandon Shores (BS), Paul Smith (PS) and Dickerson Precipitator (DP). All of the fly ashes consisted primarily of silt-size particles and contained 76 to 90% fines (passing the 75- $\mu\text{m}$  sieve). Specific gravity of fly ashes ranged between 2.17 and 2.37 per ASTM D 854. The physical properties and chemical compositions of ashes are summarized in Table 2.1 and Table 2.2. The fly ashes investigated in this study were classified as off-specification fly ashes (neither C nor F type according to ASTM C 618) due their high loss on ignition values ( $\text{LOI} > 6$ ), and high ( $\text{SiO}_2 (\%) + \text{Al}_2\text{O}_3 (\%) + \text{Fe}_2\text{O}_3 (\%) > 70 \%$ ) and very low lime ( $\text{CaO}$ ) contents (0.7-7.8 %). The LOI data along with the pH measurements were conducted according to EPA Method SW-846 Method 9045, and are also presented in Table 2.3. Since the three fly ashes do not have high cementing potential, lime kiln dust (LKD) was used to initiate pozzolanic reactions for stabilization of the soil. LKD (a disposed residue of lime production plants) was obtained from Carmeuse Lime and Stone Company, Pittsburgh, Pennsylvania and contained approximately 60%  $\text{CaO}$  by weight. The specific gravity ( $G_s$ ) of LKD by 2.97. Total elemental analyses of the three fly ashes and URM were conducted following the procedures outlined in EPA SW-846 Method 6800 and are summarized in Table 2.3.

## 2.3 METHODS

### 2.3.1 *Batch Water Leach Tests (WLTs)*

Batch water leach tests were conducted on the soil, fly ashes and soil mixtures using different percentages of fly ashes and LKD in accordance with ASTM D 3987. A constant liquid-to-solid (L:S) ratio of 20:1 was used for all materials. The air-dried soil was crushed and sieved from U.S. No. 4 sieve (4.75-mm), and the soil was mixed homogeneously with fly ash and lime kiln dust at different percentages. Each specimen was cured for 7 days in plastic bags in a moisture controlled humidity chamber (21 °C and 100% relative humidity). After curing, 2.4 g of soil mixture was added to a 50-mL plastic centrifuge tube followed by 48 mL leachant (i.e., the 0.1 M NaBr solution). The soil mixtures were rotated continuously on a rotator at 29 revolutions per minute, room temperature (~22 °C) for 18 hours for equilibration. After equilibrium, the specimens were settled for 5 minutes and placed in a Beckman GPR centrifuge machine. The mixtures were centrifuged at 3000 rpm for 20 minutes. Next, the suspended solids were filtered through the 0.2- $\mu$ m pore size, 25 mm diameter membrane disk filters fitted in a 25-mm Easy Pressure syringe filter holder by using a 60-mL plastic syringe. The filtered samples were subjected to pH measurements and then acidified to pH < 2 using high-purity nitric acid and stored in 15 mL high density polyethylene centrifuge tubes at 4 °C. Triplicate WLTs were conducted on all fly ashes, soil or soil mixtures.

### 2.3.2 *Column Leach Tests*

Column leach tests (CLTs) were conducted on soil, fly ashes alone and soil mixtures to provide more realistic results about leaching behavior of heavy metals. The soils, fly

ashes and their mixtures prepared for CLTs tests were the same materials used in WLTs. Air-dried soil was sieved from U.S. No.4 (4.75 mm) sieve. All specimens were compacted in polyvinyl chloride (PVC) molds having 101.6 mm diameter and 116.4 mm height by using standard Proctor compaction effort (ASTM D 698). PVC molds were preferred to minimize the outside effects on effluent metal concentrations. All soil mixtures were cured for 7 days in a humidity chamber with 100% relative humidity and 21 °C following compaction. The protocol for sample filtration and preservation followed those employed in WLTs. After curing, the CLTs were started immediately. A 0.1 M NaBr solution was used to provide influent with an ionic strength, which was sent to the specimen by a peristaltic pump at a rate of 60 mL/hr per Morar (2007), Gelhar et al. (1992), and Papini et al. (1999). Sampling and pH measurements were conducted every 4 hours in the first 72 hours, after which sampling 2 to 14 times a week was sufficient. Detailed information about the testing procedures can be found in Morar (2007).

### *2.3.3 Chemical Analysis*

pHs of the leachate samples collected from the CLTs and WLTs were determined following the methods outlined in ASTM D 1293. pH of the fly ashes was determined by using SW-846 Method 9045. Three replicate samples were measured for each sample and the mean values were reported. The metals selected for analysis were Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Si, Sr, Ti, V, and Zn, based on the total elemental analyses. However, initial spectroscopy analyses showed WLT and CLT effluent concentrations below the detection limits for all metals, except Al, Cr, Fe, Mn, Sb, and V. These six metals also pose health concerns based on the recommendations of

the U.S. Environmental Protection Agency (EPA), and thus were included in further analyses. The metals also represent different mobilities. For instance, at the pHs typical of soil-fly ash mixtures (pH=10-12.5), Cr forms oxyanions that can be very mobile (Fendorf 1995, Daniels and Das 2006), whereas Al forms hydroxyl compounds and their attachment to the soil surface depends on the solubility level (Sparks 2003). On the other hand, Fe, Mn, Sb and V have cationic species at high pHs and their solubility is relatively lower. (Jackson et al. 1999, Pavageau et al. 2004, Cornelis et al. 2006).

The concentrations of all metals were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX CCD Simultaneous ICP-OES instrument. Minimum detection limits (MDLs) for ICP-OES were determined for each metals and a set of calibration standards according to the U.S. Code of Federal Regulations Title 40. The MDLs for Al, Cr, Fe, Mn, Sb, and V were determined as 2.5 µg/L, 0.5 µg/L, 3.2 µg/L, 0.05 µg/L, 3 µg/L, and 0.1 µg/L, respectively.

## 2.4 RESULTS

### 2.4.1 *Batch Water Leach Tests*

Triplicate batch water leach tests (WLTs) were conducted on URM only, fly ash only, and several URM-fly ash- LKD mixtures. Table 2.4 summarizes the pH of the specimens tested. Figure 2.1 shows that the rate of increase in pH was initially high and addition of LKD above 2.5% by weight did not affect pH significantly.



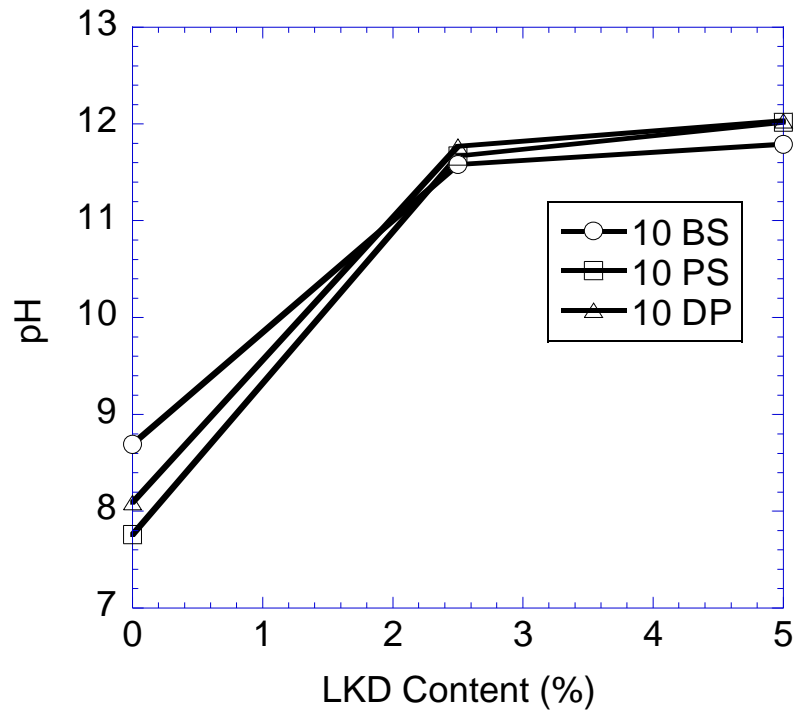
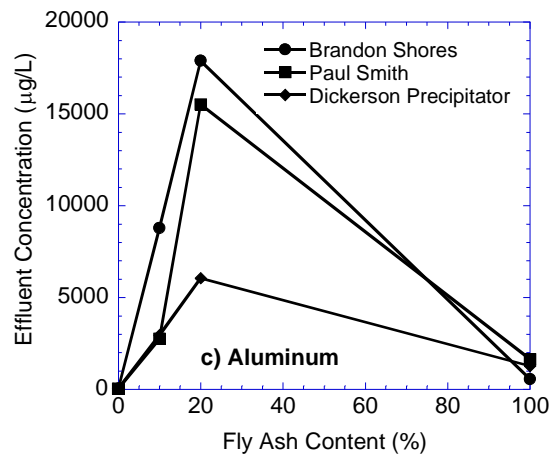
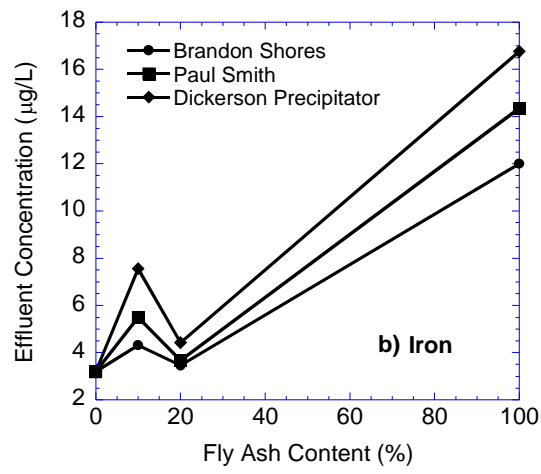
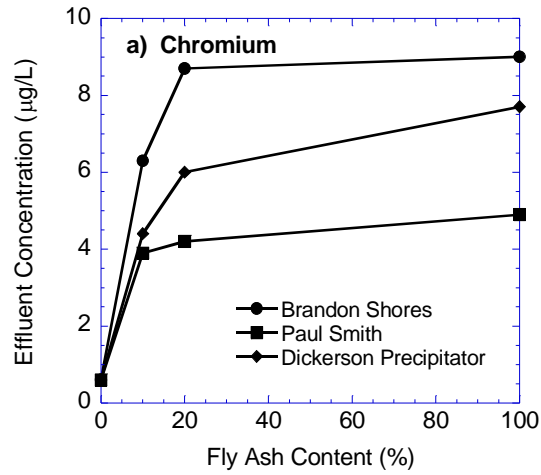


Figure 2.1. Effect of LKD content on pH of the soil mixtures. Note: 10 BS, 10 PS, 10 DP designate the specimens with 10% Brandon Shores, Paul Smith, and Dickerson Precipitator fly ash respectively. 0% LKD content corresponds to fly ash only.

It is speculated that an increase in LKD amount increased the release of free lime (CaO), hydrated calcium silicate (C-S-H) and portlandite Ca (OH)<sub>2</sub> which resulted in an increase in pH values. The fly ash, as compared to LKD, had relatively smaller effect on pH of the mixture due to its lower calcium content (Table 4). All three fly ashes except BS fly ash had calcium contents of less than 5% compared to a calcium content of approximately 60% for LKD. LKD content was the dominant factor that controlled the effluent pH of the effluent solutions due to its high CaO content (60%) compared to high carbon fly ashes used in this study.

Table 2.4 shows the concentrations of six metals for several different soil mixtures compared to the U.S. EPA maximum concentration limits for drinking waters (MCLs), EPA water quality limits (WQLs) for protection of aquatic life and human health, and Maryland aquatic toxicity limits (ATLs) for fresh water. The results show that, except Al, higher metal concentrations were obtained for fly ashes alone than URM-fly ash-LKD mixtures. Of the three fly ashes tested, generally the mixture with BS fly ash yielded the highest metal concentrations followed by the mixtures prepared with DP and PS fly ashes. Trace metal contents were also generally the highest in BS fly ash based on total element analysis (Table 2.3). However, regardless of the increase in metal concentrations all trace metal concentrations, except Al, were below the MCL, WQL and Maryland ATL.

The variation in concentrations of these six metals was plotted against fly ash content for mixtures prepared with 5% LKD in Figure 2.2. Al, Cr, V, Sb, and Mn showed similar trends, the concentrations generally increased with increasing fly ash content.



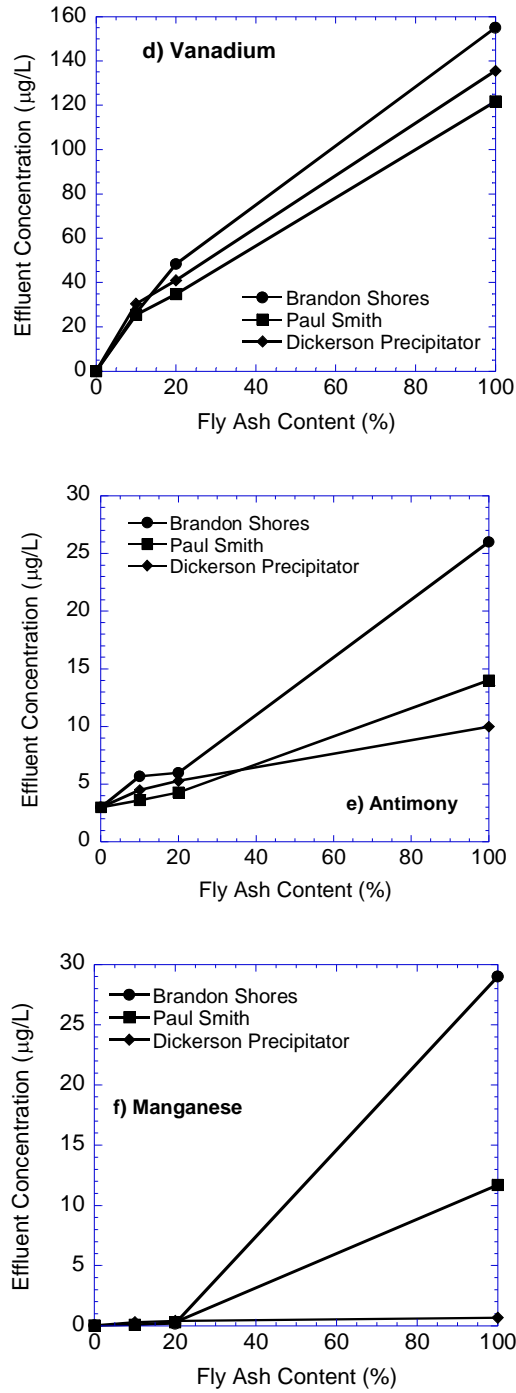


Figure 2.2. Effect of fly ash content on WLT concentrations of a) chromium, b) iron, c) aluminum, d) vanadium, e) antimony, and f) manganese. Mixtures prepared with 10% and 20% fly ash are amended with 5% LKD. 0% and 100% fly ash content corresponds to URM only and fly ash only specimens, respectively.

The rate of increase of these five metals concentrations, however, was different without a recognizably consistent variation, and partially due to differences on metal contents based on total elemental analysis (Table 2.4). The effluent concentrations of all metals were higher for the fly ash alone (100% fly ash) than the soil alone (0% fly ash). For the soil-fly ash-LKD mixtures, higher fly ash contents generally yielded higher effluent metal concentrations. However, the increase in metal concentrations was not linear with fly ash content, even though the mass of metals in soil mixture increases approximately linearly with increasing fly ash content. Therefore, the use of linear dilution calculations will underestimate the resulting concentrations of metals from soil mixtures.

Fe concentrations increased with increasing fly ash content from 0% to 10% because of the addition of the main metal source. Similar increase in Fe was observed when the ash content was increased from 20% to 100% due to increase in metal source as well as lack of LKD addition. However, an increase in fly ash content from 10% to 20% cause a decrease in Fe concentrations because of the high pH (pH >11) of the effluent solutions which was achieved by the LKD addition. Fe forms cationic species and precipitates as different complexes (e.g.,  $\text{FeCO}_3$ ) under such alkaline conditions and solubility of Fe play a more dominant role than an increase in the metal source (Pandian and Balasubramonian 2000, Goswami and Mahanta 2007).

High concentrations of Al were observed in the effluent leachates that were leached from soil-fly ash-LKD materials. The solubility of Al is minimum at a pH of about 6.5 and increases with increasing pH (Lim et al. 2004, Komonweeraket et al. 2010). As seen in Table 2.4, the aluminum concentrations in fly ashes alone were at least 3 times lower

than that of the mixtures. The addition of the LKD is most probably responsible for leaching of Al which is increasing the pH of the effluent solutions due to the release of high amount of CaO from LKD. Aluminum produces anionic species and cannot be absorbed by the negatively charged surface in alkaline conditions. High pH values may have showed a significant change in the size of negatively charged particle surface occupied by the hydrogen ions, causing a serious space decrease for Al and other metals (Sparks 2003).

Table 2.4. Stabilized pH and peak effluent concentrations in CLTs. Concentrations exceeding MCLs in **bold**.

Specimen Name	Fly Ash Content (%)	LKD Content (%)	pH	Al (µg/L)	Sb (µg/L)	Cr (µg/L)	Fe (µg/L)	Mn (µg/L)	V (µg/L)
100 BS	100	-	8.6	<b>1590</b>	<b>304</b>	43	223	<b>76</b>	1533
10 BS + 2.5 LKD	10	2.5	12.1	<b>4870</b>	<b>17</b>	28	216	2	100
10 BS + 5 LKD	10	5	12.5	<b>6850</b>	<b>9</b>	40	197	0.5	72
20 BS + 5 LKD	20	5	12.5	<b>7572</b>	<b>49</b>	44	64	0.6	649
100 PS	100	-	7.6	<b>262</b>	<b>156</b>	76	174	<b>1654</b>	891
10 PS + 2.5 LKD	10	2.5	12.3	<b>6030</b>	<b>19</b>	11	18	1	89
10 PS + 5 LKD	10	5	12.5	<b>6660</b>	<b>8</b>	12	15.2	0.3	53
20 PS + 5 LKD	20	5	12.5	<b>7230</b>	<b>24</b>	15	13	0.4	487
100 DP	100	-	7.9	<b>950</b>	<b>48</b>	<b>252</b>	162	<b>257</b>	1093
10 DP + 2.5 LKD	10	2.5	12.1	<b>5810</b>	<b>10</b>	16	30	0.5	170
10 DP + 5 LKD	10	5	12.4	<b>6250</b>	<b>7</b>	26	21	0.3	78
20 DP + 5 LKD	20	5	12.6	<b>8640</b>	<b>8.7</b>	31	16	1	195
URM	-	-	6.5	122	33	0.8	91	3.5	32
	U.S. EPA MCL			200	6	100	300	50	NA
	U.S. EPA WQL			750	NA	570	NA	NA	NA
	MD ATL			NA	NA	74 (Chronic)	570 (Acute)	NA	NA

Notes: MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. MD ATL = Maryland State aquatic toxicity limits for fresh water.

## 2.4.2 Column Leach Tests

### **pH Measurements**

Figure 2.3 shows the effluent pH of the URM alone, fly ash alone and soil mixtures as a function of pore volumes of flow. All tests were continued until a minimum of 200 pore volumes of flow were obtained to examine the behavior and persistency of pH. In all cases, pH initially decreased during the first 30-100 pore volumes of flow with few exceptions followed by an essentially constant pH. Even though the pH of the influent solutions were kept between 6.5 and 7, the stabilized pH of the effluent solutions were still relatively high (pH>11) due to buffering capacities of the fly ashes and LKD.

URM had the lowest pH, and when either fly ash or LKD were added, pH increased regardless of the percentage of additive (Figure 2.3). As with the WLT, the addition of LKD appears to have a greater effect on pH than the addition of fly ash due to relatively higher CaO content. pH can also be correlated with the Ca content of the ash. For instance, PS fly ash (CaO=0.7%) has lower calcium content than BS fly ash (CaO = 7.8%), which resulted in relatively lower stabilized pH values in CLTs (Figure 2.3).



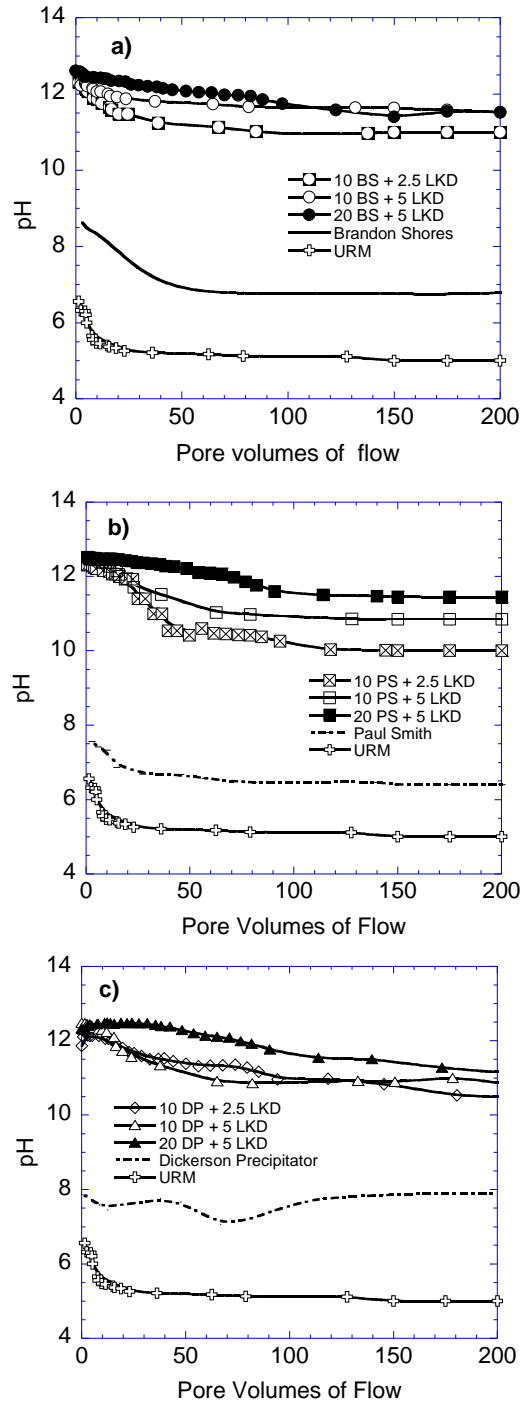
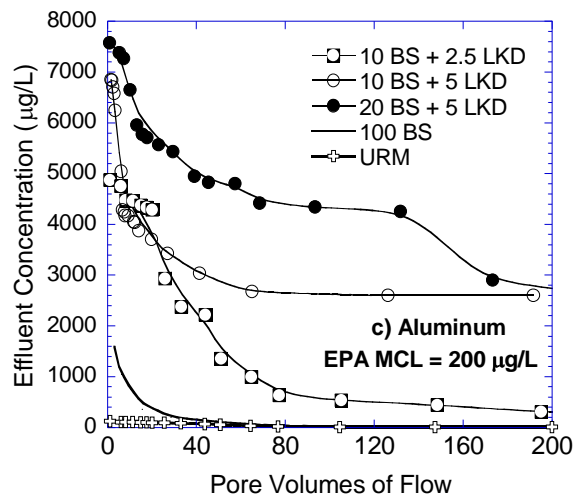
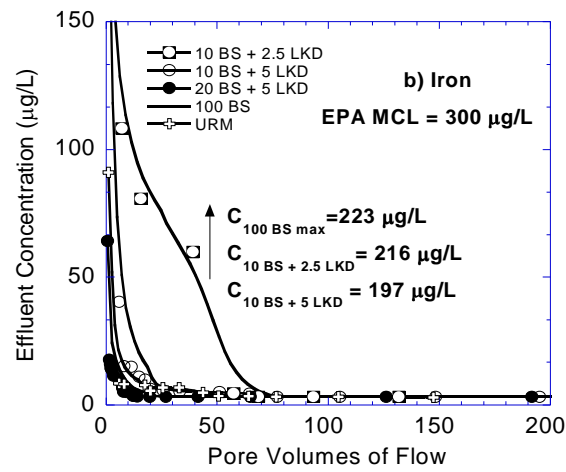
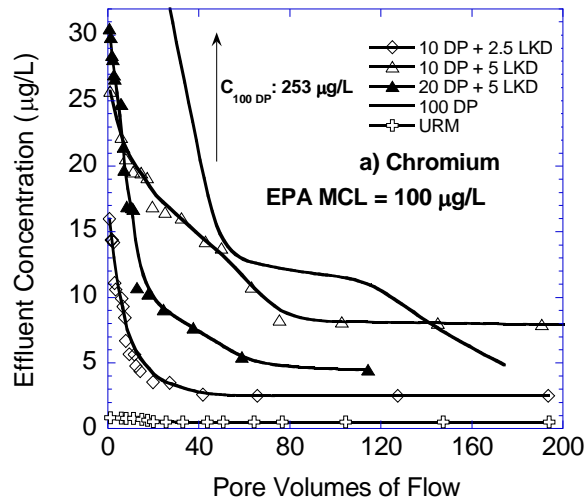


Figure 2.3 Effluent pH in CLTs conducted on mixtures prepared with a) Brandon Shores fly ash , b) Paul Smith fly ash, and c) Dickerson Precipitator fly ash.

## 2.5 METAL LEACHING

Table 2.5 shows that the peak metal concentrations in soil-fly ash mixtures, were below the groundwater quality limits. The only exception was Al. It should be noted that Al is on the EPA list of secondary drinking water regulations, and there are no limits for Al specified in Maryland groundwater protection guidelines.

Figure 4 shows a series of CLT elution curves. All elution curves are not presented herein for brevity, but similar trends were obtained in the remaining curves. The elution curves in Figure 2.4 suggest a high initial leaching of the metals followed by a sharp decrease to near constant concentrations after approximately 10-100 pore volumes of flow, with few exceptions. This type of leaching behavior is called first flush pattern and occurs due to release of the metals from the water soluble fraction as well as from the sites with low adsorption energies (Bin-Shafique et al. 2006, Morar 2008). The initially high effluent pH values of the mixtures (pH~12) provide a possible explanation for the first flush pattern leaching of Al and Cr. In this pH range, Al and Cr are likely to be available in their anionic species in the environment, and the dominant Al species are  $\text{Al(OH)}_4^-$  and  $\text{Al(OH)}_5^{-2}$ , and the Cr species are  $\text{CrO}_7^{-2}$  and  $\text{CrO}_4^{-2}$  (Quina et al. 2009). Cr (VI) is a toxic Cr species, and an acute irritant for living cells, and can be carcinogenic to humans via inhalation (Whalley et al. 1999). Of the six metals considered, Cr and Al are the only ones that increased with increasing pH. While anionic species of Fe, Sb, Mn and V may exist in the environment, the pH range observed in the current study is most conducive to the existence of their cationic species (Goswami and Mahanta 2007, Jegadeesan et al. 2008, Komonweeraket et al. 2010).



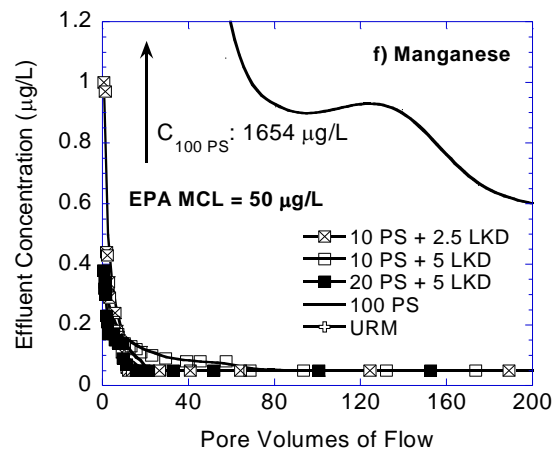
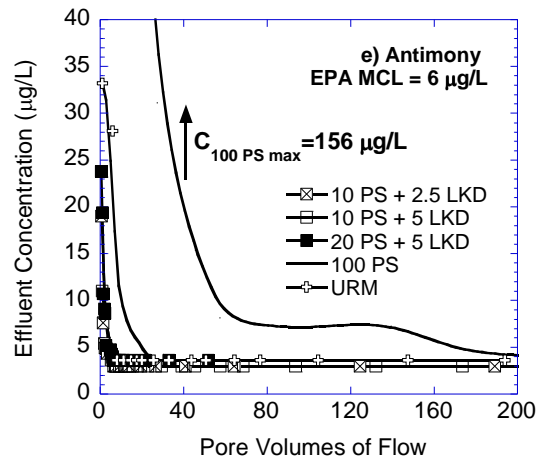
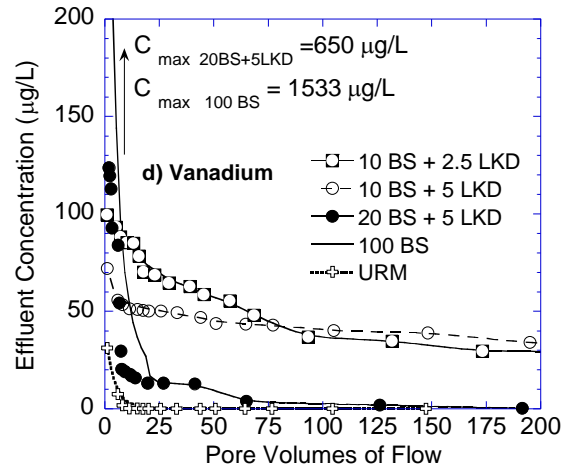


Figure 2.4 CLT elution curves for a) chromium, b) iron, c) aluminum, d) vanadium, e) antimony, and f) manganese.

At basic pHs, the availability of deprotonated (negatively charged) surface increases (Stumm and Morgan 1996), which may have led to an increase in adsorption of cationic species and caused a decrease in the concentrations of Cr, Fe, V, Sb and Mn into the solution. Since the initial pH of the effluent was high, it probably enhanced the solubility of anionic species of Cr, and Al due to unavailability of positively charged surface species for complexation. However, pH decreased from 12 to 10.5 after nearly 50-100 pore volumes of flow and caused a decrease in the solubility of anionic species of Al and Cr in the effluent solution.

The leaching of aluminum from the soil-fly ash mixtures is controlled by the solubility of aluminum hydroxides (Komonweeraket et al. 2010). The leaching behavior of Al shows an amphoteric pattern which represents higher leaching concentrations at extreme pH levels and lesser leaching concentration at neutral pH (Langmuir 1997, Kenkel 2003). Tables 2.4 and 2.5 show that the Al concentrations rose with an increase in LKD and fly ash contents, confirming an amphoteric pattern. Aluminum is very insoluble at neutral pH (Sparks 2003) and its solubility is controlled by dissolution-precipitation oxide and hydroxide minerals (Komonweeraket et al. 2010). This is in good agreement with other studies which showed that Al leaching is the lowest at neutral pH and highest under very alkaline conditions (Stumm and Morgan 1996, Lim et al. 2004, Komonweeraket et al. 2010).

Chemical compositions of the fly ashes based on total element analysis are also important to define the metal leaching behavior. The Al content, for example, is high in all three fly ashes (Table 2.3) resulting in significantly high Al concentrations in the effluent leachate.

Similar to other metals studied, Al also showed the first flush leaching behavior mainly due to basic conditions at the initial pore volumes which probably enhanced the Al solubilization. Edil et al. (1992) and Chichester and Landsberg (1996) reported similar first-flush patterns for metals with high concentrations and a sharp decrease at early pore volumes of flow (PVFs) followed by flattening of the elution curves during column testing of soil-fly ash mixtures. Ogunro and Inyang (2003) also observed wash-out and detachment of Al and Cu metals by percolating solution during the initial stages of a column test. They attributed this phenomenon to an increase in the chemical potential which initiated the leaching of metals from the solid matrix into the surrounding solution. Such an increased chemical potential continued to occur until the concentration difference between the leachant and the solid material was reduced and a steady-state condition was reached.

Figure 2.4 shows that an increase in the initial Cr metal concentrations occurs with increasing fly ash content. This level of increase is probably due to the large amounts of Cr concentrations in the fly ash itself. At initial pore volumes of flow, relatively high levels of Cr were observed in mixtures that included 20% fly ash; however, after nearly 20 PVFs the concentrations for all mixtures were comparable. Solubility of Cr is highly dependent on pH of the aqueous solution. Cr mobility is very low at a neutral pH, but the metal is very mobile at very acidic and basic conditions. As seen in Table 2.5, an increase in LKD caused an increase in pH and peak Cr concentrations in the effluent leachate. At high pHs, Cr generally produces anionic species which cannot be retained on the negatively charged fly ash surfaces. No testing was conducted to identify the oxidation

state of Cr speciation in the leachate, however Cornelis et al. (2008) claimed that Cr is generally as  $\text{Cr}^{6+}$  forms in alkaline conditions, and insoluble  $\text{Ca-Cr}^{3+}$  minerals cause low concentrations of  $\text{Cr}^{3+}$  species such as  $\text{Cr}(\text{OH})_4^-$  at high pHs. Speciation analyses conducted on Sand-BS fly ash mixtures at  $\text{pH}=11$  by Becker et al. (2011) support this claim.  $\text{Cr}^{3+}$  could be found only in the soil mixtures having high reduction potential which may cause an increase in the concentrations of  $\text{Cr}^{3+}$  species in the aqueous solutions. (Cornelis et al. 2008, Samaras et al. 2008).  $\text{Ca-Cr}^{3+}$  compounds may also exist in the effluent solutions having high pHs as  $\text{Ca}_2\text{Cr}_2\text{O}_5$  (Jing et al. 2006). At basic conditions, the solubility of  $\text{CaCrO}_4$  is very high compared to other Cr containing compounds (Allison et al. 1991). On the other hand, most of the oxyanionic species tend to produce surface adsorption complexation with Fe oxides (Goswami and Mahanta 2007). Dzombak and Morel (1990) showed that  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  can be released from Fe oxides at  $\text{pH} > 12.5$  and  $\text{pH} > 7$ , respectively. Pourbaix diagrams for the Cr-O-H system indicate that Cr measured in WLT and CLT leachates is likely to exist as  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$  for the pH conditions present in the current study ( $\text{pH}= 10$  to  $12.5$ ) (Brookins 1988). Thus, it should be kept in mind that most of the Cr concentrations determined in the leachate are likely to be  $\text{Cr}^{6+}$  which is of concern to environmental safety (Whalley et al. 1999).

Table 2.5 shows that the leaching of antimony decreases with increasing pH, albeit not consistently, and increases with increasing fly ash amount most probably due to an increase in main metal source in the mixture. Leaching of antimony (Sb) is significantly related to the redox potential and pH conditions of the aqueous solution. Cornelis et al.

(2008) suggests that  $\text{Sb}^{5+}$  is more commonly found in alkaline waste leachates ( $\text{pH} > 10$ ). However, Leuz et al. (2006b) claimed that the  $\text{Sb}^{3+}$  is oxidized more and faster than  $\text{Sb}^{5+}$  at high pH due to its lower solubility. Jackson et al. (1999) and Komonweeraket et al. (2010) found that the leaching of Sb is the highest around neutral pH and decreases at extreme pH conditions which is in agreement with the findings of the current study.

There is growing interest in studying leaching behavior of vanadium (V) from fly ashes over the past years. Similar to antimony, V is also very redox- and pH-sensitive (Cornelis et al. 2008, Komonweeraket et al. 2010). Some oxidation states of V can form oxyanions at very alkaline conditions which cause a desorption of V from the soil surfaces due to the negatively charged surfaces on the soil surface. **Table 5** shows retention of total V is higher than the release of its oxyanionic species, which may be a cause in decrease in V concentrations with increasing LKD content (from 2.5% to 5% by weight). Since the oxidation states of the both influent and effluent solutions were not constant, the oxidation states of V may fluctuate and may not transform the oxyanionic vanadium species  $\text{V}(\text{OH})_2^+$ ,  $\text{VO}(\text{OH})_2^+$ ,  $\text{VO}_4^{3-}$ .

Concentrations of Fe and Mn in aqueous solutions decreased or remain nearly the same with increasing pH (Table 2.5). Both Mn oxides and Fe oxides are very important for the surface complexation of other oxyanions in the aqueous solutions (van der Hoek et al. 1996, Piantone et al. 2004, Kumpiene et al. 2007). Most of the oxyanions can complex during the co-precipitation of iron metals in the vadose zone (Dixit and Hering 2003, Peacock and Sherman 2004, Jegadeesan et al. 2008, Dutta et al. 2009). Precipitation of  $\text{Fe}^{3+}$  starts as  $\text{Fe}_x(\text{OH})_y$  at  $\text{pH} > 6$  (Espana et al. 2005, Cornelis et al. 2008 and Dutta et al.



2009) and metal adsorption of iron oxides increases with pH, causing a decrease in the effluent metal concentrations (Cornell and Schwertmann 2003). The current study showed that both Mn and Fe concentrations decrease with pH, consistent with the study of Cornelis et al. (2008), Dutta et al. (2009), and Komonweeraket et al. (2010).

## 2.6 COMPARISON OF WLTS AND CLTS

Attempts were made to compare the WLT and CLT results. The peak effluent concentrations in the CLTs ( $C_i$ ) are consistently higher than the WLT concentrations ( $C_w$ ), as shown in Figure 2.5. Differences in L: S ratio between the two leaching tests (a ratio of 20:1 in WLTS versus 0.1:1 in CLTs at the initial PVFs) could be responsible for the metal concentration differences measured in these two leaching tests. Figure 5 shows that  $C_i$  for Al is 2 times higher than  $C_w$ . Similarly,  $C_i$  for Cr, Fe, V, Sb and Mn are up to 20, 100, 10, 10 and 500 times higher than  $C_w$ , respectively. The lack of linear relationship between the  $C_w$  and  $C_i$  for most metals could be attributed to the variation in effluent pHs. Bin Shafique et al. (2006) made similar observations during comparison of WLTS and CLTs.

The scale factors mentioned above should be used with caution as the testing conditions between the CLT and WLT are different. First, the liquid-to-solid ratio remains constant in WLTS but varies in CLTs (Ogunro and Inyang, 2003). A second issue of concern is the difference in duration of the tests. CLT is a dynamic test and the data fluctuates for an extended period of time, while WLTS are finalized in 24 hours. The peak concentrations in CLTs typically occur in the transient stage, and may be different than the ones observed in WLTS.

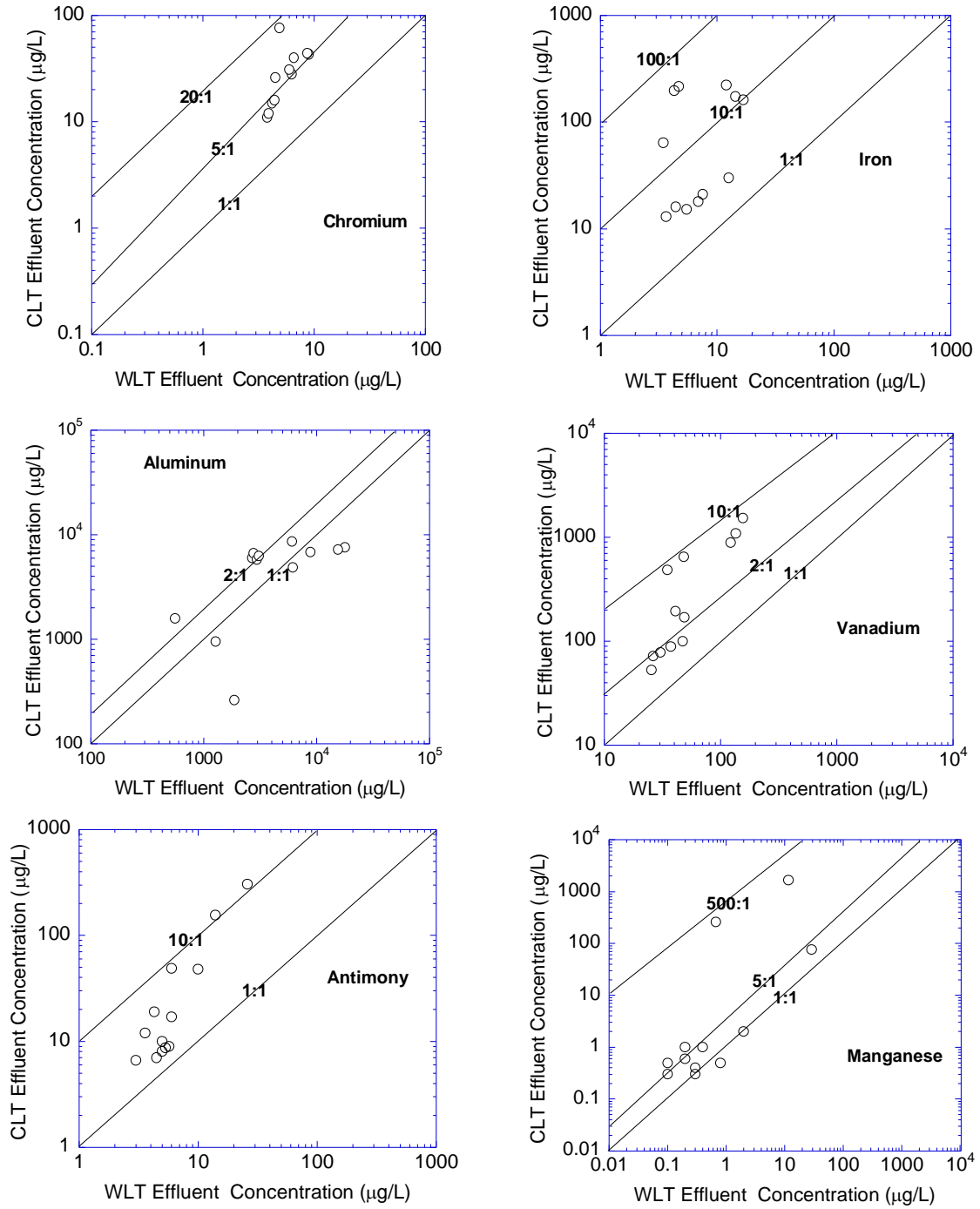


Figure 2.5 Comparison of peak effluent concentrations of six metals from the CLTs and the WLTs

Third, the water flows smoothly through the column set-up while the WLT samples are agitated aggressively, likely enhancing the surface contact of the leaching solution and the solid particulates. This may result in both a higher leaching rate of the metals and a shorter period of time to the equilibrium state between the liquid and solid phases. The pH conditions may also be influenced by this agitation as well as by the dissolution of the mineral components of the metals that were tested. Because the speciation of Al, Cr, V and Sb are highly dependent on redox conditions, the different environments for the two tests are likely to contribute to the difference in the test results.

## 2.7 CONCLUSIONS

A laboratory study was conducted to investigate the environmental feasibility of reusing chemically stabilized road surface material in construction of highway bases. Non-cementitious off-spec high carbon fly ash was activated with lime kiln dust and used to stabilize an unpaved road material (URM). The effects of both fly ash and lime kiln dust addition on environmental suitability of highway base layers were studied through laboratory leaching tests. The observations from the current study are as follows:

1. The concentrations of Cr, Sb, V, Mn, and Fe were below the EPA MCLs, WQLs and Maryland ATLS. Al was only the exception. It should be noted that Al is on the EPA list of secondary drinking water regulations, and there are no limits for Al specified in Maryland groundwater protection guidelines.
2. The initial pH values from CLTs were relatively higher than those measured in WLTs most likely due to difference between the liquid-to-solid-ratio in two tests (a ratio of 20:1 in WLTs versus 0.1:1 in the initial PVFs in CLTs).

3. The metal concentrations increased with increasing fly ash content in WLTs which can be a result of the increased total metal amount in the soil compound. The addition of fly ash, on the other hand, caused an increase in pH values and in concentrations of Sb, V, Cr, Al and Mn.
4. The addition of lime kiln dust (LKD) had different effects on the leaching of the six metals analyzed. LKD addition caused a decrease in CLT concentrations of Fe, Sb, V and Mn due to an increase on the negative surface charge of the solid surface. However, Al and Cr concentrations increased with LKD addition due to an increase in the solubility of their anionic species.
5. The release of all metals from the soil mixtures in CLTs exhibited a first-flush pattern followed by a decrease in concentrations. Most of the metals leached out at the initial stages, and steady-state conditions were reached within 10-120 pore volumes of flow. The higher initial pH values of the effluent solutions may have contributed to an increase in the solubility of anionic species, especially for Al and Cr.

An attempt was made to correlate CLT and WLT concentrations. The concentrations of Al, V, Fe, Sb, Cr and Mn can be conservatively estimated from WLTs by multiplying the concentrations with 2, 10, 100, 10, 20 and 500, respectively. However, caution should be exercised in using these correlation factors as the testing conditions are different for these two systems, due to different liquid-to-solid ratios, test durations, and agitation motion in the batch procedure as compared to the relatively smooth fluid movement inside the column set-up.

### 3 EXPERIMENTAL AND NUMERICAL ANALYSIS OF METALS LEACHING FROM FLY-ASH AMENDED HIGHWAY BASES

#### 3.1 INTRODUCTION

Over 100 million tons of fly ash is produced in the United States as a by-product of burning coal in electric power plants (ACAA 2009). Approximately, 39% of this fly ash is reused and majority of the remaining amount is stockpiled in landfills, thus occupying valuable land space. Benson et al. (2010) indicates that only 24% of the fly ashes generated in the United States are used in concrete production, and an increasing number of power plants are producing high carbon fly ash (HCFA) with loss on ignition (LOI) contents greater than 6%. These fly ashes cannot be used as a concrete additive as unburned carbon content adsorbs the air entrainment agents that are used to prevent crack formation and propagation in the cement matrix (Cetin et al. 2010). HCFAs in the eastern parts of the United States contain very small amounts of calcium oxides and they often need to be activated with a cementitious agent for use in geotechnical applications (Baykal et al. 2004, Edil et al. 2006, Kumar et al. 2007, Yoon et al. 2009, Cetin et al. 2010).

American Society of Civil Engineers estimates that \$2.2 trillion is needed over a five-year period to bring the nation's infrastructure to good condition (Cetin et al. 2010). A large portion of the earthen materials needed for these transportation infrastructure projects have the potential to use recycled materials to aid in their stabilization; however, these materials must also be safe for the environment in which they are placed. One area

for their large volume reuse is highway base stabilization. Even though mechanical properties of the fly ash-amended highway base layers are deemed satisfactory, one key issue that precludes highway base layer stabilization with fly ash is the potential for groundwater impacts caused by metals in the fly ash (Jankowski et al. 2006, Wang et al. 2006, Bin-Shafique et al. 2006, Goswami and Mahanta 2007, Li et al. 2007).

The objective of this study was to evaluate the leaching potential of HCFA-stabilized highway base layers and to assess their potential impact on groundwater through laboratory batch water leach and column leach tests, and computer modeling. One type of soil and three different HCFAs were used. The study focused on leaching of four trace metals: barium (Ba), boron (B), copper (Cu) and zinc (Zn).

### 3.2 MATERIALS

An unpaved road material (URM) was used as the primary soil source for the highway base mixtures. URM was stockpiled in various locations in Maryland and required immediate attention for recycling. The URM was collected from a stock-pile in Caroline County, Maryland satisfied the gradation and maximum dry unit weights requirements by the Maryland State Highway Administration (SHA). The materials larger than 19-mm sieve were removed before starting any laboratory tests. Physical and chemical properties of URM are summarized in Table 3.1.

Three HCFAs were used as stabilizing agents in highway base layers. All fly ashes were obtained from power plants located in Maryland: Brandon Shores (BS), Paul Smith (PS), and Dickerson Precipitator (DP). The physicochemical properties and particle size distributions of all materials are presented in Table 3.1 and Figure 3.1, respectively.

Table 3.1 Physical and chemical properties of the materials used in current study. Chemical compositions and metal concentrations are based on X-ray fluorescence spectroscopy and total elemental analysis, respectively.

Property		Unpaved road material	Brandon Shores (BS) fly ash	Paul Smith (PS) fly ash	Dickerson Precipitator (DP) fly ash	
Index Properties	$G_s$	2.64	2.17	2.2	2.37	
	$w_{opt}$ (%)	13.4	26	22	36	
	$\gamma_{d\ max}$ (kN/m <sup>3</sup> )	18.8	11.9	10	9.9	
	PI (%)	NP	NP	NP	NP	
Chemical Properties	Chemical Composition (%)	LOI	NA	13.4	10.7	20.5
		SiO <sub>2</sub>	NA	45.1	50.8	35
		Al <sub>2</sub> O <sub>3</sub>	NA	23.1	26.9	24.4
		Fe <sub>e</sub> O <sub>3</sub>	NA	3.16	5.5	12.6
		CaO	NA	7.8	0.7	3.2
	Total Metal Concentration (mg/L)	Barium	4.62	13.7	30	19.7
		Boron	2.86	17.3	45.3	24.5
		Copper	1.28	74.7	25.3	58.7
		Zinc	82.3	58.2	28.5	45.6
		pH	6.5	9.6	7.6	8.8

Note: LOI: Loss on ignition.  $G_s$ : Specific gravity,  $w_{optm}$ : Optimum water content,  $\gamma_{dmax}$ : Maximum dry unit weight, NP: Nonplastic, NA: Not available.

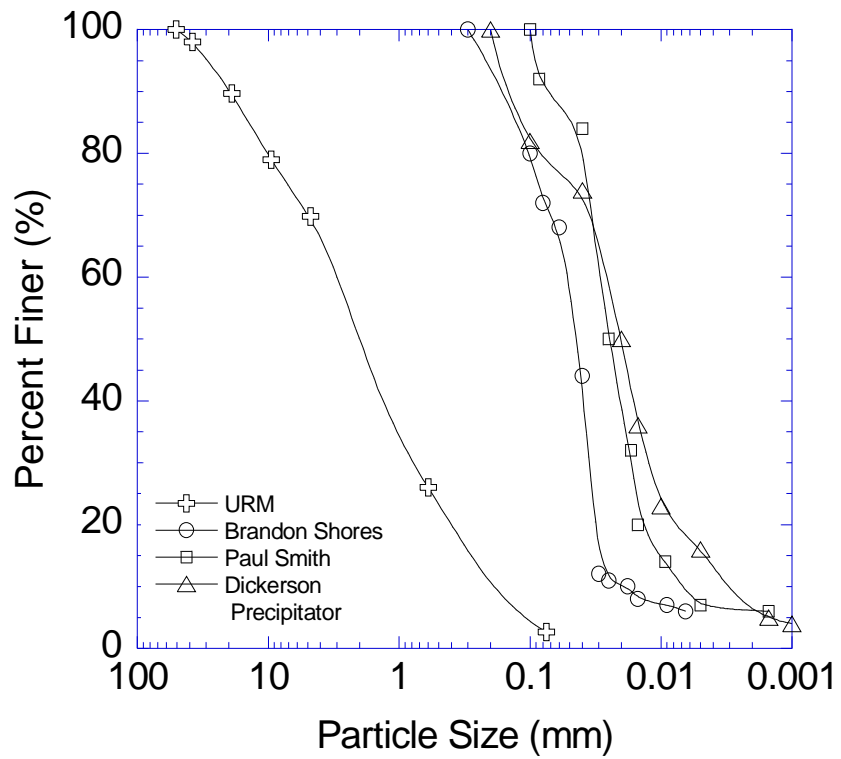


Figure 3.1 Particle size distributions of unpaved road material (URM) and fly ashes.



The LOI and CaO contents of the ashes range from 10.7% to 20.5%, and from 0.7% to 7.8%, respectively, indicating that the fly ashes can not be classified as C or F fly ashes according to Standard Specification for Coal Fly Ash (ASTM C 618). All three ashes are slightly alkaline (pH = 7.6 to 9.6). Due to non-cementitious nature of HCFAs, Lime Kiln Dust (LKD) with CaO content 60% obtained from Pittsburgh, Pennsylvania was used to initiate the pozzolanic reactions.

### 3.3 METHODS

#### 3.3.1 *Batch Water Leach Test (WLT)*

Batch water leach tests were conducted on the URM, fly ashes and URM-fly ash-LKD mixtures using different percentages of fly ashes and lime kiln dusts in accordance with the Test Method for Shake Extraction of Solid Waste with Water (ASTM D 3987). Non-activated fly ashes (i.e., 100% fly ash specimens) are not used in highway base construction but the ashes, along with 100% URM, were still employed in laboratory testing for comparison purposes. Two modifications were made to the standard method. The specimens were prepared at a liquid-to-solid ratio (L:S) of 20:1. All soil materials were air-dried and sieved through the No. 4 (4.75-mm) sieve before use. The specimens were cured in plastic bags for 7 days (21 C° and 100% relative humidity) to allow pozzolanic reactions to occur. 2.4 g of URM mixture was then added to 48 mL of influent solution in 50 mL high-density polyethylene (HDPE) bottles. Next the solutions were rotated at a rate of 29 rpm at room temperature (24 C°) for 18 hours in accordance with ASTM D 3987. After rotation, the samples were allowed to sit for 5 minutes and centrifuged at 3000 rpm for 20 minutes. Upon centrifugation, the suspended solids were

filtered through the 0.2- $\mu\text{m}$  pore size, 25 mm diameter membrane disk filters fitted in a 25-mm Easy Pressure syringe filter holder by using a 60-mL plastic syringe. pH and electrical conductivity (EC) measurements were conducted and the samples were acidified to  $\text{pH} < 2$  with 2%  $\text{HNO}_3$ . Before use, all equipment (centrifuge tubes, filter holders syringe etc.) was washed with 2 %  $\text{HNO}_3$  acid solutions and rinsed with DI water. All samples were stored at 4 C° for chemical analysis. Triplicate WLTs were conducted on all mixtures using each soil solution.

Two different influent leaching solutions were used in water leach tests (WLTs). The influent solutions were prepared with 0.1M NaBr solution (IS= 0.1) and 0.02 M NaBr solution (IS= 0.02) to determine the effect of ionic strength on leaching of heavy metals.

### *3.3.2 Column Leach Tests*

The column leach test (CLTs) were conducted on URM, fly ashes alone and URM-fly ash-LKD mixtures. All specimens were compacted at optimum moisture contents in a PVC mold having 101.6 mm diameter and 116.4 mm height by using standard Proctor compaction effort with the Method of Laboratory Compaction Characteristics of Soil using Standard Effort (ASTM D 698). In the original grain size distribution of the URM, approximately 25% of the grain particles are larger than 4.75 mm in width. When placed in a mold of diameter 101.6 mm, the larger grain particles would make the specimen highly permeable and would decrease the total solid surface area in the soil matrix. Therefore, air-dried URM was sieved from a No.4 (4.75-mm) sieve to remove these larger particles. PVC molds were preferred to minimize the outside effects on effluent

metal concentrations. All mixtures were cured for 7 days in a humidity chamber with 100% relative humidity and 21 C° following compaction.

After curing, the CLTs were started immediately. The columns were operated in an up-flow mode with flow provided by a peristaltic pump on the influent line. The polypropylene (PP) influent lines were connected to a polyethylene reservoir tank which was filled with the 0.1 M NaBr solution with adjusted pH (pH 6.5~7). On the effluent end of the column, polytetrafluoroethylene (PTFE) tubing transferred the effluent solution into the collection bottle.. An inflow rate of 60 mL/hr was used for all tests following the recommendations of Gelhar et al. (1992) and Morar (2007).

A 0.1 M NaBr solution prepared with ASTM Type II water was used to provide influent with an ionic strength comparable to that of salt-laden percolate similar to that encountered in regions where salt is applied to roadways for deicing (Papini et al. 1999, Bin-Shafique 2006). Br was selected because it is a non-reactive tracer. pH of the influent solution was adjusted by adding 0.5 M NaOH solution to stay between 6.5 and 7. During the first three days of testing, frequent sampling (every 4 hours) was necessary in order to catch the breakthrough curve describing the leaching of each metal studied. After 72 h, the sampling frequency was decreased to twice a day for two days, and 2 to 7 times a week as the temporal changes in the metals concentrations became less significant. pH and electrical conductivity measurements were recorded immediately after the sample collection. The protocol for sample filtration and preservation followed those employed in WLTs. A series of falling-head hydraulic conductivity tests were conducted on the specimens before dismantling the columns.

### 3.3.3 *Chemical Analysis*

The metals selected for analysis were Ba, B, Cu and Zn. These metals were selected on the total elemental analyses presented in Table 1 and due to their potential risk to the environment and human health as well as their range of mobilities in groundwater (Praharaj et al. 2002, Kim et al 2006, Bankowski et al. 2004, Jankowski et al. 2006, Goswami and Mahanta 2007, Quina et al. 2010, Chavez et al. 2010). In adults, B can cause nausea, vomiting, redness of the skin, difficulty swallowing and diarrhea. In animals, acute excessive exposure to B may cause rapid respiration, eye inflammation, swelling of the paws and may affect male reproductive organs (Ischii et al. 1993, Wegman et al. 1994, US-EPA 2008). Long-term Ba exposure may cause hypertension in humans (Wones et al. 1990, Perry et al. 1989). Exposure to Potassium with Ba may cause cardiac and skeletal effects in human body (US EPA 1990). Furthermore, copper and zinc metals are the most metals listed in the priority list by US.EPA. These 2 metals are very soluble and non-biodegradable and can accumulate in animals, plants and human body over an extended period of time (Svilovic et al. 2009, Elsayed-Ali et al. 2011).

The total elemental analyses method covers the digestion and analysis of fly ash samples for major and minor element contents by using an ICP-OES (Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer). The digestion process was started by weighing the sample in a 50-mL glass digestion tube. 5 mL of concentrated HNO<sub>3</sub> (trace element grade) was added per tube and the tubes were loosely capped and placed on a digestion block heated to 120<sup>0</sup> C. The fly ash and URM samples were digested for 15-16 hours at 120<sup>0</sup> C and then removed from the block. After

cooling, 1 mL of H<sub>2</sub>O<sub>2</sub> was added to each tube and the tubes were put back on the block for 30 min. The last step was repeated twice and the samples were then removed from the block and allowed to cool down. The sample volume was brought to 50 mL, mixed and allowed to sit for 3 hours before analysis on the ICP-OES was performed.

The concentrations of all metals were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX CCD Simultaneous ICP-OES instrument. All sampling equipment that contacted the leachate samples was acid cleaned, dried, and stored in clean and sealed bags. Blanks were run every 10-20 analyses and the calibration was verified every 10 analyses. A reagent blank was tested every 20 samples and a spiked sample was analyzed every 10 samples. Minimum detection limits (MDLs) for ICP-OES were determined for each metal and a set of calibration standards according to the U.S. Code of Federal Regulations Title 40. The MDLs for Ba, B, Cu, and Zn were determined as 2 µg/L, 4 µg/L, 0.7 µg/L, and 1 µg/L, respectively.

### *3.3.4 Chemical Transport Modeling*

The transport of metals in a highway environment was simulated using WiscLEACH, a recent and verified algorithm for simulating water and solute movement in two-dimensional variably saturated media (Li et al. 2007). Three analytical solutions to the advection-dispersion-reaction equation are combined in WiscLEACH to develop a method for assessing impacts to groundwater caused by leaching of trace elements from fly ashes used in highway layers. The analytical method in WiscLEACH has been verified with the predictions made with HYDRUS-2D, a well-known software package for simulating flow and transport in variably saturated media (Li et al. 2007).

WiscLEACH simulations were conducted to study the locations of maximum soil vadose zone and groundwater concentrations (e.g., at the centerline of the pavement structure, at the vicinity of point of compliance) and contours of trace metals were developed at different years as a function of depth to groundwater, thickness of the base layer, percent fly ash by weight, hydraulic conductivity of the base layer, hydraulic conductivity of the aquifer material and initial concentration of the metal in the fly ash (Figure 3.2). Input to the model included annual precipitation rate in Maryland was obtained from the National Weather Service records, point of compliance and physical properties of the pavement layers were selected according to the MD -SHA roadway design manual (2004), and transport parameters and hydraulic conductivities were determined in the current laboratory study.

WiscLEACH assumes all materials in the profile are homogeneous and isotropic. Precipitation falling on the pavement surface, the shoulders, and surrounding ground infiltrates into the ground surface or is shed as runoff (Li et al. 2007).

As water percolates down through the profile, trace elements leach from the fly ash and migrate downward through the subgrade soils until they reach the ground water table. Flow in the fly ash and subgrade is assumed to occur only in the vertical direction. Steady 1D unit gradient flow is assumed in the pavement layers and the vadose zone, with the net infiltration rate controlled by the least conductive layer in the profile and the annual precipitation rate. Surface runoff and evaporation from the pavement surface, the shoulders, and the surrounding ground are not considered. Infiltration of runoff along the edges of the pavement structure is ignored.

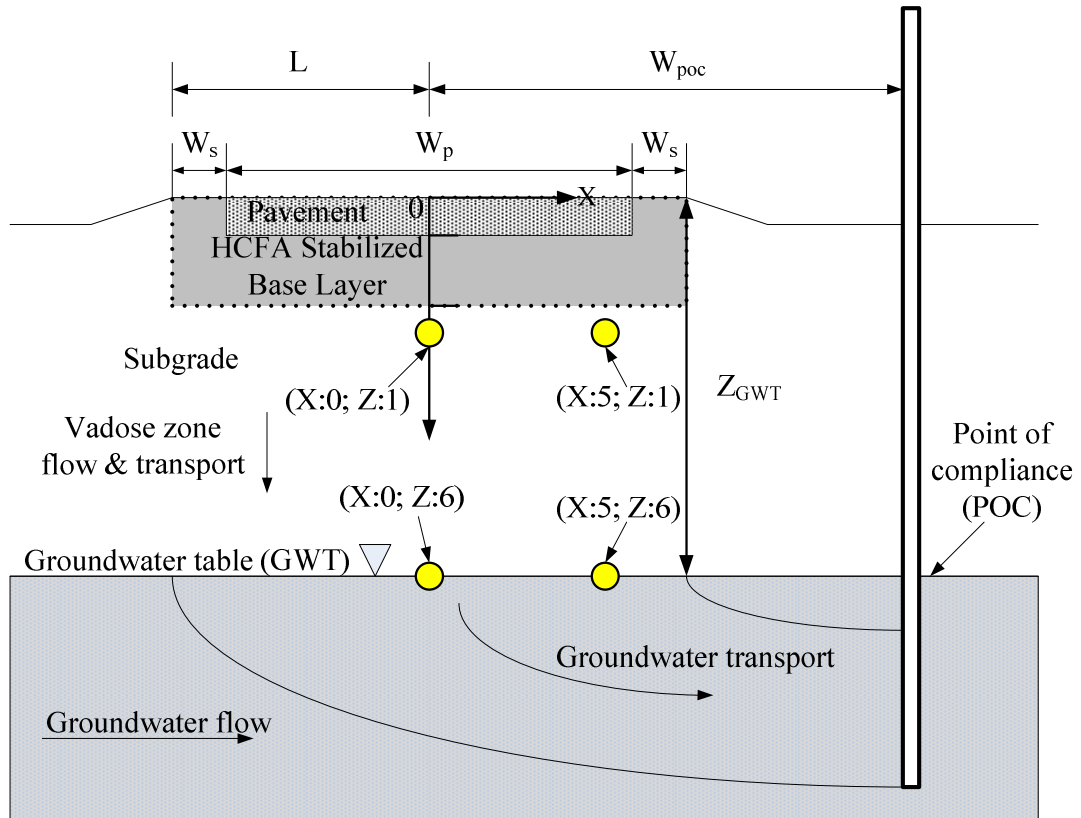


Figure 3.2 Conceptual model in WiscLeach for predicting impacts to the vadose zone and groundwater from HCFA stabilized highway base layer,

Transport in the vadose zone beneath the fly ash layer is assumed to follow the advection-dispersion-reaction equation (ADRE) for 1D steady state vertical flow with 2D dispersion and linear, instantaneous, and reversible sorption. Trace elements that reach the groundwater table are transported horizontally and vertically, although the flow of ground water is assumed to occur predominantly in the horizontal direction. Steady saturated groundwater flow is assumed, and transport in groundwater is assumed to follow the ADRE with instantaneous, reversible, and linear sorption. Chemical and biological reactions that may consume or transform trace elements are assumed to be absent. In addition, flow in the fly ash and subgrade is assumed to occur only in the vertical direction. Steady 1D unit gradient flow is assumed in the pavement layers and the vadose zone, with the net infiltration rate controlled by the least conductive layer in the profile and the annual precipitation rate. Transverse flow on top of the subgrade toward the edge of the road structure is ignored.

### *3.3.5 Model Formulation in Vadose Zone*

WiscLEACH considers only steady 1D unit gradient flow in the pavement layers and the soil vadose zone and the rate of flow  $q_v$  is determined by the comparison of the least conductive layer in the profile and the annual precipitation rate. The lowest of these values are used as the rate of flow in the program. It is assumed that possible horizontal movement of the flow is ignored whereas the rate of vertical flow may change with depth, but the net infiltration rate is assumed to equal  $q_v$ . No water loss is assumed and the water infiltrates to the soil vadose zone toward groundwater without any loss on the



pavement and ground surface. Surface runoff and evaporation from the pavement surface are ignored (Li et al. 2007). In the current study leaching pattern is first-flush leaching from the HCFA stabilized base layer. In WiscLEACH a first-flush leaching from the HCFA base layer is assumed to follow the ADRE with linear, instantaneous and reversible sorption (Li et al. 2007).

In WiscLEACH, transport in the vadose zone beneath the HCFA layer is assumed to follow the ADRE for 1D steady state vertical flow with 2D dispersion and linear, instantaneous and reversible sorption (Li et al. 2007).

$$R \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} \quad (1)$$

where C is metal concentration, T is time, x is horizontal distance from the centerline of the pavement, z is depth below ground surface,  $v_z$  is seepage velocity in vertical direction,  $D_x$  is dispersion coefficient in x direction,  $D_z$  is dispersion coefficient in z direction and R is retardation factor.

The analytical solution to Equation 1 is obtained by applying the following initial and boundary conditions (Li et al. 2007):

$$C(x, z, t = 0) = \begin{cases} C_0 & \text{at } z_t < z < z_B \quad \text{and } -L < x < L \\ 0 & \text{otherwise} \end{cases} \quad (2a)$$

$$\theta_z C - D_z \frac{\partial C}{\partial z} \Big|_{z=0} = 0 \quad (2b)$$

$$\frac{\partial C}{\partial x}(\pm\infty, z, t) = 0 \quad (2c)$$

$$\frac{\partial C}{\partial z}(x, \infty, t) = 0 \quad (2d)$$

where  $C_0$  is initial metal concentration,  $Z_T$  is depth of the top of the fly ash stabilized layer,  $Z_B$  is depth of the bottom of the fly ash stabilized base layer,  $L$  is sum of the shoulder and half of the pavement width.

Equation 2a and 2b indicate that the fly ash stabilized base layer is the only source of trace elements and no trace elements leached from the pavements or ground surface that is above the fly ash stabilized base layer. Equations 2c and 2d imply that the effect of dispersion and diffusion in the soil vadose zone is insignificant with a distance from the pavement surface and the centerline of the pavement structure. The analytical solution to Equations 1 and 2 is (Li et al. 2007):

$$\begin{aligned} C(x, z, t) = & \frac{C_0}{4} \left\{ e^{\left(\frac{\theta_z z}{D_z}\right)} \left[ \left( \frac{1 + \theta_z z}{D_z} \left( z + Z_T + \frac{\theta_z t}{R} \right) \right) x \operatorname{erfc} \left( \frac{R(z + Z_T) + \theta_z t}{\sqrt{4RD_z t}} \right) \right] - \exp \left( \frac{\theta_z z}{D_z} \right) \right. \\ & x \left[ \left( 1 + \frac{\theta_z}{D_z} \left( z + Z_B + \frac{\theta_z t}{R} \right) \right) \operatorname{erfc} \left( \frac{R(z + Z_B) + \theta_z t}{\sqrt{4RD_z t}} \right) \right] + \operatorname{erfc} \left( \frac{R(z - Z_B) - \theta_z t}{\sqrt{4RD_z t}} \right) - \\ & \left. \operatorname{erfc} \left( \frac{R(z - Z_T) - v_z t}{\sqrt{4RD_z t}} \right) \right] \quad (3) \\ & + \sqrt{\frac{4v_z^2 t}{\pi RD_z}} \exp \left( \frac{v_z z}{D_z} \right) \left[ \exp \left( -\frac{[R(z - Z_B) + v_z t]^2}{4RD_z t} \right) - \exp \left( -\frac{[R(z + Z_T) + \theta_z t]^2}{4RD_z t} \right) \right] \left\} x \right. \\ & \left. \left[ \operatorname{erfc} \left( \frac{x - L}{\sqrt{\frac{4D_x t}{K}}} \right) - \operatorname{erfc} \left( \frac{x + L}{\sqrt{\frac{4D_x t}{K}}} \right) \right] \right\} \end{aligned}$$

Equation 3 is applied from the surface of the pavement to the groundwater table (Fig. 3.2).

### 3.3.6 Model Formulation in Groundwater

The transportation of the trace metal elements that leach into the groundwater is at horizontal and vertical direction, although the direction of horizontal flow movement is dominant in the groundwater (Li et al. 2007). The groundwater flow is assumed to be saturated, and the transport of the trace elements is assumed to follow the ADRE with instantaneous, reversible and linear sorption as assumed in transportation in soil vadose zone (Li et al. 2007).

$$R_w \frac{\partial C}{\partial t} = D_{xw} \frac{\partial^2 C}{\partial x^2} - v_h \frac{\partial C}{\partial x} + D_{zw} \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} \quad (4)$$

Where C is metal concentration, T is time,  $v_h$  is groundwater seepage velocity in the horizontal direction,  $D_{xy}$  is hydrodynamic dispersion coefficient in horizontal direction,  $D_{zw}$  is hydrodynamic dispersion coefficient in vertical direction,  $R_w$  is retardation factor in groundwater.

In Equation 4 the cross – dispersion terms are ignored due to the dominant horizontal flow in a uniform and isotropic medium (Li et al. 2007). An analytical solution to Equation 4 for the following initial and boundary conditions:

$$C(x, z, t = 0) = 0 \quad (5a)$$

$$\left( v_z C - D_{zw} \frac{\partial C}{\partial z} \right) \Big|_{z=z_{GWT}} = f(x) = \begin{cases} v_z g(x, z_{GWT}, t), & x_1 < x < x_2 \\ 0, & \text{otherwise} \end{cases} \quad (5b)$$

$$\frac{\partial C}{\partial x} (\pm\infty, z, t) = 0 \quad (5c)$$

$$\frac{\partial C}{\partial z}(x, \infty, t) = 0 \quad (5d)$$

where  $z_{\text{gwt}}$  is depth of groundwater table,  $g(t)$  is metal concentration at the groundwater table and  $x_1, x_2$  are lateral extents over  $g(t)$  applies.

It is assumed that initially groundwater is not contaminated with any trace elements or any other elements that can effect to the sorption of the trace elements which is suggested by Equation 5a. Equation 5b indicates that the amount of trace elements in the vadose zone of the soil directly above the groundwater table is equal to the amount in the groundwater. Equations 5c and 5d indicate that the effect of diffusion and dispersion in groundwater are ignorable at the locations that are very far from the centerline of the pavement and the groundwater table. The solution to Equations 4 and 5 for a condition if  $Z$  is larger than  $Z_{\text{GWT}}$  is (Li et al. 2007):

$$C(x, z, t) = \int_0^t \frac{\theta_z g(t-\tau)}{2R_W} \left[ \operatorname{erfc} \left( \frac{R_W(x-x_2) - \theta_z \tau}{\sqrt{4R_W D_{ZW} \tau}} \right) - \operatorname{erfc} \left( \frac{R_W(x-x_1) - \theta_z \tau}{\sqrt{4R_W D_{ZW} \tau}} \right) \right] x \left[ \sqrt{\frac{R_W}{\pi D_{ZW} \tau}} \exp \left( -\frac{(R_W(z-z_{\text{GWT}}) - \theta_z \tau)^2}{4R_W D_{ZW} \tau} \right) - \frac{\theta_z}{2D_{ZW}} \exp \left( \frac{\theta_z (z-z_{\text{GWT}})}{D_{ZW}} \right) \right] x \operatorname{erfc} \left( \frac{R_W(z-z_{\text{GWT}}) + \theta_z \tau}{\sqrt{4R_W D_{ZW} \tau}} \right) \quad (6)$$

Equation 6 estimates the metal concentrations that leached from a line source at the groundwater table between  $X_1$  and  $X_2$ .

### 3.4 RESULTS OF WATER LEACH TESTS

WLT concentrations of four metals (Ba, B, Cu and Zn) for all mixtures are shown in Table 2. All concentrations are below the U.S. EPA maximum concentration limits for

drinking waters (MCLs). The results show that, except for Zn, higher concentrations were obtained for fly ashes alone than URM-fly ash-LKD mixtures. Based on total element analysis (TEA), the Brandon Shores fly ash has the highest concentrations of Cu and Zn, and Paul Smith fly ash has the highest concentrations of Ba and B (Table 3.1). However, no consistent relationship exists between TEA-based and WLT-based metal concentrations indicating that leaching of metals is not only dependent on the metal concentrations in the main source but factors such as pH and electrical conductivity may also play a role.

The variation in concentrations of these four metals was plotted against fly ash content for mixtures prepared with 5% LKD in Figure 3.3. The data for URM only (0% fly ash content) as well as fly ash only (100% fly ash content) were also added for comparison purposes. Ba, B and Cu showed similar trends and the concentrations of these three metals generally increased with an increase in fly ash content. Figure 3.3 indicates that the rate of increase in Ba, B and Cu concentrations in the effluent solutions was generally higher when the fly ash content was increased from 0% to 10% than when fly ash content was increased from 10% to 20%. For the URM-fly ash-LKD mixtures, higher ash content generally yielded higher effluent concentrations of Ba, B, and Cu as fly ash contained high amounts of these metals (Table 3.1). However, the linear dilution calculations can not be used since the rate of increase in metal concentrations in the mixtures is not consistent with the increase in fly ash content.

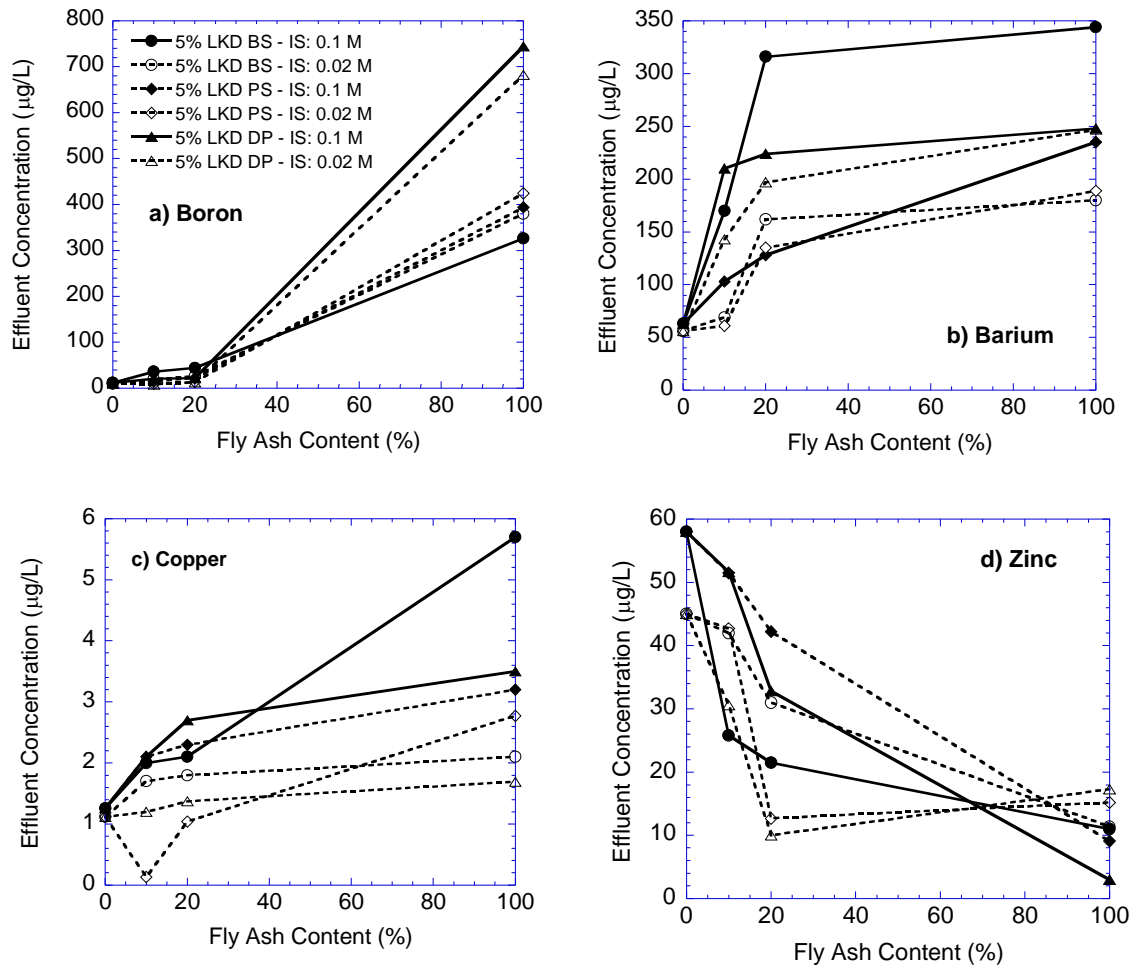


Figure 3.3 Effect of fly ash content on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs. 0% and 100% fly ash content corresponds to URM only and fly ash only specimens, respectively.

Figure 3.3 shows that an increase in fly ash content caused a decrease in Zn concentration as URM contains higher amounts of Zn than the three fly ashes based on total elemental analyses. On the other hand, an increase in LKD content from 2.5% to 5% increased the Zn concentrations in the aqueous solution even under moderate increases in pH (Table 3.3 and Figure 3.4). Goh and Tay (1993) and Ghosh and Subbaroa (1998) also showed that Zn concentrations increased when pH was increased from 9 to 12.

It is widely known that Ba, B, and Cu follow a cationic pattern where the concentrations of these metals decrease dramatically with increasing pH. Since an increase in LKD caused an increase in pH of the solution, a decrease in Ba, B, and Cu concentrations is expected, as seen in Figure 3.4. Similar observations were made by Karuppiah and Gupta (1997), Jankowski et al. (2006), and Liu et al. (2008). Conversely, Zn tends to follow an amphoteric pattern, indicating that the metals leaching are highest at extreme pH conditions and the lowest at neutral pH (Ricou et al. 1999, Lim et al. 2004, Komonweeraket et al. 2010). Jegadeesan et al. (2008) showed that a decrease in leaching of Zn with pH is due to its surface complexation with Fe- Al-oxide or silicate material or the formation of insoluble hydroxides. Furthermore, beyond neutral pH, the Zn metals start precipitating as  $Zn(OH)_2$  and dissolve completely under very alkaline conditions as  $Zn(OH)_3^-$  (Cotton and Wilkinson 1999). The cationic pattern for Ba, B, and Cu and the amphoteric pattern for Zn can be clearly observed when the WLT concentrations are plotted against pH (Figure 3.5).

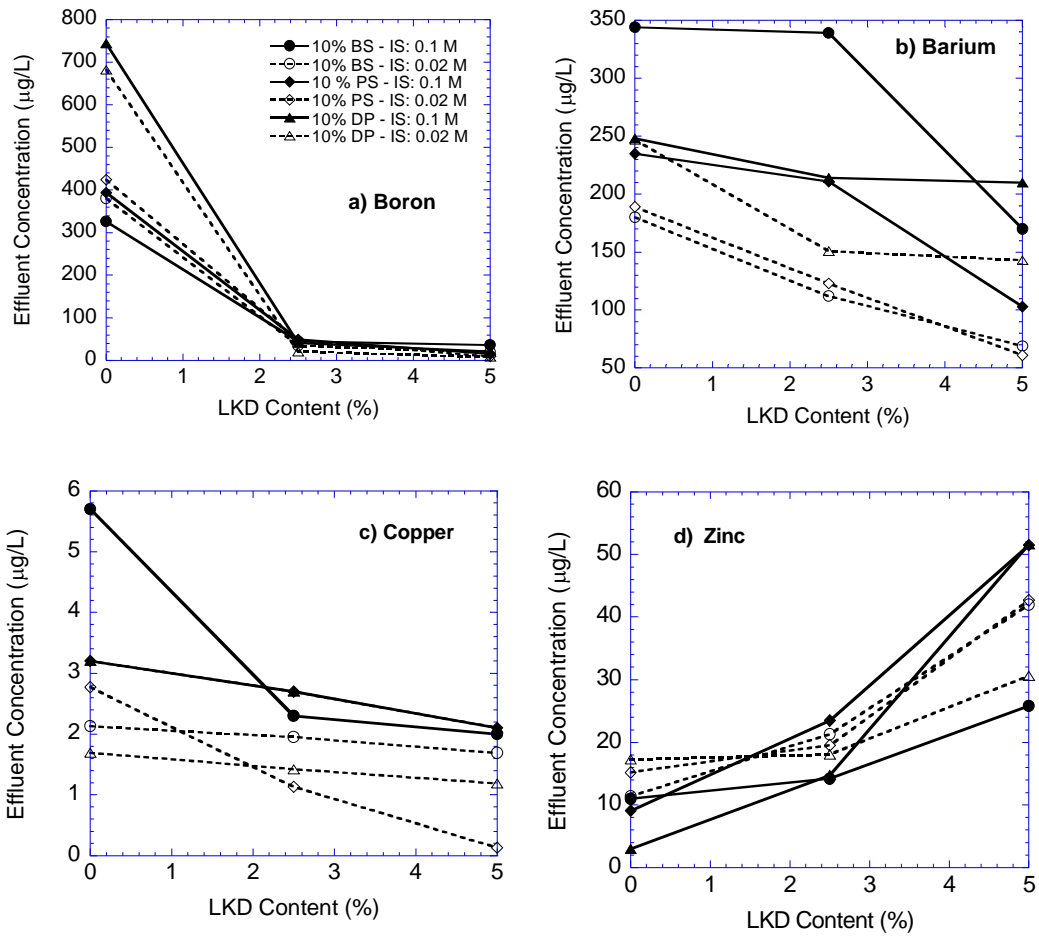


Figure 3.4 Effect of lime kiln dust content on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs. 0% lime kiln dust content corresponds to fly ash only.



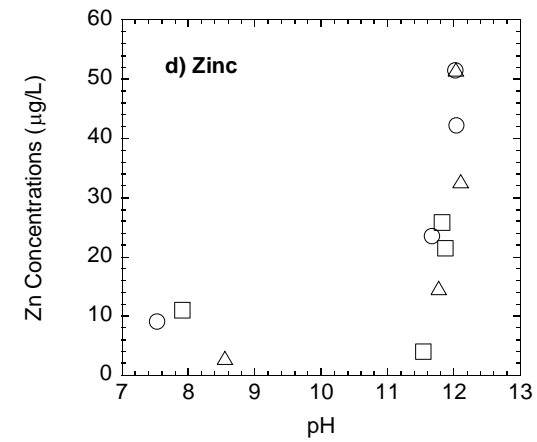
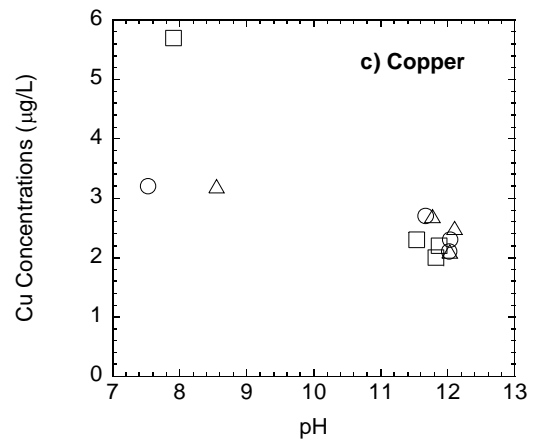
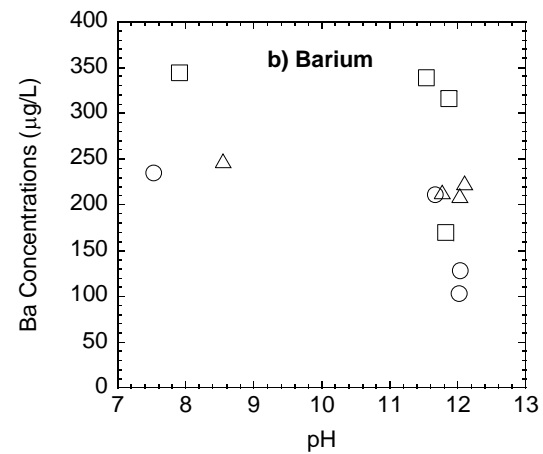
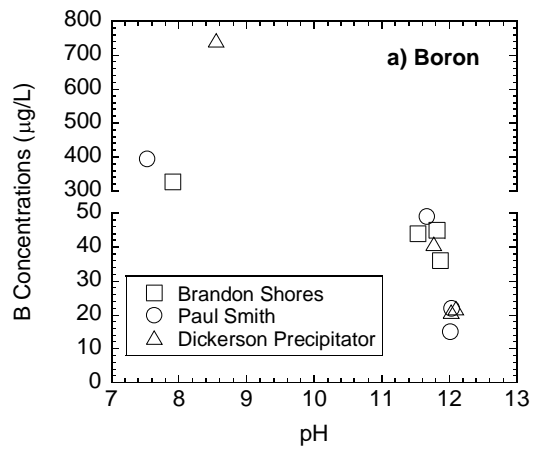


Figure 3.5 Effect of pH on effluent concentrations of a) boron, b) barium, c) copper, and d) zinc in WLTs.

Table 3.2 Aqueous concentrations of metals from WLTs.

Specimen Name	Fly Ash Content (%)	LKD Content (%)	pH <sup>IS=0.1</sup>	pH <sup>IS=0.02</sup>	Barium (µg/L)		Boron (µg/L)		Copper (µg/L)		Zinc (µg/L)	
					C <sub>aq</sub> <sup>IS=0.1</sup>	C <sub>aq</sub> <sup>IS=0.02</sup>	C <sub>aq</sub> <sup>IS=0.1</sup>	C <sub>aq</sub> <sup>IS=0.02</sup>	C <sub>aq</sub> <sup>IS=0.1</sup>	C <sub>aq</sub> <sup>IS=0.02</sup>	C <sub>aq</sub> <sup>NaBr</sup>	C <sub>aq</sub> <sup>DI</sup>
100 BS	100	-	7.9	8.1	344	180	326	380	5.7	2.1	11	11
10 BS + 2.5 LKD	10	2.5	11.5	11.6	339	112	44	34	2.3	1.9	14	21
10 BS + 5 LKD	10	5	11.8	11.8	170	69	45	26	2.0	1.7	26	42
20 BS + 5 LKD	20	5	11.8	11.9	316	162	36	20	2.2	1.8	22	31
100 PS	100	-	7.5	7.8	235	189	394	424	3.2	2.8	9.1	15
10 PS + 2.5 LKD	10	2.5	11.7	11.7	211	123	49	46	2.7	1.1	24	20
10 PS + 5 LKD	10	5	12	11.9	103	61	15	9.4	2.1	0.13	52	43
20 PS + 5 LKD	20	5	12	12.1	128	135	22	14	2.3	1.1	42	13
100 DP	100	-	8.6	8.7	248	247	744	682	3.2	1.7	3	17
10 DP + 2.5 LKD	10	2.5	11.8	11.9	214	151	41	21	2.7	1.4	15	18
10 DP + 5 LKD	10	5	12	12	210	143	21	8	2.1	1.2	52	31
20 DP + 5 LKD	20	5	12.1	12	224	197	22	13	2.5	1.4	33	10
URM	100	-	4.8	5.1	63	56	12	10	1.3	1.1	58	45
U.S. EPA MCL (µg / L)					2000		NA		1300		5000	

Notes: MCL:maximum contaminant levels for drinking water; NA: Not available.

Table 3.3 Peak effluent concentrations of Ba, B, Cu, and Zn for column leach tests and pH at peak concentrations. Concentrations exceeding MCLs in **bold**.

Specimen Name	Fly Ash Content (%)	LKD Content (%)	pH	Barium (µg/L)	Boron (µg/L)	Copper (µg/L)	Zinc (µg/L)
100 BS	100	-	8.6	1507	15000	26	128
10 BS + 2.5 LKD	10	2.5	12.1	1030	590	25	92
10 BS + 5 LKD	10	5	12.5	590	225	15	113
20 BS + 5 LKD	20	5	12.5	<b>2220</b>	2227	57	51
100 PS	100	-	7.6	1460	26400	43	129
10 PS + 2.5 LKD	10	2.5	12.3	677	539	15	141
10 PS + 5 LKD	10	5	12.5	334	314	9	151
20 PS + 5 LKD	20	5	12.5	1263	599	40	88
100 DP	100	-	7.9	<b>3193</b>	11900	181	78
10 DP + 2.5 LKD	10	2.5	12.1	1444	568	18	64
10 DP + 5 LKD	10	5	12.4	377	174	17	94
20 DP + 5 LKD	20	5	12.6	<b>2038</b>	291	24	60
URM	100	-	6.5	209	112	49	258
U.S. EPA MCL (µg / L)				2000	NA	1300	5000

Notes: MCL:maximum contaminant levels for drinking water; NA: Not available.

The data in Table 3.2 suggest that the pHs of the WLT effluents are not affected by the change in ionic strength of the influent solutions. However, metal leaching, with few exceptions, was generally enhanced by an increase in ionic strength of influent solution. An increase in  $\text{Na}^+$  concentrations in the soil matrix by adjusting ionic strength from 0.02 M to 0.1 M may have decreased the surface negativity of the fly ash and URM particles, and released the  $\text{Ba}^{2+}$ ,  $\text{B}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from the solid surface into the aqueous solution by electrostatic effects (Sparks 2003). Praharaj et al. (2002) claimed that the surface area of the fly ash particles decrease and coarseness of the particles increase upon leaching. These changes may have contributed to a decrease on the active surface sites and caused the loosely attached soluble species to be released into the aqueous solution.

### 3.5 RESULTS OF COLUMN LEACH TESTS

CLTs were conducted on URM alone, fly ash alone and URM-fly ash-LKD mixtures to evaluate the leaching of metals under flow-through conditions. All CLTs continued until the pHs of the effluent solutions were stabilized and a minimum of 200 pore volumes of flow was observed. pH of the influent solutions was kept between 6.5 and 7 to simulate typical field conditions in Maryland. pHs of the effluent solutions were relatively high (pH=11-12) compared to that of influent solution due to release of CaO from LKD (Wehrer and Totsche 2008). Table 3.3 indicates that an increase in fly ash content did not influence effluent pH. The effect of LKD addition on effluent pH was more clearly pronounced due to higher CaO content of LKD as compared to fly ashes (60% versus 0.7-7.8%). Small amounts of LKD addition (2.5% by weight) increased the pH of URM by ~5.6 pH units and further addition of LKD had a moderate effect on pH increase.

The peak CLT concentrations of four metals for all specimens are shown in Table 3.3. Most of the concentrations are below the U.S. EPA maximum concentration limits, except the Ba concentrations for 100% Dickerson Precipitator fly ash and two mixtures. Maryland aquatic chronic toxicity limit for copper in fresh water was exceeded for all specimens, whereas 38% of the specimens exhibited Zn concentrations above the Maryland ATLS.

Figure 3.6 shows a series of CLT elution curves. The elution curves for all mixtures are not presented herein for brevity. All specimens exhibited a first-flush leaching pattern, consistent with the past studies (Chichester and Landsberger 1996, Sauer et al. 2005). First-flush pattern generally occurs for the metals having cationic species. An addition of LKD may have caused significant release of CaO into the aqueous solution, which may have contributed to the existence of a such leaching pattern. At the initial leach stages of CLTs, most of the metals were probably washed out and released from the surface of the fly ash and URM particles into the aqueous solution until the concentration difference between the metal source and aqueous solution was reduced (Ogunro and Inyang 2003). A first-flush pattern is expected for boron since the metal is usually attached onto the fly ash and URM particles, and remains present in the water-soluble fraction which increases its leaching rate significantly (Jankowski et al. 2006).

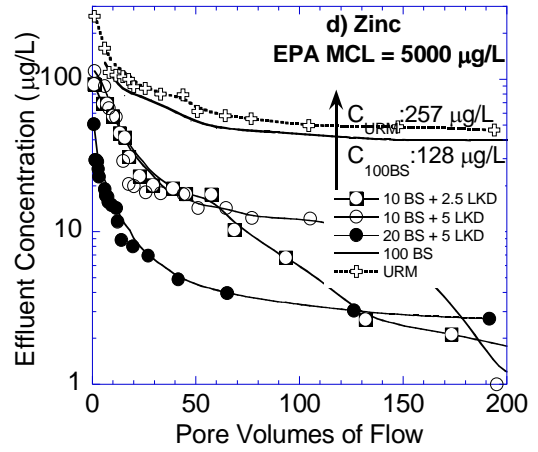
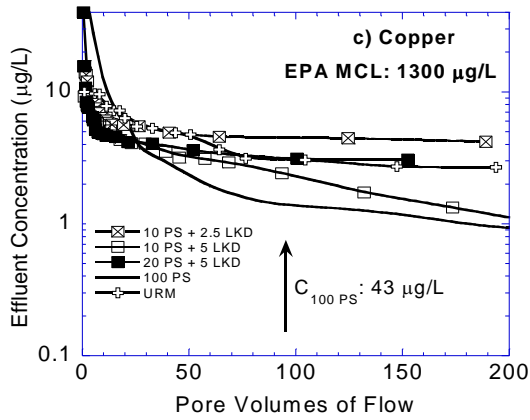
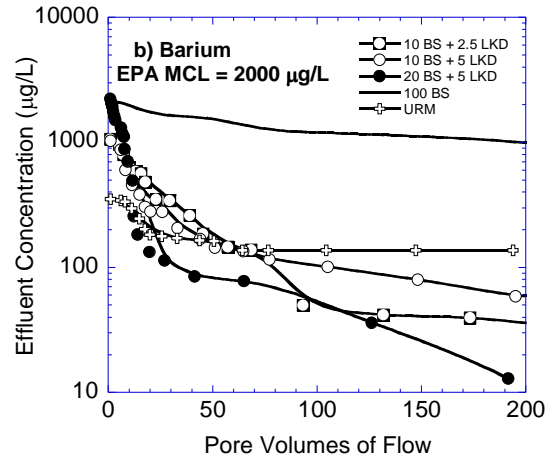
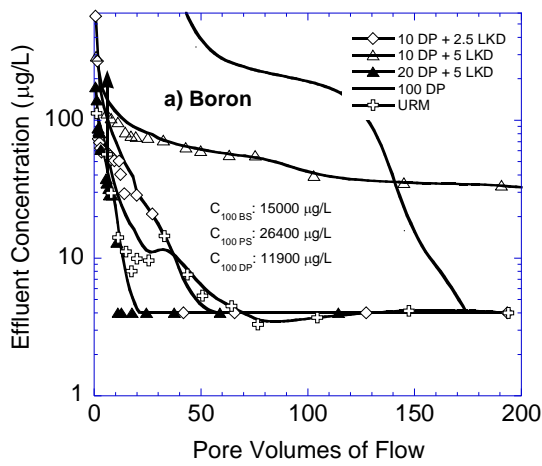


Figure 3.6 CLT elution curves for a) boron, b) barium, c) copper, and d) zinc.

The solubilities of all four metals are highly dependent on the effluent pH. Table 3.3 shows that pH of the mixtures was high (pH > 11.5), indicating a very basic effluent solution. It is recognized in previous studies that the solubility of Cu decreases significantly with increasing pH (Ricou et al. 1999, Yan et al. 2001, Goswami and Mahanta 2007, Liu et al. 2008). It is assumed in alkaline conditions that Cu metals are either included in low-solubility minerals or fixed in precipitates (Wehrer and Totsche 2008), which is consistent with the findings obtained in this study. As seen in Table 3.3, an increase in LKD amount from 2.5% to 5% by weight increased the effluent pH, which may have resulted in reduced Cu concentrations in the aqueous solution due to adsorption of Cu metals onto the fly ash surface (Sparks 2003). Jegadeesan et al. (2008) also showed that the leaching of cationic metals such as Cu can be very low under alkaline conditions (pH > 10). Material amendments into soils that include Fe oxides and alkaline materials can also reduce the mobility and availability of metals in soil by adsorption, complexation, precipitation or combination (Brown et al. 2005, Kumpiene et al. 2007). The relatively high amounts of Fe<sub>2</sub>O<sub>3</sub> (3.16-12.6% by weight, see Table 3.1) may have enhanced the sorption of Cu and caused a reduction in metal concentrations in the current study

The highest Zn concentrations were observed for URM only and Zn concentrations decreased with increasing fly ash content (Figure 3.6). Table 1 indicates that the Zn content of URM is higher than the Zn contents of fly ashes used in this study. This may yield releasing of higher amount of Zn metals into the aqueous solutions with an increase in URM content in the mixtures. Komonweeraket et al. (2010) showed that Zn leaching

follows an amphoteric pattern; however, no relationship was observed when peak CLT zinc concentrations were plotted against effluent pH (data not shown). Even though an amphoteric pattern was evident for Zn in WLTs (Figure 3.5), the dynamic flow conditions in CLTs may have inhibited the formation of such a pattern.

Boron generally tends to show an amphoteric leaching pattern. Recent studies indicated that B is in anionic form in alkaline solutions (Querol et al. 2001, Jankowski et al. 2006). B (III) atoms generally do not exist in their cationic forms and tends to present as boric acid,  $B(OH)_3$ . Moreover, in basic conditions ( $pH > 7$ ) boric acid is being hydrolyzed and being converted into borate ions (Baes and Mesmer 1976). In the current study, the concentrations of B in the effluent solutions from fly ash alone specimens were significantly higher than the concentrations of B from URM-fly ash-LKD specimens even though the pH of specimens was around 12. These results indicated that the amount of main metal source was more dominant than the influence of the pH on the leaching behavior of B. Elsewi et al. (1980) showed that leaching of B is usually higher at low pHs and decreases with an increase in pH. On the other hand, an increase in LKD amount from 2.5% to 5% increased the pH of the specimens only 3 to 5 % which is not a significant increase in pH. Therefore, this minimal change in pH may not be an accurate representation of the effect of pH on leaching behavior of B at these alkaline conditions. In addition, at basic conditions, it is expected to see the precipitation of B with  $CaCO_3$  (Hollis et al. 1988) which may have also caused a decrease in the B concentrations in the aqueous solutions.



Table 3.3 shows that the Ba concentrations in the effluent increased with fly ash content most probably due to an increase in the amount of the main metal source in the mixtures. On the other hand, Ba concentrations decreased with increasing effluent pH. Bankowski et al. (2004) claimed that formation of precipitates and complexation of Ba with silicates may have caused a decrease in Ba concentrations in the aqueous solutions as  $Ba^{2+}$  ions tend to attach to the surface of fly ash and URM, and exist as  $Ba(OH)^+$  at extreme pH conditions.

### 3.6 TOTAL LEACHED AMOUNT OF METALS FROM WLTS AND CLTS

The high carbon fly ashes used in this study contain high amounts of toxic metals. However, high concentrations of toxic metals do not necessarily mean that the material will release significant amounts of heavy metals to into the environment (Apul et al. 2007). Leached amounts of Ba, B, Cu and Zn metals along with the total metal concentrations in WLTS and CLTs are shown in Figures 3.7 and 3.8, respectively. An increase in total metal contents for all specimens generally yielded an increase in metal concentrations in the leachates of WLTS and CLTs with few exceptions. This indicates that the amount of total metal source used in the specimens had direct affect on the leaching amount of metals to the aqueous solutions.

The leached amounts of Ba, B, Cu and Zn from the WLT specimens were up to 98%, 65%, 2.3%, and 1.2% respectively. This indicates that the initial metal content used in the mixtures had significant effects on the leaching of Ba and B metals. Leaching of Cu and Zn, on the other hand, is solubility controlled indicating that their leaching amount is

highly dependent on the pH of the effluent solutions (Quina et al. 2009). Therefore, it is expected that the pH of the effluent solutions has a greater effect on the leached amount of Cu and Zn metals than the total Cu and Zn metal amount in the mixtures.

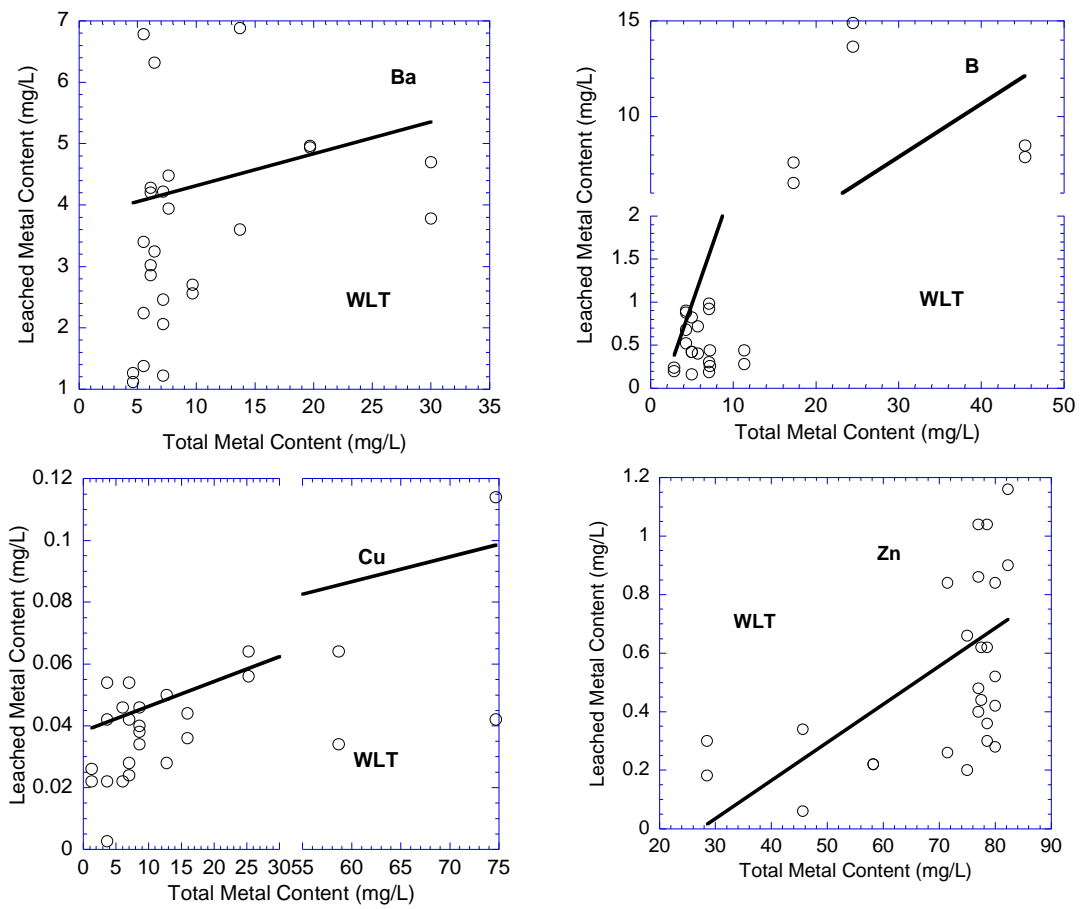


Figure 3.7 Relationship between leaching amounts and concentration of metals in fly ashes (WLTs)

Note: WLT=Water Leach Test.

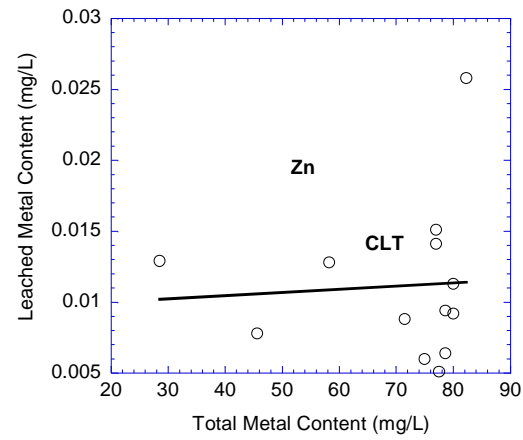
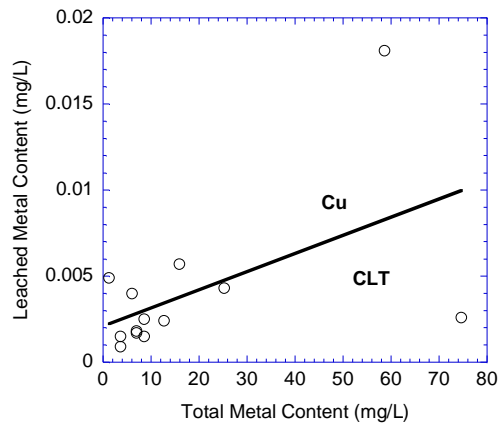
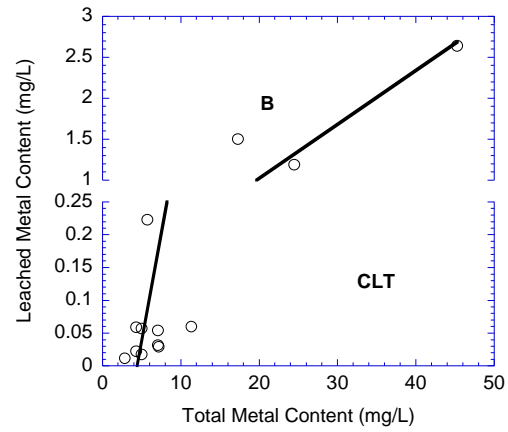
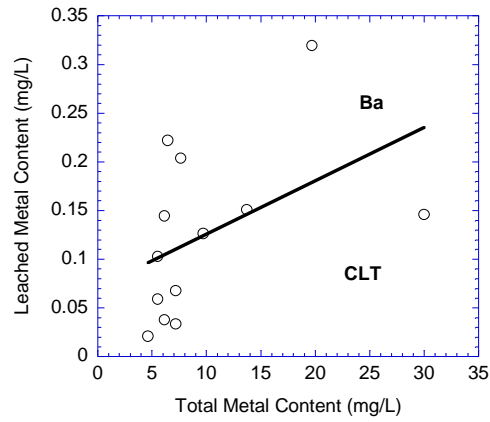


Figure 3.8 Relationship between leaching amounts and concentration of metals in fly ashes (CLTs).  
 Note: CLT=Column Leach Test

Figure 3.8 indicates that the leached amounts of Ba, B, Cu and Zn in CLTs were up to 3.5%, 8.7%, 0.4%, and 0.05%, respectively (Figure 8). Even though CLT peak effluent concentrations were much higher than the WLT concentrations for all four metals, the mass of leached metals in WLTs were higher than those in CLTs. A lower liquid-to-solid ratio (L:S) is probably responsible for the metal concentrations in the CLTs than the WLTs. On the other hand, the agitation motion in the WLTs as compared to the smooth fluid movement inside the column set-up may have increased the surface contact between the influent solution and the solid particles (Morar 2007), and resulted in higher leached metal amounts into the effluent solutions in WLTs.

### 3.7 NUMERICAL MODELING

WiscLEACH was used to predict metal concentrations at different depths and years under field conditions. Input to the model, including the transport parameters and hydraulic conductivities determined in the current study, are provided in Tables 3.4 and 3.5. The pavement width ( $W_p$ ) and shoulder width ( $W_s$ ) were assumed to be 10.4 and 1.5 m, respectively, with a point of compliance ( $W_{poc}$ ) 20 m from the center of the roadway and a depth to the ground water table ( $Z_{GWT}$ ) of 6 m. Over a maximum simulation time ( $T_{max}$ ) of 100 years, an annual precipitation rate of 1 m/year was assumed. Br tracer tests were conducted to determine the transport parameters. Effective porosities and dispersion coefficients were determined by fitting the Ogata-Banks (1961) equation to the effluent Br concentrations in the tracer tests. By using the dispersion coefficients obtained from tracer tests, the longitudinal dispersivities of each specimen was determined and the transverse dispersivity was assumed to be equal to 10% of the longitudinal dispersivity

(Apul et al. 2007). The retardation factors for each metals were obtained by fitting van Genuchten (1981) analytical leaching model to the metal concentrations in the effluent of the column leaching tests.

Figures 3.9 and 3.10 show the contour plots for the predicted concentrations of Zn and Cu, respectively. Contour plots for all metals and mixtures are not shown in Appendix B. The contour plots provide the predictions of the metal concentrations after 1, 2, 4 and 8 years of construction. As expected, metal concentrations decreased significantly with time and distance from the HCFA-stabilized layer surface most probably due to the dispersion of the metals in the soil vadose zone. The concentrations of Cu and Zn metals even after 1 year is much lower than peak Cu and Zn concentrations obtained from CLTs suggesting conservative concentration measurements in CLTs. The metal concentrations mostly were adsorbed in the soil vadose zone before reaching to the ground water. High retardation factors of subgrade would be increasing the rate of adsorption of metals before reaching to the groundwater.

WiscLEACH simulations were also conducted to study the locations of maximum groundwater concentrations (e.g. at the centerline of the pavement structure, in the vicinity of the point of compliance) as a function of depth to groundwater. Figure 3.11 shows the variation of the B and Zn concentrations at different depths and horizontal distance for a base layer comprised of 85% URM, 10% DP fly ash and 5% LKD. The same tests were run on all other mixtures and similar results were obtained but they are not shown here for brevity. Figure 3.11 shows a decrease in B and Zn concentrations with increasing depth and distance from the center alignment of the fly ash stabilized layer in

the vadose zone and groundwater, most probably due to dispersion and adsorption of metals in the vadose zone.

Figure 3.12 shows that the WiscLEACH-based concentrations of B, Ba, and Cu increased and Zn concentrations decreased with increasing fly ash content (10% to 20% by weight), consistent with the observations made in laboratory water leach and column leach tests. WiscLEACH-based maximum field concentrations are lower than those measured in the laboratory column leach tests. Furthermore, all metal concentrations estimated by WiscLEACH are below the EPA MCLs indicating that the use of these mixtures has minimal threat to the environment.

In WiscLEACH, the geometric variables (pavement width, depth to groundwater, shoulder width and thickness of stabilized base layer) and hydraulic variables (porosity and hydraulic conductivity of the fly ash stabilized base layer) could have significant effects on the leaching of metal concentrations in the groundwater. In order to study these effects, a series of sensitivity analyses were conducted at a point of compliance (POC) of 20 m from the center of the roadway in the current study. POC was chosen as the target location as Li et al. (2007) claimed that the concentrations of metals at point of compliance (POC) are less sensitive to the pavement width and shoulder width. In addition, the pavement and shoulder width are less important because the source is distributed over a broad area for all pavement and shoulder widths used in the simulations.

Table 3.4 Hydraulic conductivities and transport parameters for all materials

Specimen	Layer Thickness (m)	Hydraulic Conductivity, $K_s$ (m/s)	Effective Porosity, $n_e$	Hydraulic Gradient	Longitudinal dispersivity, $\alpha_L$ (m)	Transverse dispersivity, $\alpha_T$ (m)
10 BS + 5 LKD	0.407	$1.34 \times 10^{-7}$	0.23	1.0	0.04	0.004
20 BS + 5 LKD	0.356	$1.04 \times 10^{-7}$	0.31	1.0	0.07	0.007
10 PS + 5 LKD	0.375	$2.22 \times 10^{-7}$	0.26	1.0	0.06	0.006
20 PS + 5 LKD	0.396	$2.5 \times 10^{-7}$	0.33	1.0	0.03	0.003
10 DP + 5 LKD	0.375	$2.86 \times 10^{-7}$	0.24	1.0	0.01	0.001
20 DP + 5 LKD	0.396	$1.87 \times 10^{-7}$	0.29	1.0	0.02	0.002
URM	0.791	$8.2 \times 10^{-5}$	0.32	1.0	0.085	0.0085
Pavement	0.125	$5.8 \times 10^{-7}$	0.35	1.0	0.1	0.01
Subgrade	NA	$3.2 \times 10^{-8}$	0.35	1.0	0.1	0.01
Aquifer	NA	$1.2 \times 10^{-4}$	0.30	1.0	0.1	0.01

Notes: The properties for the mixtures were determined from the laboratory tests in the current study. The properties for pavement, subgrade and aquifer are adopted from Li et al. (2006), NA: Not available.

Table 3.5 Retardation factors of the soil mixtures for different metals

Specimen	Retardation Factor, $R_d$			
	Barium	Boron	Copper	Zinc
10 BS + 5 LKD	3.1	5	5.8	3.4
20 BS + 5 LKD	4	2.6	1.2	2.8
10 PS + 5 LKD	3.2	3.6	3.5	2.8
20 PS + 5 LKD	4.1	1.8	1.2	1.8
10 DP + 5 LKD	2.4	1.4	1.7	2.3
20 DP + 5 LKD	1.6	1.8	1.2	1.8
URM	1.93	2.2	2.22	2.04
Pavement	1	1	1	1
Subgrade	3.5	3.5	3.5	3.5
Aquifer	2	2	2	2



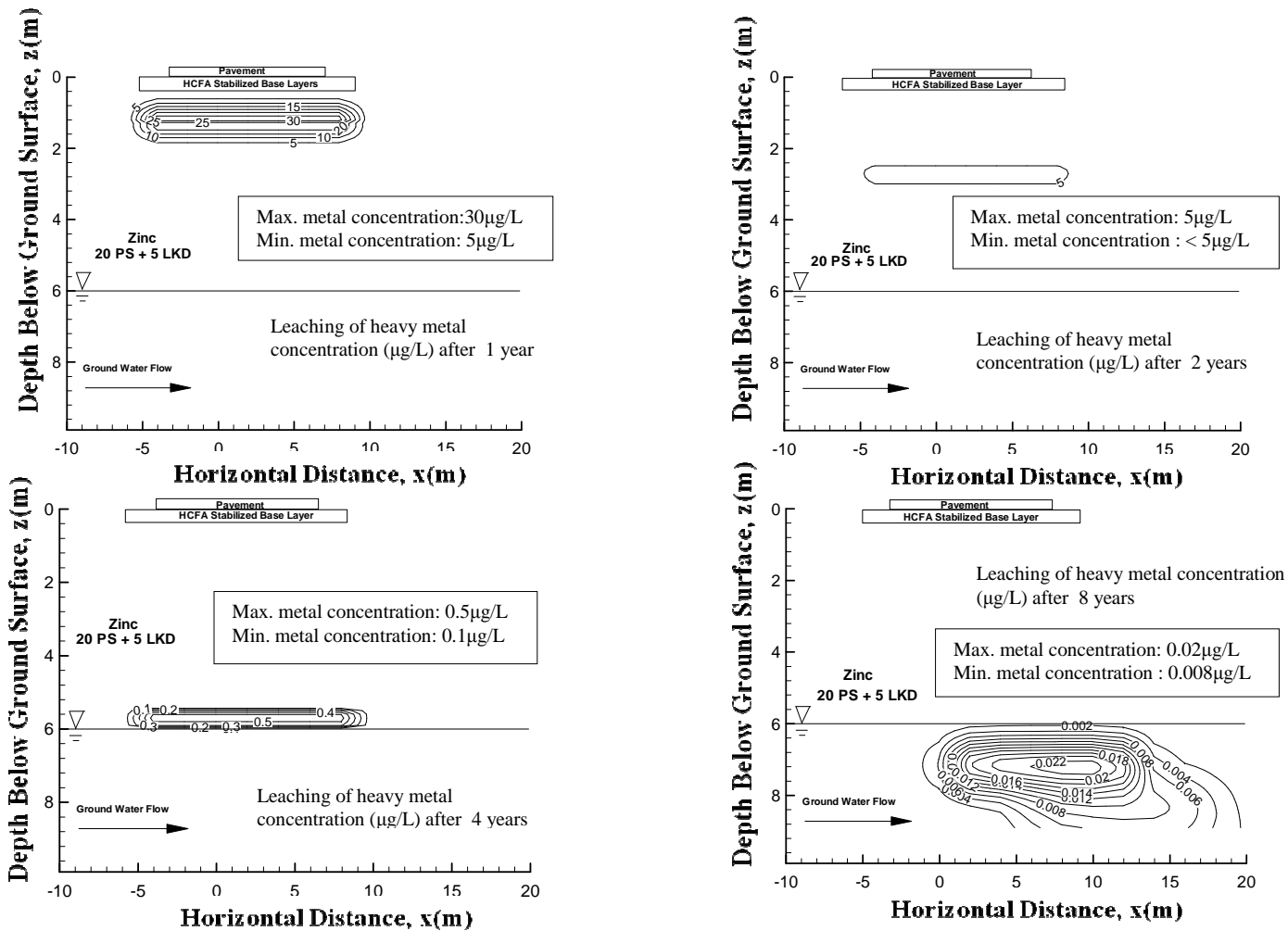


Figure 3.9 Predicted Zn concentrations in vadose zone and ground water. Note: 20 PS + 5LKD designate the specimens with 20% Paul Smith fly ash and 5% lime kiln dust by weight.

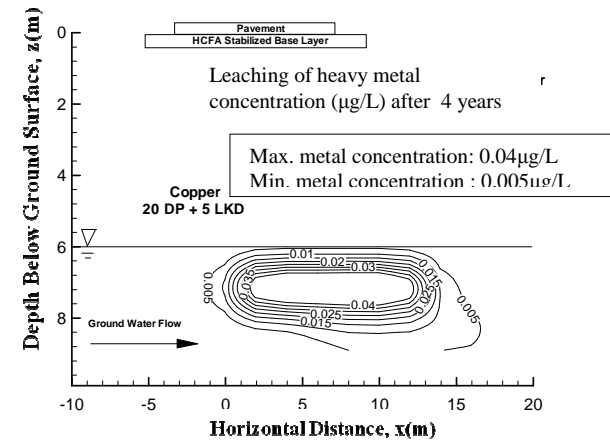
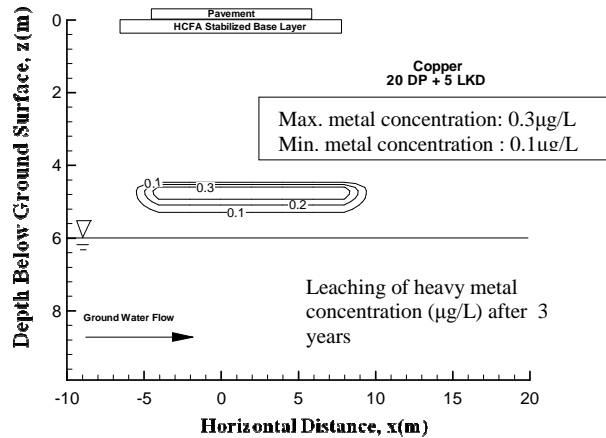
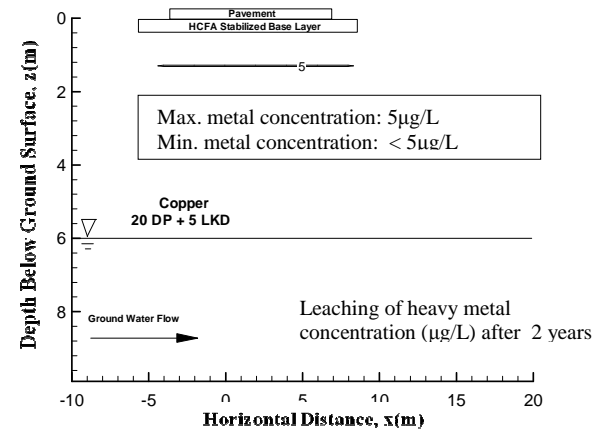
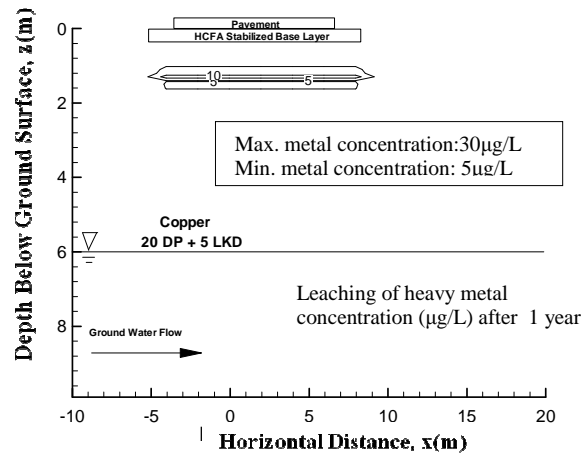


Figure 3.10 Predicted Cu concentrations in vadose zone and ground water Note: Note: 20 DP + 5LKD designate the specimens with 20% Dickerson Precipitator fly ash and 5% lime kiln dust by weight.

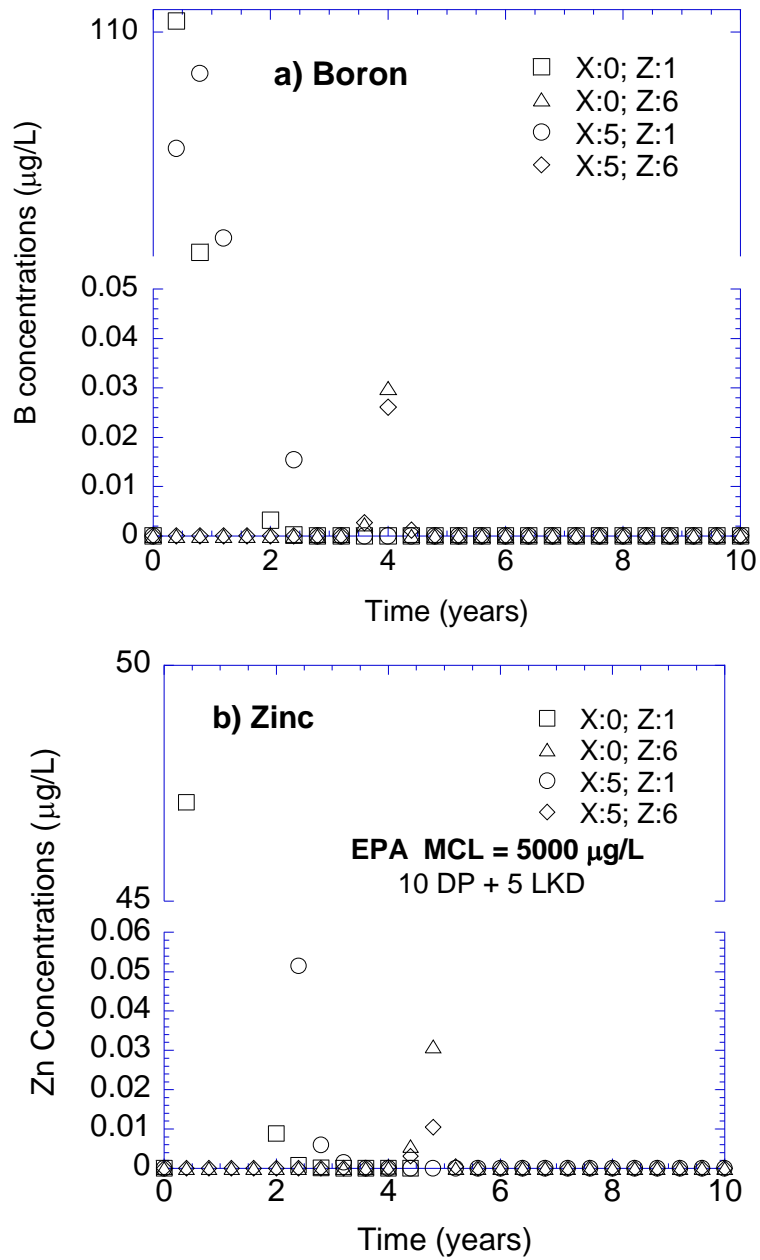


Figure 3.11 WisCLEACH-based concentrations of a) boron and b) zinc at different locations beneath the pavement. X and Z are the horizontal and vertical distances measured from the center alignment of fly ash stabilized layer.

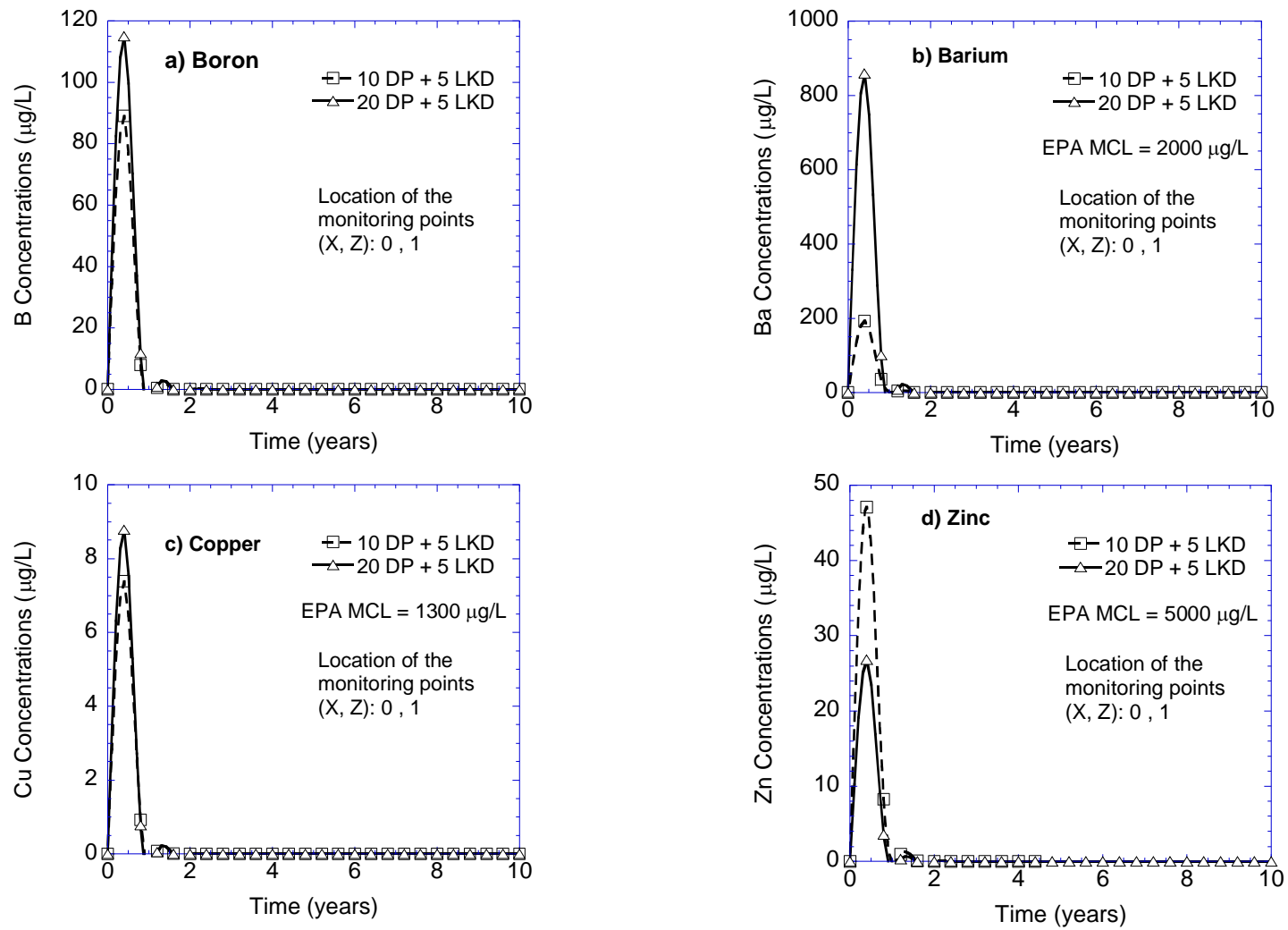


Figure 3.12 Effect of fly ash content on WiscLEACH-based concentrations of a) and b) boron, and c) and d) zinc. X and Z are the horizontal and vertical distances measured from the center alignment of fly ash stabilized layer.

An example set of analyses for Zn concentrations from a specimen prepared with 75% URM, 20% DP fly ash, and 5% LKD is shown in Figure 3.13. These preliminary analyses show that depth to groundwater table, thickness of the fly ash stabilized base layer, and annual precipitation rate are critical parameters that can affect the metal concentrations in WiscLEACH. Depth to groundwater table is important since it may affect the amount of dispersion and dilution that occurs between the fly ash stabilized base layer and the POC (Li et al. 2007). Figure 3.13a shows that an increase in depth to the groundwater table decreased Zn concentrations at the POC due to the dispersion. On the other hand, thicker fly ash stabilized base layer yielded an higher Zn concentrations at the POC, due to an increase in the total Zn mass in the base layer structure (Figure 3.13b).

In WiscLEACH, the least conductive layer in the highway profile controls the seepage velocity. The same is true for the precipitation rate. If the precipitation rate is less than the hydraulic conductivity of the least conductive layer in the highway profile, the seepage velocity is controlled by the precipitation rate (Li et al. 2007). Since the precipitation rate in State of Maryland is fairly lower than the hydraulic conductivities of the soil profiles used in this study, the amount of metal concentrations at the POC will be dependent on the annually precipitation rate significantly. Figure 3.13c confirms that an increase in precipitation rate resulted in increasing the Zn concentrations at the POC due to higher dilution rate in the groundwater.

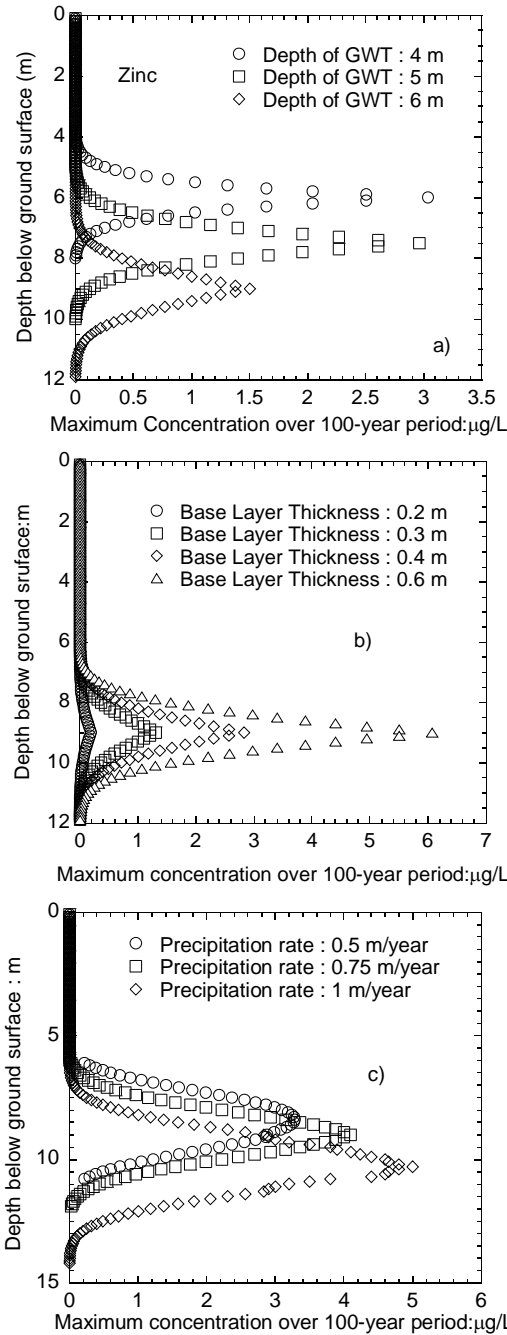


Figure 3.13 Maximum concentrations at POC over a 100 year-period: a) effect of groundwater depth, b) effect of base layer thickness, c) effect of precipitation rate. POC is 20 m down gradient from pavement centerline. Groundwater table (GWT) is fixed at 6 m below ground surface for b) and c).

### 3.8 CONCLUSIONS

A study was conducted to investigate the leaching of Ba, B, Cu and Zn metals from high carbon fly ash (HCFA) stabilized highway base layers through laboratory tests and numerical modeling. The following conclusions are warranted:

- 1) Concentrations of all four metals (Ba, B, Cu and Zn) were below the regulatory limits determined by EPA MCLs (Maximum Contaminant Limits) in 98% of the tests. Ba concentrations were 2% to 60% over the MCLs in three CLTs. Field predicted concentrations of all these metals were also significantly below the EPA MCLs.
- 2) An increase in LKD content caused an increase in pHs of the effluent solutions. Ba, B and Cu concentrations decreased with LKD addition, indicating a cationic leaching pattern, characterized by greater leaching at acidic pHs. The Zn concentrations in the effluent showed an amphoteric pattern, characterized by greater leaching at extreme acidic and basic pH conditions.
- 3) Ba, B and Cu concentrations increased with fly ash content even though the pHs of the leachates was very basic. This demonstrates that an increase in the amount of total metal source in the mixtures contributes more to the increase in leaching of these three metals than the increase of pH due to addition of fly ash. On the other hand, Zn concentrations decreased with an increase in fly ash content since the URM had more Zn metals than the fly ashes.
- 4) An increase in ionic strength (IS: 0.02 M to IS: 0.1 M) did not change the effluent

pH consistently but generally enhanced metal leaching. An increase in the cation amount in aqueous solutions may have decreased the surface negativity of the fly ash and URM particles, and thus increased the leaching of  $Ba^{2+}$ ,  $B^+$ ,  $Cu^{2+}$  and  $Zn^{2+}$  metals from the solid surface into the aqueous solution by electrostatic effects.

- 5) Column leach test elution curves exhibited a first-flush leaching pattern for all mixtures tested. Initial leaching rates were the highest, and then stabilized after 70-75 pore volumes of flow with few exceptions.
- 6) WiscLEACH numerical simulations suggest that the metal concentrations decreased over time and distance and that all the metals were sufficiently dispersed in the vadose zone. WiscLEACH results also indicated that the metal concentrations of metals were much lower than the metal concentrations obtained from the column leach tests suggesting that the results of laboratory tests are likely to provide a conservative estimate of field metal leaching.
- 7) The leaching of heavy metals from fly ash stabilized base layers to the groundwater did not exceed the EPA MCLimits, EPA WQLimits and Maryland ATLimits according to the WiscLEACH results due to the adsorption and dispersion of heavy metals in the soil vadose zone.
- 8) WiscLEACH results indicated that the leaching of metal concentrations to the groundwater would change depending on the site conditions. It was seen that an increase in depth to groundwater table decreases the heavy metal concentrations reached to groundwater. On the other hand, a higher infiltration rate and a thicker



HCFA stabilized base layer yielded an increase in the leaching concentrations of heavy metals.

- 9) On the other hand it should be kept in mind that in WiscLEACH the flow in the fly ash and subgrade is assumed to occur only in the vertical direction. Steady 1D unit gradient flow is assumed in the pavement layers and the vadose zone, with the net infiltration rate controlled by the least conductive layer in the profile and the annual precipitation rate. This also ignores the transverse flow on the top of the base layers toward the edge of the highway structures in case of subgrade has the least hydraulic conductivity.

## 4 LEACHING OF TRACE METALS FROM HCFA-AMENDED STRUCTURAL FILLS

### 4.1 INTRODUCTION

The objective of the current study in this section is to evaluate the leaching potential of embankment construction materials mixed with fly ash relative to those stabilized with conventional materials, and to evaluate the potential groundwater and surface water impacts. The beneficial reuse of fly ash in embankments construction not only helps ease one of the most pressing environmental problems (safe disposal), but may result in significant cost savings as well.

Utilization of fly ash in embankment construction has been documented in earlier studies (Baykal et al. 2004, Zhang and Solis 2008, Yoon et al. 2009). However, previous studies, in general, focused on the mechanical improvement of fly ash-amended embankments and no information was available for leached concentrations of metals and other inorganic under field conditions. Even though, mechanical properties of the fly ash-amended embankments deemed satisfactory, one key issue that precludes embankment stabilization with fly ash is the potential for surface and groundwater impacts caused by metals in the fly ash. Public perception on fly ash use was also affected by the failure of a dike in Tennessee. The failure of a dike built with 100% fly ash at the Kingston Fossil Plant, Tennessee in 2008 led to the release of approximately 5.4 million cubic yards of impounded fly ash onto surrounding land and into the adjacent Emory River. This event most directly affected citizens living in close proximity to the plant and indirectly impacted all coal burning utilities and other large coal users. For example, as a result of

this event, the U.S. Environmental Protection Agency (EPA) directed plant operators and power companies to conduct on-site assessments to determine the structural integrity and vulnerabilities of all ash management facilities and to order repairs where needed. EPA determined in 1993 and in 2000 that waste from the combustion of coal and other fossil fuels is to be regulated as nonhazardous; however, many organizations, including the U.S. Congress, are urging EPA to propose new rules regulating coal combustion waste under the Resource Conservation and Recovery Act (RCRA).

The Kingston release has focused new attention on all aspects of CCP management. Even though it was quickly recognized that the dike material was pure fly ash, additional research was warranted to ensure the environmental suitability of future soil-fly ash embankments. Moreover, high carbon fly ashes (HCFAs) may have different behavior than conventional Class F or C fly ashes and such behavior needs to be studied. In order to study the water quality impacts of fly ash amendment into embankments in Maryland, a research program was initiated. The objectives of this chapter of the current study are to determine the leaching patterns of the heavy metals as well as the effects of fly ash content and type on the leaching behavior of the trace metals from the embankments constructed with HCFA.

## 4.2 MATERIALS

Sandy soil (borrow material) that is commonly used in embankment construction by the Maryland State Highway Administration was utilized in preparing the soil-fly ash mixtures. Soil was collected from a pit in Denton, Maryland, and was sieved through No 4 sieve (4.75 mm) upon transporting to the laboratory. The soil was classified as poorly

graded sand with silt (SP-SM) according to the Unified Soil Classification System, and A-3 (fine sand) according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System. The soil showed no plasticity based on consistency limit tests per ASTM D4318-10. The physical properties of the soil along with the fly ashes are summarized in Table 4.1.

The fly ashes used in this study were collected from Brandon Shores (BS), Paul Smith Precipitator (PSP), Dickerson Precipitator (DP), Morgan Town (MT) and Columbia power plants. All fly ashes, except Columbia, were obtained from the power plants in Maryland were classified as off-spec fly ashes according to ASTM 618C. The Columbia ash, a Class C fly ash, was collected from a power plant in Wisconsin and was included in the testing program due its high CaO content and low loss on ignition value. All of the fly ashes consisted primarily of silt-size particles and contained 80 to 90% fines (passing the 75-mm sieve). Specific gravity of fly ashes ranged between 2.1 and 2.5 (ASTM D 854), and the pHs ranged between 4.5 and 9.5 (EPA Method SW- 846 Method 945), respectively. The physical properties and chemical compositions of the materials are summarized in Tables 4.1 and 4.2, respectively. Total elemental analyses of the 5 fly ashes and sandy soil were conducted following the procedures outlined in EPA SW-846 Method 6800 and summarized in Table 4.3.

Fly ash addition to the soil was 10, 20, and 40% by weight. The lower percentages are within the typical range used in soil stabilization and the higher percentage (40%) was chosen to study the effect of ash content on the leaching behavior. All column leach test specimens were compacted at their 2% dry of optimum moisture contents (OMCs) in an

acrylic tube having a 101.6 mm inside diameter and 305 mm height. By compacting to the dry of OMC, higher hydraulic conductivities could be achieved that allow enough sample to be collected in a reasonable amount of time. Standard Proctor effort (ASTM D 698) was used during compaction consisting of 8 layers with 29 blows per layer to achieve a target dry unit weight of  $19.2 \text{ kN/m}^3$ , which is a minimum value for highway embankments specified by the Maryland State Highway Administration. The mixtures prepared with Maryland fly ashes were used directly after compaction. However, due to their high calcium content, Columbia fly ash mixtures were then cured for 7 days at 95% relative humidity and  $23 \text{ C}^\circ$ . Table 4.4 provides the list of soil mixtures that are used in the current study along with their maximum dry unit weights and optimum moisture contents.

Table 4.1 Physical properties of the soil and fly ashes

Sample	$G_s$	$w_{opt}$ (%)	$\gamma_d$ ( $kN/m^3$ )	LL (%)	PI (%)	Fines Content ( $<75 \mu m$ ) (%)	Fineness ( $>45 \mu m$ ) (%)
Soil	2.6	11	19.2	NP	NP	2	-
BS	2.28	16	11.87	NP	NP	84	13
PSP	2.17	22	9.96	NP	NP	87	20
DP	2.43	36	9.93	NP	NP	82	15
MT	2.4	25	13.8	NP	NP	80	16
Co	2.7	21	15.6	NP	NP	90	14.4

BS: Brandon Shores, PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, BS: Morgantown fly ash, Co: Columbia fly ash,  $G_s$ : Specific gravity,  $w_{optm}$ : optimum water content,  $\gamma_{dmax}$ : maximum dry unit weight, LL: liquid Limit, PL: plastic limit, NP: Nonplastic.

Table 4.2 Chemical compositions of the fly ashes tested. Concentrations of major minerals were determined by X-ray fluorescence spectroscopy analysis. All concentrations are in percentage by weight.

Fly ash	Chemical Composition								
	pH	LOI (%)	$SiO_2$ (%)	$Al_2O_3$ (%)	$Fe_2O_3$ (%)	CaO (%)	MgO (%)	$SiO_2 + Al_2O_3 + Fe_2O_3$ , min (%)	Moisture Content, (max)(%)
BS	6.1	6.2	45	27	3.2	1.1	0.6	75	0.007
PSP	6.6	6.8	53	21	6.7	0.4	1.2	81	0.004
DP	8.1	16	40	32	14.7	0.6	1.5	87	0.006
MT	9.5	8.1	49	26	13.7	2.5	1.9	88	0.011
Co	12.4	0.4	31	18	6.1	19.4	3.7	56	0.004
Class C (ASTM C618)	NA	6	40	17	6	24	5	70	3
Class F (ASTM C618)	NA	6	55	26	7	9	2	50	3

BS: Brandon Shores PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, BS: Morgan Town fly ash, Co: Columbia fly ash, LOI: Loss on ignition. FW: Future Work, NA : Not applicable.

Table 4.3. Total metal content of the fly ashes and sandy soil material from the total elemental analysis results.

Sample	Al (mg/L)	As(mg/L)	B (mg/L)	Cr (mg/L)	Mn (mg/L)	Se (mg/L)
Soil	28760	<3	3	16	38	<3
BS	21333	24.16	21	50	34	39
PSP	11770	52.08	30	30	216	21
DP	17638	41.63	79	42	62	9
MT	29123	39.68	241	68	208	46
Co	91848	15.01	600	65	92	24

Table 4.4 Legend and compositions of the mixtures.

Legend of Mixtures	Fly Ash Content (%)	Optimum Water Content (%)	Maximum Dry Unit Weight (kN/m <sup>3</sup> )
100 Soil	0	11	19.2
S – 10 BS	10	9	19.3
S – 20 BS	20	11	18.8
S – 40 BS	40	13	16.7
100 BS	100	26	11.9
S – 10 PSP	10	11	19.1
S – 20 PSP	20	13	18.7
S – 40 PSP	40	17	16
100 PSP	100	22	10
S – 10 MT	10	10	19.2
S – 20 MT	20	11	19.
S – 40 MT	40	12	18
100 MT	100	25	13.2
S – 10 DP	10	14	16.8
S – 20 DP	20	15	15.6
S – 40 DP	40	18	13.2
100 DP	100	36	10
S – 10 Co	10	11	119
S – 20 Co	20	13	18..9
S – 40 Co	40	16	16.4
100 Co	100	21	15.6

*Note:* BS: Brandon Shores fly ash, PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, MT: Morgan Town fly ash, Co: Columbia fly ash. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

### 4.3 METHODS

The procedures listed in sections 2 and 3 were also followed for the water leach tests and column leach tests. In addition, a series of toxicity leaching characteristic procedure (TCLP) tests were also conducted on the same soil alone, fly ash alone and soil-fly ash mixtures.

The soils, fly ashes their mixtures prepared for TCLP tests were the same materials prepared for WLTs. The TCLP test is designed to determine the mobility of organic and inorganic compounds present in liquid, solid and multiphase wastes. EPA Method 1311 was followed during TCLP tests. The soil mixtures were sieved through U.S. No. 3/8 inches sieve. A liquid-to-solid (L: S) ratio of 20:1 was used for all test specimens. An acetic acid solution with a pH of 5 was used as an extraction fluid, and was added only once, at the start of the extraction. pH and electrical conductivity measurements were recorded immediately after the sample collection. The protocol for sample preparation and preservation followed those employed in WLTs except the filtration procedure. The samples were vacuum filtered through TCLP glass fiber filters. Then filtered leachates were acidified to pH<2 with 2% HNO<sub>3</sub> acid solution and preserved in 4 C° for chemical analysis.

### 4.4 RESULTS

#### 4.4.1 *Water Leach Tests*

Duplicate batch water leach tests (WLTs) were conducted on fly ash alone, soil alone and soil – fly ash mixtures. The pH values for each specimen were measured and are summarized in Table 4.5. The pH values of mixtures, in descending order, are Columbia



(Co), Morgantown (MT), Dickerson Precipitator (DP), Paul Smith Precipitator (PSP) and Brandon Shores (BS) fly ashes. The pHs of the effluent solutions was between 5.5 and 12.2 (Table 4.5). The specimens prepared with Co and MT fly ashes had the highest pHs while specimens prepared with the PSP and BS fly ashes had the lowest. Table 4.2 shows the chemical compositions of the fly ashes obtained from X-ray diffraction analysis. It is well known that there is a strong relationship between the pH of the leachate and the CaO and MgO contents of the materials used in the soil mixtures due to the basic nature of these minerals (Jankowski et al. 2006, Quina et al. 2009, Mudd et al. 2004, and Gitari et al. 2009). Johnson et al. (1999) also claimed that release of Ca from CaO minerals yields  $\text{Ca(OH)}_2$  in aqueous solutions.  $\text{Ca(OH)}_2$  is the oxide mineral that significantly contributes to alkalinity. Therefore, it was an expected behavior for the specimens prepared with Co and MT fly ashes to produce higher pH values than the specimens prepared with BS and PSP fly ashes.

Figure 4.1a shows the impact of fly ash addition into the sandy borrow material. As expected, an increase in fly ash contents in the soil- fly ash mixtures increased the pH values of the effluent solutions significantly. Generally the rate of increase in pH values was the highest when fly ash content was increased from 0% to 10% by weight in the soil-fly ash mixtures. The increase rate was the lowest in pH values while increments in fly ash contents were varied from 40% to 100% by weight. An increase in BS, PSP and DP fly ash contents did not affect the increase rate of the pHs in the effluent solutions as it did in Co and MT fly ashes because of the relatively lower CaO and MgO contents of BS, PSP and DP fly ashes.

Table 4.5 Stabilized pH and effluent concentrations in WLTs. Concentrations exceeding EPA MCL are in **bold**.

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (µg/L)	B (µg/L)	Cr (µg/L)	Mn (µg/L)	Se (µg/L)
S – 10 BS	10	6.3	0.08	<0.01	<0.02	<0.001	0.028	<0.03
S – 20 BS	20	6.4	0.001	<0.01	0.18	<0.001	0.034	<0.03
S – 40 BS	40	6.81	0.05	0.01	0.12	<0.001	<b>0.075</b>	<0.03
100 BS	100	5.5	<b>0.15</b>	<0.01	0.34	<0.001	0.031	<0.03
S – 10 PSP	10	6	<b>0.22</b>	<0.01	NA	<0.001	0.017	<0.03
S – 20 PSP	20	6.4	<0.05	<0.01	0.16	<0.001	0.027	<0.03
S – 40 PSP	40	7.02	<0.05	<b>0.21</b>	0.34	0.01	<b>0.12</b>	<b>0.09</b>
100 PSP	100	7.7	<b>0.68</b>	<b>0.23</b>	0.58	0.007	0.018	<b>0.13</b>
S – 10 MT	10	7.2	0.2	<0.01	0.75	0.011	<0.001	<0.03
S – 20 MT	20	8.7	<b>0.35</b>	<0.01	1.36	0.021	<0.001	<b>0.076</b>
S – 40 MT	40	9.64	<b>2.4</b>	<b>0.06</b>	2.23	0.06	<0.001	<b>0.12</b>
100 MT	100	9.8	<b>6.7</b>	<b>0.08</b>	6.56	<b>0.13</b>	<0.001	<b>0.28</b>
S – 10 DP	10	7.05	<0.05	<0.01	0.2	0.002	<b>0.07</b>	<0.03
S – 20 DP	20	7.11	<0.05	<0.01	0.33	0.008	0.03	0.04
S – 40 DP	40	7.78	<0.05	<b>0.04</b>	0.74	0.01	0.01	<b>0.12</b>
100 DP	100	7.96	0.07	<b>0.05</b>	1.45	0.015	0.03	<b>0.17</b>
S – 10 Co	10	11.88	<b>45</b>	<0.01	0.65	0.04	<0.001	<0.03
S – 20 Co	20	11.95	<b>48</b>	<0.01	0.22	0.06	<0.001	<0.03
S – 40 Co	40	12.07	<b>57</b>	<0.01	0.16	0.06	<0.001	<0.03
100 Co	100	12.15	<b>55</b>	<0.01	<0.02	0.04	<0.001	<0.03
Soil	-	6.74	<0.05	<0.01	<0.02	<0.001	<0.001	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	0.57	NA	NA

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

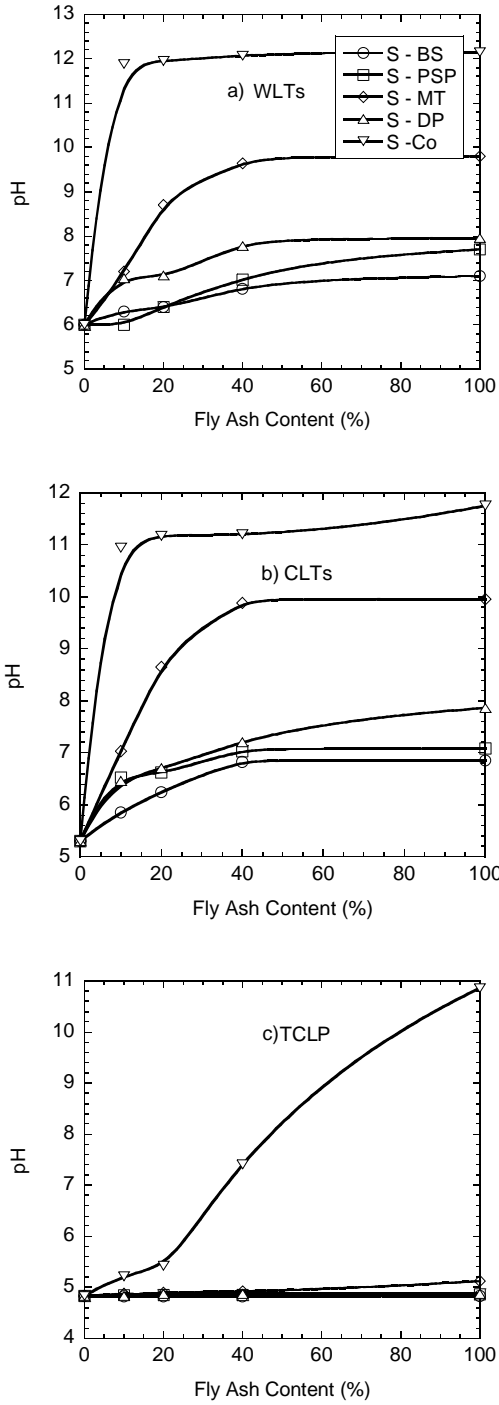


Figure 4.1 Effect of fly ash content on pH of the soil mixtures a) Water leach tests, b) Column leach tests, c) TCLP tests. (Note: BS: Brandon Shores Fly Ash, PSP: Paul Smith Precipitator Fly ash, MT: Morgantown Fly ash, DP: Dickerson Precipitator Fly Ash, Co: Columbia Fly Ash)

Table 4.5 shows that, with few exceptions, the concentrations of six metals (Al, As, B, Cr, Mn and Se) that leached from the soil-fly ash mixtures prepared with 10% and 20% fly ash contents by weights are below the U.S EPA maximum concentration limits for drinking water (MCLs), EPA water quality limits (WQLs) for the protection of aquatic life and human health, and Maryland aquatic toxicity limits (ATLs) for fresh water. Arsenic and selenium concentrations are below the detection limits in soil mixtures, except the specimens prepared with 40% and 100% PSP, MT and DP fly ashes by weight. This indicates that by increasing the total metals source greatly in the soil-fly ash mixtures, leaching potential of these heavy metals also increases, posing a potential threat to the environment. This trend suggested that extra care should be taken in the design of soil-fly ash mixtures, to be sure that the leached metals concentrations do not exceed the environmental regulation limits. Specimen prepared with 100% MT fly ashes was the only specimen that leached Cr concentration was above the limits.

Figure 4.2 shows the effects of fly ash content on leaching concentrations of the 6 metals analyzed. An increase in fly ash contents in the soil-fly ash mixtures increased concentrations of As, B and Se metals regardless of fly ash type. However; no consistent increase were observed for the leaching of Al and Mn metals with addition of fly ash in the soil-fly ash mixtures. The pH of the effluent solutions were between 6.5 and 7.5 especially specimens prepared with BS, PSP and DP fly ashes. The mobility of Al and Mn metals at this pH range is minimal and it is expected to have very low concentrations of these metals under this condition.

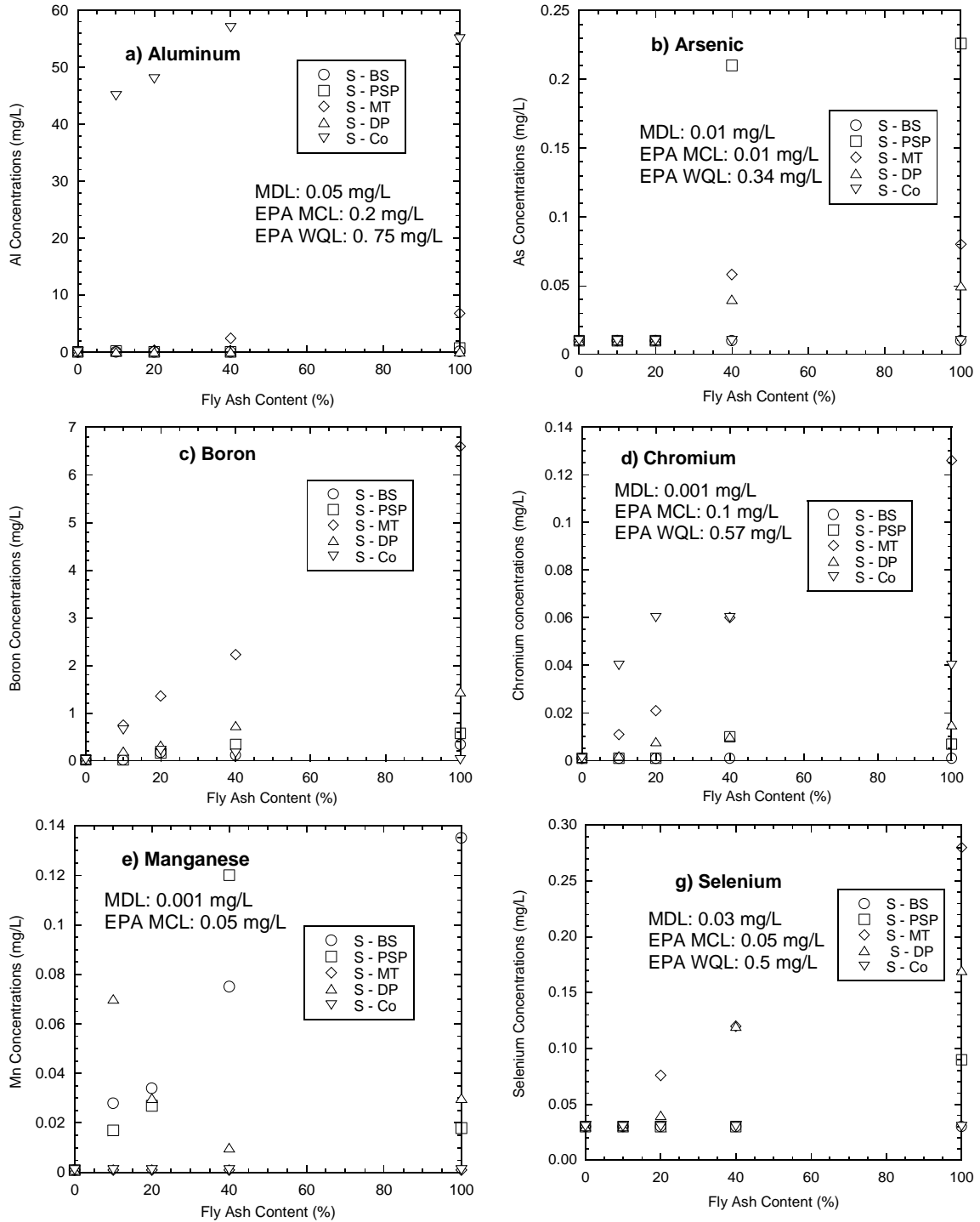


Figure 4.2 Concentrations of six metals in the effluent from WLTs (Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgan Town)

It seems that the pH effect of the aqueous solution was more dominant than the increase of fly ash content on leaching of Al and Mn metals for specimens prepared with certain type of fly ashes such as BS, PSP, and DP.

On the other hand, leached Al concentrations from the soil-fly ash mixtures prepared with Co fly ash were the highest most probably due to the higher total Al content in this fly ash (Table 4.3). In addition, Al tends to show an amphoteric leaching pattern (Cetin et al. 2012, Komonweeraket et al. 2010) which indicates that release of Al increases at extreme pH conditions. The pHs values of the Co mixed soil mixtures were between, 11.9 and 12.15. Under these alkaline conditions, the surface charge of the soil and fly ash particles are negative and anionic forms of Al metal tends to be released significantly into the aqueous solutions which also probably raise Al concentrations (Gitari et al. 2009). These findings are consistent with Johnson et al. (1999), which also found that an increase in pH increases the Al concentrations leached from similar waste materials significantly.

Even though an increase in fly ash content increased the As and Se concentrations in the effluent solutions, the concentrations were mostly below the detection limits. Thus, it was not possible to define the leaching pattern of these two toxic metals. Table 4.5 shows that a change in pH from neutral to alkaline pHs also increased the concentrations of As and Se metals, consistent with a behavior observed from previous studies (Jankowski et al. 2006, Komonweeraket et al. 2010). At these pHs arsenic and selenium start producing anionic forms as  $\text{HAsO}_4^{2-}$  and  $\text{HSeO}_3^-$  released from the fly ashes (Izquierdo et al. 2011).

Cr concentrations leached from specimens prepared with BS and PSP fly ashes were below the detection limits with few exceptions. Specimens prepared with MT fly ashes

released the highest Cr concentrations into the aqueous solutions. Table 4.3 indicates that MT fly ashes contain the highest amount of total Cr content which results in higher Cr release than the other fly ashes. Moreover, Cr leaching is highly dependent on the pH of the effluent solutions (Komonweeraket et al. 2010, Jegadeesan et al. 2008, and Cetin et al. 2012). The pH of the specimens prepared with MT fly ashes were varied between 7.2 and 9.8 and at these pHs, the insoluble form of Cr metals which is Cr(III) starts being oxidized to soluble Cr(VI) and create the  $\text{CrO}_4^{2-}$  anionic form (Geelhoed et al. 2002, Gitari et al. 2009, Engelsen et al. 2010). Therefore, an increase in pH would increase the oxidation rate of insoluble Cr(III) to highly soluble Cr(VI) which would increase the released Cr concentrations into the aqueous solutions.

B concentrations were increased with the addition of fly ash except specimens prepared with Co fly ashes. Leaching of B is very sensitive to pH of the aqueous solutions and it tends to show cationic leaching pattern indicating that its solubility is very high at low pHs and decrease with an increase in pH (Elseewi et al. 1980, Gitari et al. 2009). As shown in Table 4.5 the pHs of the specimens prepared with Co fly ash were very high and this could be the reason to observe a decrease in B concentrations with an increase in Co content in the soil-fly ash mixtures. In addition, at high pHs adsorption of cationic species are very likely and increase in pH with addition of Co fly ash may have caused an increase in the adsorption of B by soil and fly ash surfaces and yield a decrease in B concentrations in the aqueous solutions (Mudd et al. 2004). Furthermore, B may co-precipitate with  $\text{CaCO}_3$  minerals and it is expected to observe large amount of these

minerals in the effluent solutions of the soil-fly ash mixtures prepared with Co fly ash due to its high CaO content (Hollis et al. 1988).

The Mn concentrations increase with an increase in fly ash content in the soil-fly ash mixtures, except those prepared with MT and DP fly ashes (Table 4.5). The increase in Mn concentrations is not linear with fly ash content, even though the mass of metals in soil mixtures increases approximately linearly with fly ash content. Therefore, the use of linear dilution calculations will underestimate the resulting concentrations of Mn from soil-fly ash mixtures. Mn concentrations below the detection limits for the specimens prepared with Co fly ashes. Mn metals tends to show cationic leaching pattern and it is very unlikely to determine Mn concentrations at very basic conditions such as provided by soil-fly ash mixtures prepared with Co fly ash (pH 11-12.5) (Gitari et al. 2009, Engelsen et al. 2009).

Mn concentrations decreased with increasing fly ash content in soils amended with MT and DP fly ashes. The leaching pattern of Mn is generally dominated by the pH of the effluent solutions (Goswami and Mahanta 2007). Since the pH of the effluent vary between 7.2 and 10 for the soil-MT fly ash mixtures and the soil-DP fly ash mixtures, precipitation of Mn with Al-oxides and Fe-oxides occur and generate a decrease in Mn concentrations in the aqueous solutions even though the main source of metals was increased. (McBride 1994, Jegadeesan et al. 2008).

#### *4.4.2 Column Leach Tests*

Figure 4.3 shows the variation of the effluent pHs as a function of pore volumes (PVs) of flow. All CLTs were continued until a minimum of 50 pore volumes of flow was



obtained to examine the behavior and persistency of the pH of the soil mixtures. The pHs of the effluent solutions fluctuate for all specimens until 20 PVs of flow is reached, and then the pHs remains constant. Similar to the observations made in batch water leach tests (WLTs), there is a strong correlation between the CaO and MgO contents of the fly ashes and pH of the leachate solutions. The pHs of the CLT specimens prepared with Morgantown (MT) and Columbia (Co) fly ashes has the highest pH values and the pH of the effluents leached from the specimens prepared with Brandon Shores (BS) and Paul Smith Precipitator (PSP) had the lowest (Table 4.6). An increase in fly ash caused an increase in the effluent pHs of the all specimens as observed in WLTs. Pure sandy soil had the lowest pH values.

Table 4.6 provides the peak metal concentrations along with the stabilized pH values of the aqueous solutions. The maximum leaching concentrations of some of the metals exceeded the EPA MCLs, EPA WQLs and Maryland ATLS. However, column leach tests provide relatively high metal concentrations that are typically unrepresentative of field conditions (Bin-Shafique et al. 2006, Li et al. 2007). Thus, computer models, such as WiscLEACH, become useful in predicting concentration profiles in the field.

Figure 4.4 shows that, except Mn, the concentrations of Al, As, Cr, B and Se tend to increase with an increase in fly ash content. The soil-fly ash mixtures prepared with PSP fly ash were the only ones for which an increase in fly ash content increased the Mn concentrations in the effluent solutions. Mn is very mobile in acidic pHs and an increase in pH decreases the mobility (solubility) of Mn in the aqueous solutions because Mn starts precipitating as  $Mn(OH)_2(s)$  (Dutta et al. 2009). Furthermore, Mn usually exists in

its cationic form  $Mn^{2+}$  in the aqueous solutions, and with an increase in pH the surface of the soil and fly ash particles are being deprotonated.

The cationic species, such as  $Mn^{2+}$ , attach to negatively charge surfaces which yields a reduction in the leached Mn concentrations (Su et al. 2011, Gitari et al. 2009). Mn tends to decrease with pH. In addition, Mn metals precipitate by complexing with cationic metals that exist in the aqueous solutions such as, As and Ca (Komonweeraket et al. 2010). Table 4.6 and Figure 4.2b show that the leaching trend of the Mn is strongly dominated by the pH of the effluent solutions except for the specimens prepared with PSP fly ash. An increase in fly ash content increased the Mn concentrations in the leachates for the soil-PSP fly ash mixtures. Table 4.3 indicates that total Mn content of PSP fly ash is approximately 1.2 to 8 times higher than the total Mn contents of other fly ashes. Therefore, it was expected to observe main metal source to be the dominant factor on leaching of Mn from the soil-PSP fly ash mixtures.

Table 4.6 Stabilized pH and peak effluent concentrations in CLTs. Concentrations exceeding EPA MCL are in **bold**.

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (mg/L)	B (mg/L)	Cr (mg/L)	Mn (mg/L)	Se (mg/L)
S – 10 BS	10	5.75	0.13	<0.01	1.46	<0.001	<b>0.90</b>	<0.03
S – 20 BS	20	6.25	0.14	<b>0.04</b>	1.63	<0.001	<b>0.82</b>	<0.03
S – 40 BS	40	6.7	0.16	<b>0.09</b>	8.68	0.03	<b>0.82</b>	<0.03
100 BS	100	7.3	0.16	<b>0.73</b>	19.11	0.05	<b>3.1</b>	0.04
S – 10 PSP	10	6.3	0.062	<0.01	1.05	<0.001	<b>0.25</b>	0.031
S – 20 PSP	20	6.6	0.1	<b>0.09</b>	2.78	0.003	<b>0.33</b>	<b>0.09</b>
S – 40 PSP	40	7	<b>0.34</b>	<b>1.58</b>	30.54	0.06	<b>1.68</b>	<b>1.74</b>
100 PSP	100	7.1	<b>0.38</b>	<b>2.06</b>	56	<b>0.44</b>	<b>3.88</b>	<b>2.08</b>
S – 10 MT	10	7.2	0.11	<0.01	13.8	<b>0.32</b>	0.023	<b>0.063</b>
S – 20 MT	20	8.3	<b>0.3</b>	<b>0.075</b>	26.4	<b>1.59</b>	0.006	<b>0.202</b>
S – 40 MT	40	9.8	<b>2.7</b>	<b>0.34</b>	115	<b>3.23</b>	0.005	<b>1.79</b>
100 MT	100	10	<b>12.6</b>	<b>0.36</b>	166	<b>3.48</b>	0.01	<b>5.84</b>
S – 10 DP	10	6.6	0.07	<0.01	11.6	0.002	<b>1.28</b>	<b>0.11</b>
S – 20 DP	20	6.72	0.17	<b>0.34</b>	23.8	0.003	<b>0.6</b>	<b>0.37</b>
S – 40 DP	40	7.2	<b>0.32</b>	<b>0.5</b>	42.12	0.01	<b>0.39</b>	<b>1.12</b>
100 DP	100	7.9	<b>2.41</b>	<b>0.75</b>	43.2	0.03	0.048	<b>1.68</b>
S – 10 Co	10	11.88	<b>98.3</b>	<b>0.03</b>	1.44	<b>0.17</b>	0.003	0.05
S – 20 Co	20	11.95	<b>187</b>	<b>0.07</b>	1.52	<b>0.36</b>	<b>0.58</b>	0.08
S – 40 Co	40	12.07	<b>95</b>	<b>0.08</b>	7.86	<b>0.12</b>	<0.001	0.36
100 Co	100	12.15	<b>206</b>	<b>0.05</b>	23.6	<b>1.13</b>	0.0025	0.94
Sandy Soil	-	5.2	<0.05	<0.01	0.7	<0.001	<b>0.64</b>	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	NA	NA	NA

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

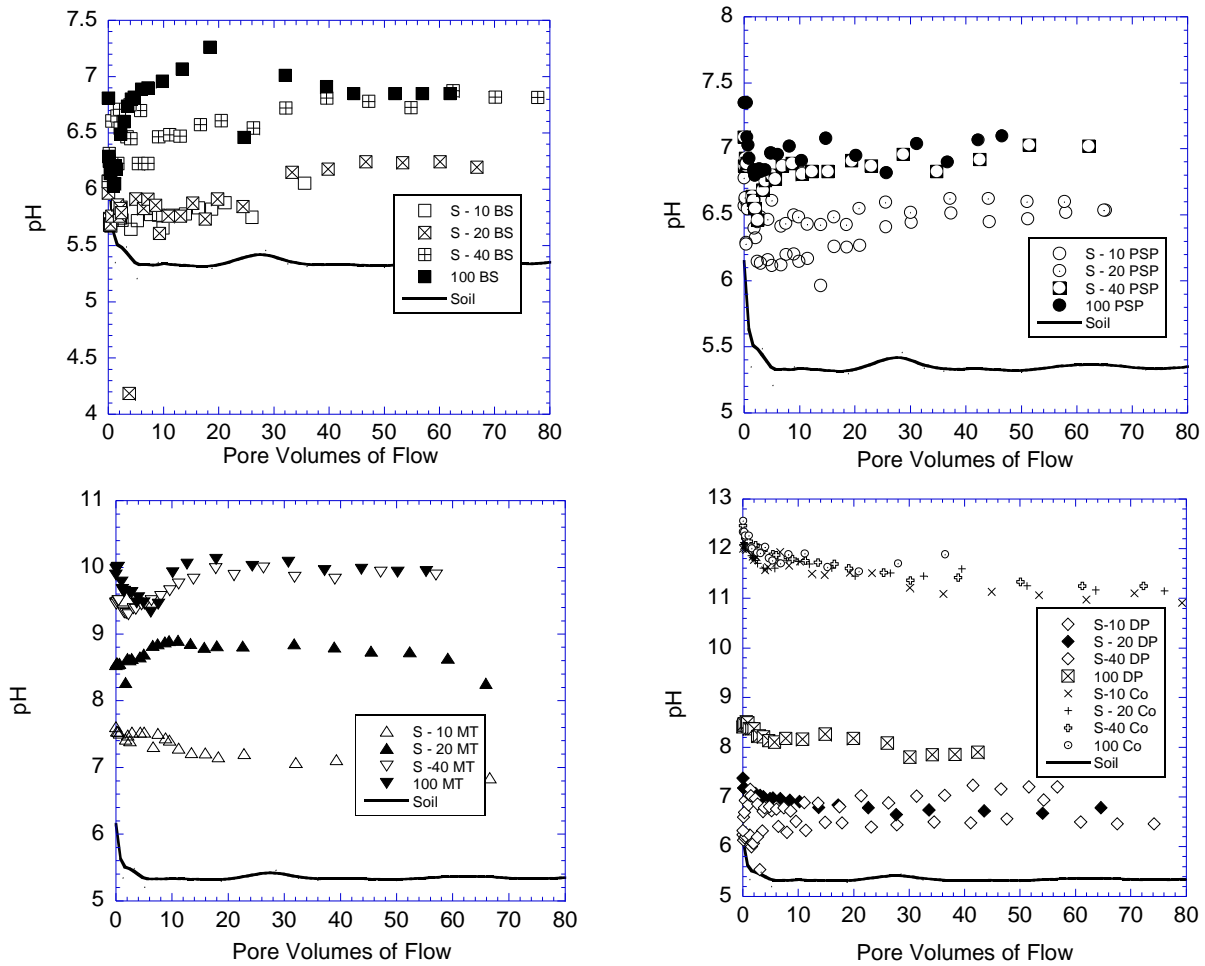


Figure 4.3 pH of the effluents from CLT on soil, fly ash and their mixtures.

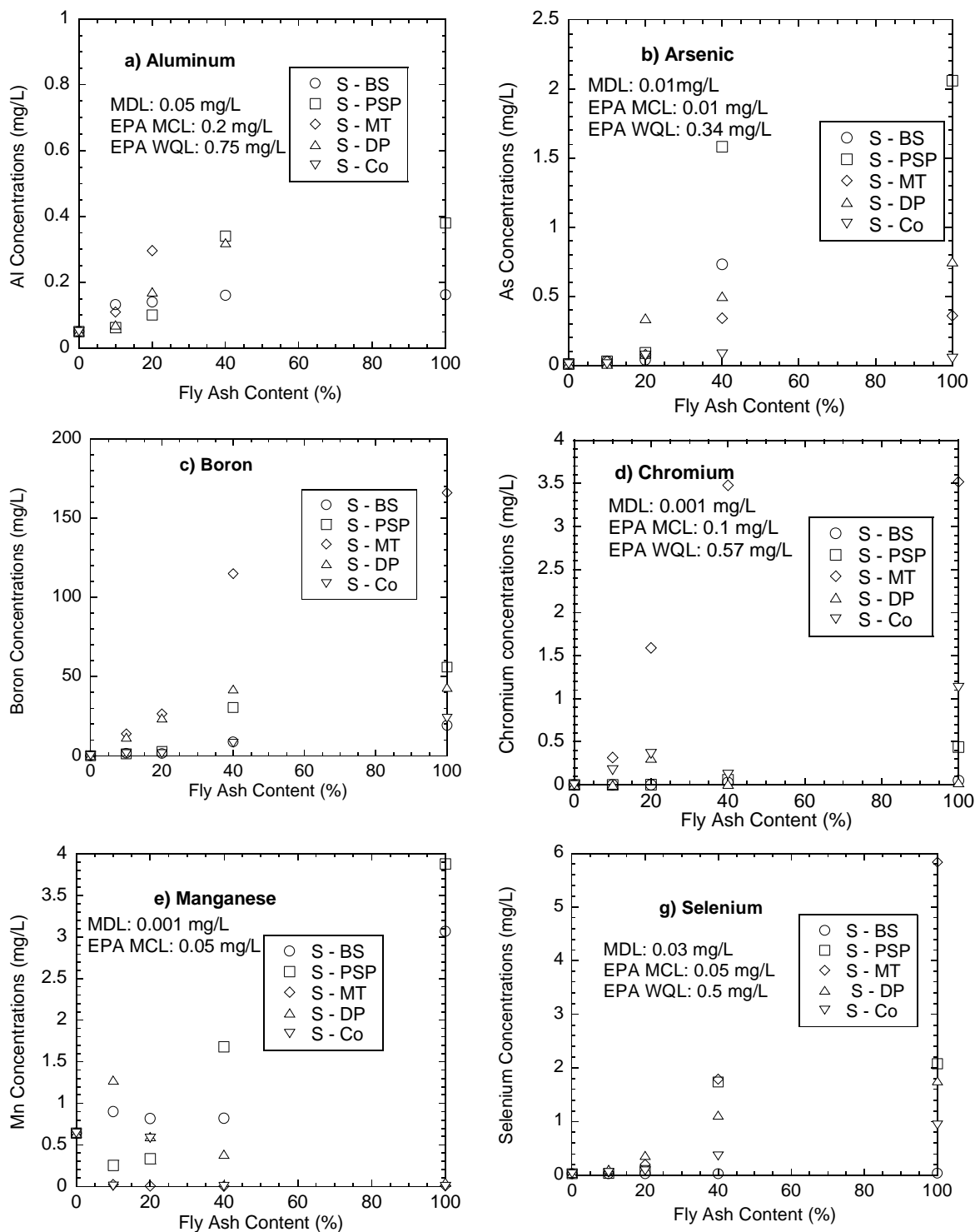


Figure 4.4 Concentrations of six metals in the effluent from CLTs (Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgan Town)

As, Cr, Al and Se metals generally show an amphoteric leaching pattern (Cetin et al. 2012, Komonweeraket 2010). An increase in fly ash content causes an increase in the amount of main metal source and an increase in the pH of the effluent solution due to the dissolution of CaO and MgO minerals (Izquierdo et al. 2011). Considering the observed pH range in the effluent of the column leach tests (pH = 5.75 – 12.5) Al solubility is likely to be available in both its cationic and anionic species. Solubility of Al is generally controlled by the dissolution of precipitation of the Al carrier mineral and Al-(hydr)oxides solid phases existing in the aqueous solutions (Murarka et al. 1991). At pH range of 5.75 to 9, the free  $Al^{3+}$  starts precipitating as  $Al(OH)_3$  (gibbsite) and  $Al(OH)_3$  (amorphous) which reduces the concentrations of  $Al^{3+}$  in the leachate (Astrup et al. 2006). This indicates that an increase in pH between the pH ranges of 5.75 to 9 should cause a decrease in Al concentrations. However, in this study an increase in fly ash content increased the Al concentrations in the leachates regardless of the fly ash type. This behavior occurred most probably due to the high total Al content in all fly ashes used (Table 4.3). On the other hand, an increase in Columbia (Co) fly ash content, Co fly ash (pH > 10) yielded Al concentrations more than 200 times higher than those leached from specimens prepared with other fly ashes. Table 4.3 indicates that total Al content of Co fly ash is 3 to 8 times higher than the other fly ashes. The pHs of the effluent solutions of the soil-Co fly ash mixtures were the main reason for the release of significantly high Al concentrations because at pH >10, the anionic Al species start dissolving from the fly ash particles and particle surfaces and complex with other metals or become freely available in the aqueous solutions (Sparks 2003).

Figure 4.4d indicates that an increase in fly ash content increased the Cr concentrations in the aqueous solutions. Specimens prepared with 10% by weight BS and PSP fly ashes and specimens prepared with 20% by weight BS fly ash did not release Cr at concentrations above the detection limit (MDL for Cr=0.001mg/L). The pH of the effluent solutions was the main reason for this low Cr release since at pH of 5.75 to 6.3 Cr is usually present at its insoluble form and do not leach significantly (Engelsen et al. 2010). At pH>6.5-7 will increase the oxidation of these Cr(III) to Cr(VI) and also will release the anionic forms of Cr metals such as  $\text{HCrO}_4^-$  and  $\text{CrO}_7^{2-}$ ,  $\text{CrO}_4^{2-}$  (Komonweeraket et al. 2010, Goswami and Mahanta 2007). This trend was observed especially with the specimens prepared with MT and Co fly ashes. The concentrations of Cr leached from these specimens were at least 7 times higher than those leached from soil-fly ash mixtures prepared with BS, PSP and DP fly ashes, owing to the high pHs of these specimens (Table 4.6). The relatively higher Cr concentrations observed from the MT fly ash mixtures as compared to Co fly ash mixtures was attributed to total Cr content of MT fly ash (Table 4.3). Cr concentrations of all soil-MT fly ash mixtures exceeded the EPA limits, Cr (VI) is a toxic Cr species and an acute irritant for living cells and can be carcinogenic to humans via inhalation (Whalley et al. 1999). Therefore, extra care should be taken in the design of embankments with MT fly ash.

Se concentrations leached from soil-fly ash mixtures prepared with BS fly ash were below the detection limits except for the specimens prepared with 100% BS. For the remaining mixtures, an increase in fly ash content increased the Se concentrations in the effluent solutions (Figure 4.4g). For soil-BS fly ash mixtures it was expected to have very

low Se concentrations due to its relatively low pH values (pH=5.75 to 7.3). Se tends to show amphoteric leaching pattern and its leaching is minimum at neutral pH values (Komonweeraket et al. 2010, Su et al. 2011). At alkaline pHs Se is remained in its anionic forms such as  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  (Izquierdo et al. 2011, Morar et al. 2012). Leaching of Se oxyanions is affected by the fly ash surface and soil surface site concentrations, pH and other anions and cations (Su et al. 2011). An increase in pH of the aqueous solutions will cause cationic species to be adsorbed by the surfaces of soil and fly ash particles and create competitions between cationic and anionic species of the metals. A decrease in the available space on the surface sites of the soil fly ash particles would cause dissolution of anionic Se species and increase the Se concentrations in the leachates (Wang et al. 2008). Therefore, the specimens prepared with MT fly ash yielded the highest Se concentrations since the pH of these soil mixtures were between 7.2 and 10. Specimens prepared with Co fly ash leached lower Se concentrations than the ones prepared with MT fly ashes even though the pHs of specimens prepared with Co fly ash were higher than those prepared with MT fly ashes. This trend is attributed to the relatively higher total Se content of the MT fly ashes (Table 4.3).

Figure 4.4b shows that an increase in fly ash content in the soil-fly ash mixtures increases the As concentrations in the effluent solutions regardless of fly ash type. Solubility of As is highly pH dependent (Komonweeraket et al. 2010, Pandey et al. 2011, Vitkova et al. 2009). Leaching of As also tends to show an amphoteric leaching pattern and has a high affinity to exist in its anionic forms such as  $\text{HAsO}_4^{2-}$ ,  $\text{HAsO}_3^-$  (Narukawa et al. 2005, Ettler et al. 2009). In neutral pH conditions (pH=6 to 7.5), leaching of As is minimal due



to the maximum adsorption of As metals onto soil and fly ash surfaces. However, the soil-fly ash mixtures prepared with PSP fly ash had the highest As concentrations in the leachates, even though the effluent pHs of these soil-PSP mixtures was neutral.

Specimens prepared with MT and Co fly ashes leached lower As concentrations than the specimens prepared with PSP fly ash, even though the effluent pHs of the specimens prepared with MT and Co fly ashes were around 10 and 12, respectively. PSP fly ash had the highest total As content of all the fly ashes used in the current study. Gitari et al. (2009) also claimed that availability of As depends on the quantities in the fly ashes.

Sorptions of As onto metal oxide minerals are very likely occur at neutral pHs (Pandey et al. 2011, Kim et al. 2009, Sadiq et al. 2002). Fe-(hydro)oxides are one of the most dominant oxide minerals that have significant effects on the leaching of As (Apul et al. 2005). Fe-oxides have a strong affinity for As species. Adsorption reaction between As and Fe-oxides becomes very rapidly and the reaction continues at a slower rate after the initial reaction (Sadiq et al. 2002). Fe contents of the fly ashes and leached Fe concentrations in the aqueous solutions are very critical in the leaching behavior of As (Kim et al. 2009). Relatively lower Fe<sub>2</sub>O<sub>3</sub> contents of the PSP fly ash could be another reason for having the highest As concentrations in the leachates (Table 4.2). Since PSP fly ash had the lowest Fe<sub>2</sub>O<sub>3</sub>, it was expected to observe lower leached Fe concentrations from the soil-PSP fly ash mixtures as compared to MT-based mixtures. However, in this study Fe concentrations were not measured, therefore; it was not possible to make a certain conclusions about the effects of Fe-As association on the leaching behavior of As.

Boron (B) concentrations also increase with increasing fly ash content with few exceptions. B has cationic species and these species are adsorbed by the soil and fly ash particles in the aqueous solution or precipitated with Al-oxides and iron oxides at pH > 6.5 (Pagenkof and Connolly 1982). Therefore, the B concentrations are expected to decrease with an increase in pH of the effluent solution. However, an opposite trend is observed for the specimens tested in the current study (Figure 4.4c and Table 4.6). It is speculated that the large amounts of boron in the fly ash is the main cause for the observed pattern. Table 4.3 indicates that total B content of Co fly ash is 600 mg/kg which is the highest among all the fly ashes used in the current study. However, specimens prepared with MT fly ashes yielded the highest B concentrations in the leachates. Precipitation of B metals with ettringite minerals at very alkaline conditions by substitution with other cations on the soil and fly ash surfaces may have yielded relatively lower B concentrations in the aqueous solutions of the soil-fly ash mixtures prepared with Co fly ash (Gitari et al. 2009).

Figure 4.5 to 4.10 show a series of column leach test elution curves for the specimens tested in the current study. The curves for all metals, except As, suggest an initial leaching of metals followed by a sharp decrease to near constant concentrations after 5-15 pore volumes of flow. This is called first-flush of leaching and occurs due to the release of metals from the water soluble fraction as well as from the sites with low adsorption energies. This CLTs results suggest that, in a real field application, aqueous samples should be collected especially during the construction phase since metal concentrations in leachates that come out of the mixtures are expected to be higher at the

initial stages. However, the leaching curves for As metals showed a lagged flush response. The leaching of As metals increases until 10-20 pore volumes of flow then decreases dramatically. The As concentrations that were leached out from the specimens prepared with 10% and 20% by weight fly ashes were generally below the detection limit (0.01 mg/L) and did not exhibit any clear leaching trend. The specimens prepared with 40% and 100% fly ashes showed a lagged response type leaching pattern. The As concentrations decreased significantly in the first 3-4 pore volumes of flow then increased to 35 – 40 pore volumes of flow followed by a dramatic decrease. In general, the immobility of the metals causes a lagged response type leaching pattern in the aqueous solution (Sauer et al. 2005). Arsenic is very mobile at extreme acidic and basic conditions (Dutta et al. 2009, Komonweeraket et al. 2010). The pHs of the effluent solutions of all specimens in the current study are either lower than 10 or higher than 6, which could be a reason for observing a lagged response leaching pattern for As.

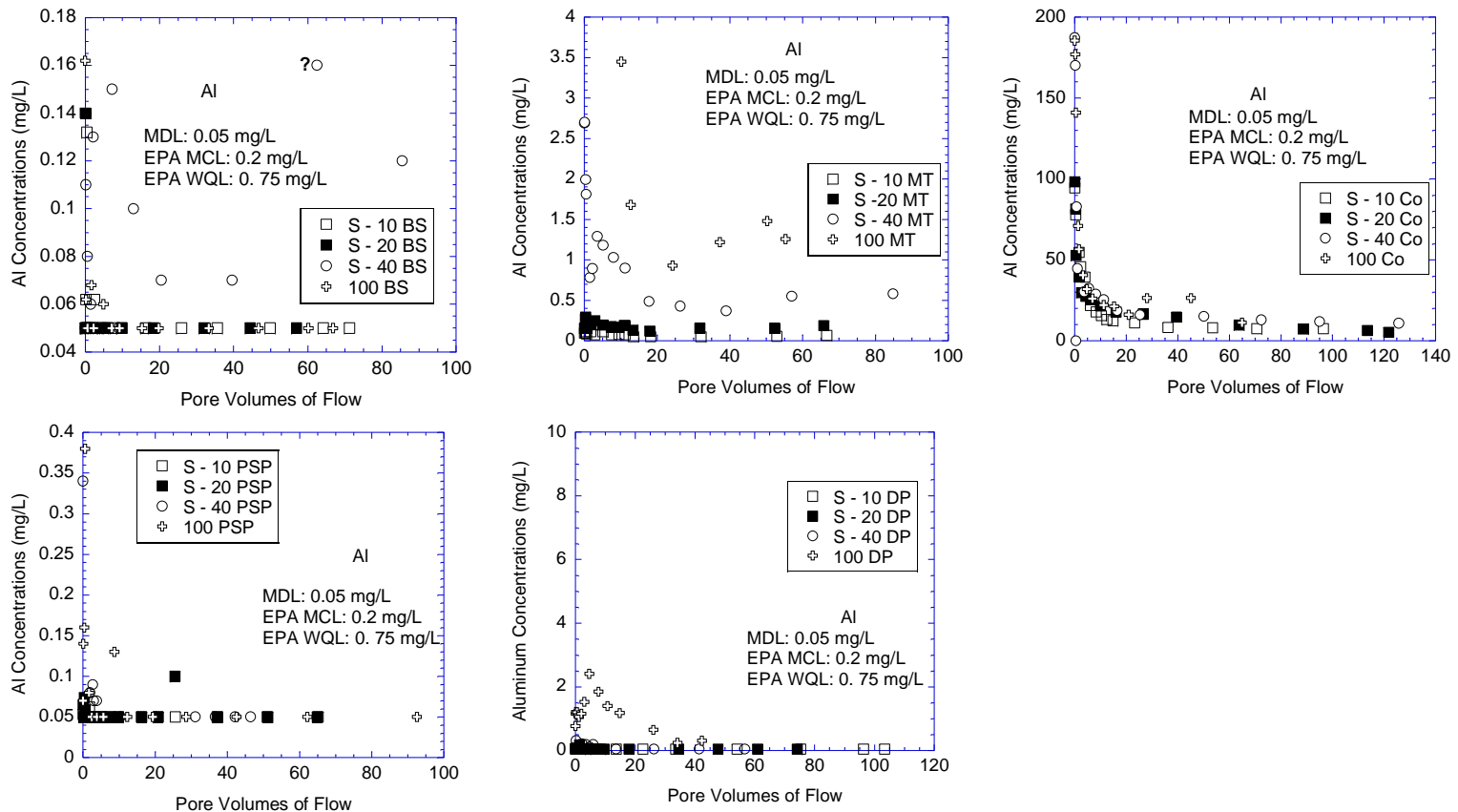


Figure 4.5 Elution curves for Aluminum Metal.

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

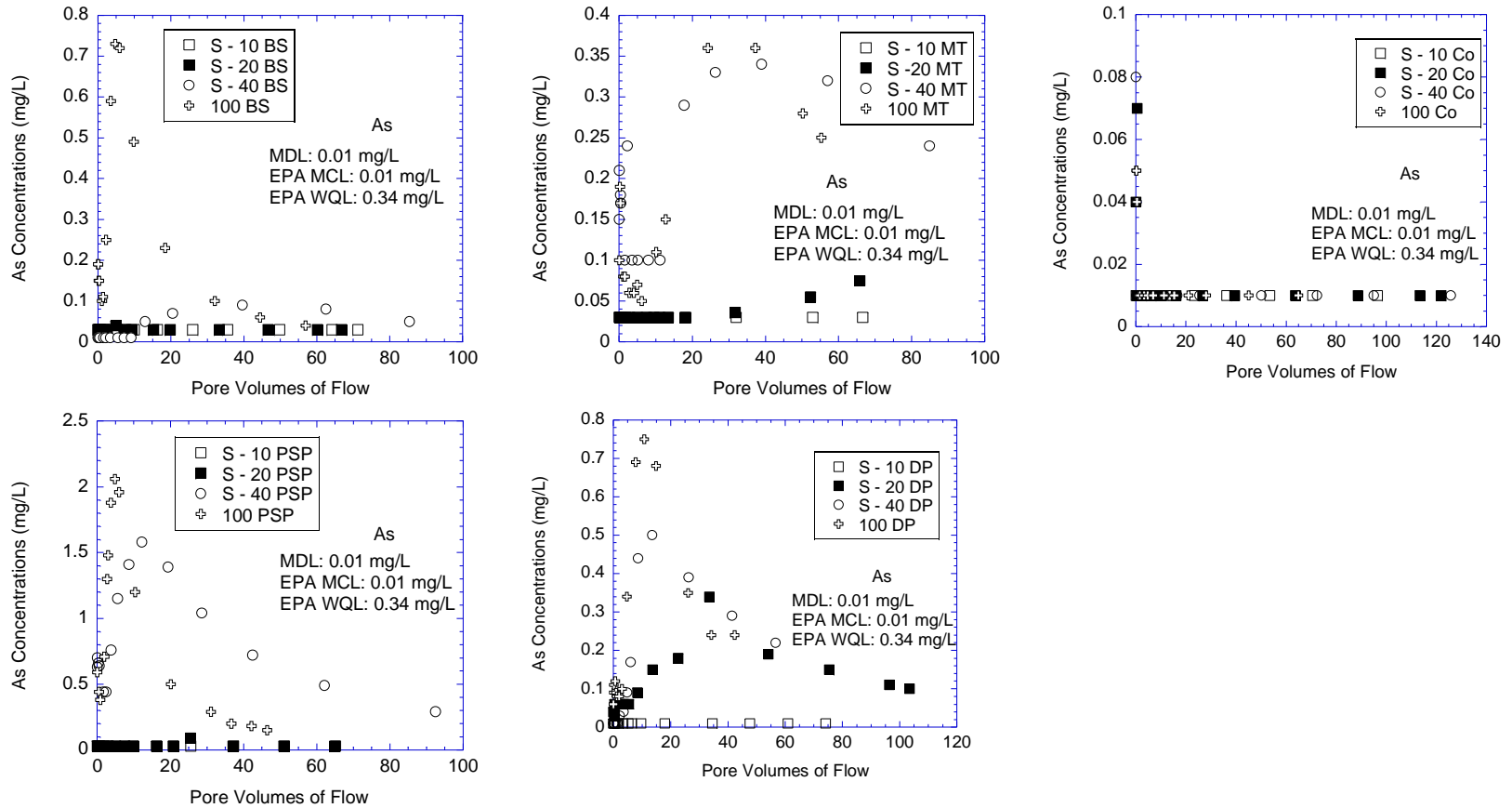


Figure 4.6 Elution curves for Arsenic Metal

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; WQL= water quality limits for protection of aquatic life and human health in fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

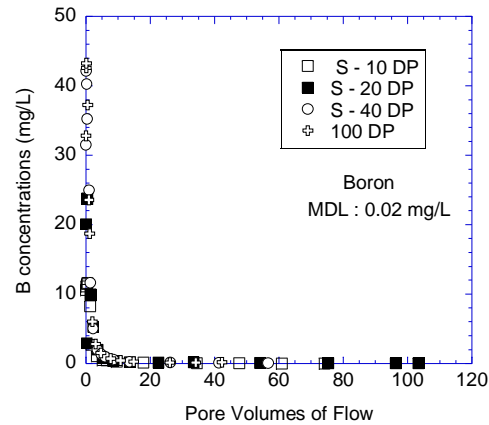
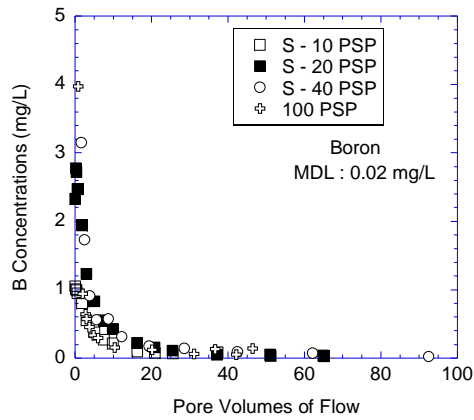
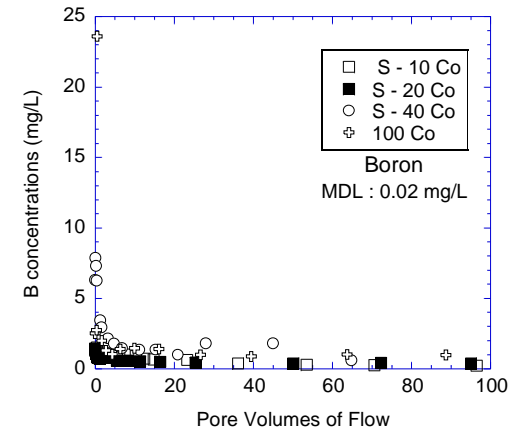
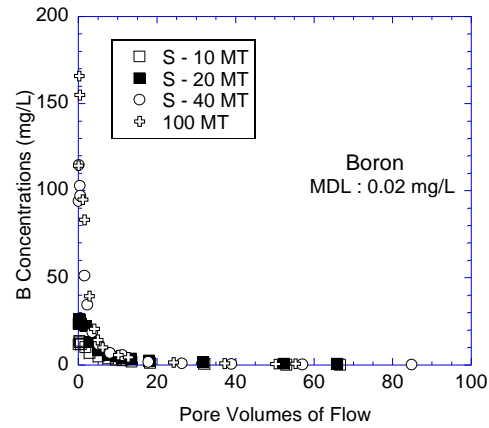
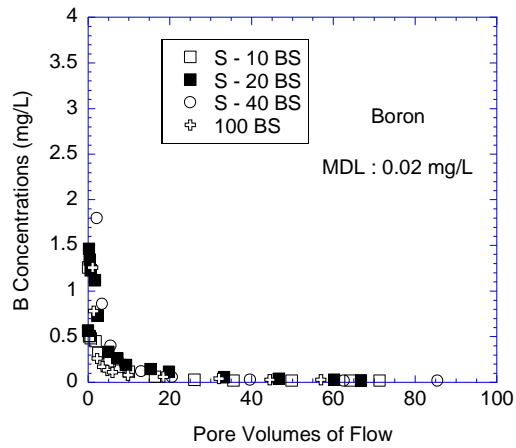


Figure 4.7 Elution Curves for Boron metal

Note: MDL: Minimum Detection Limits. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

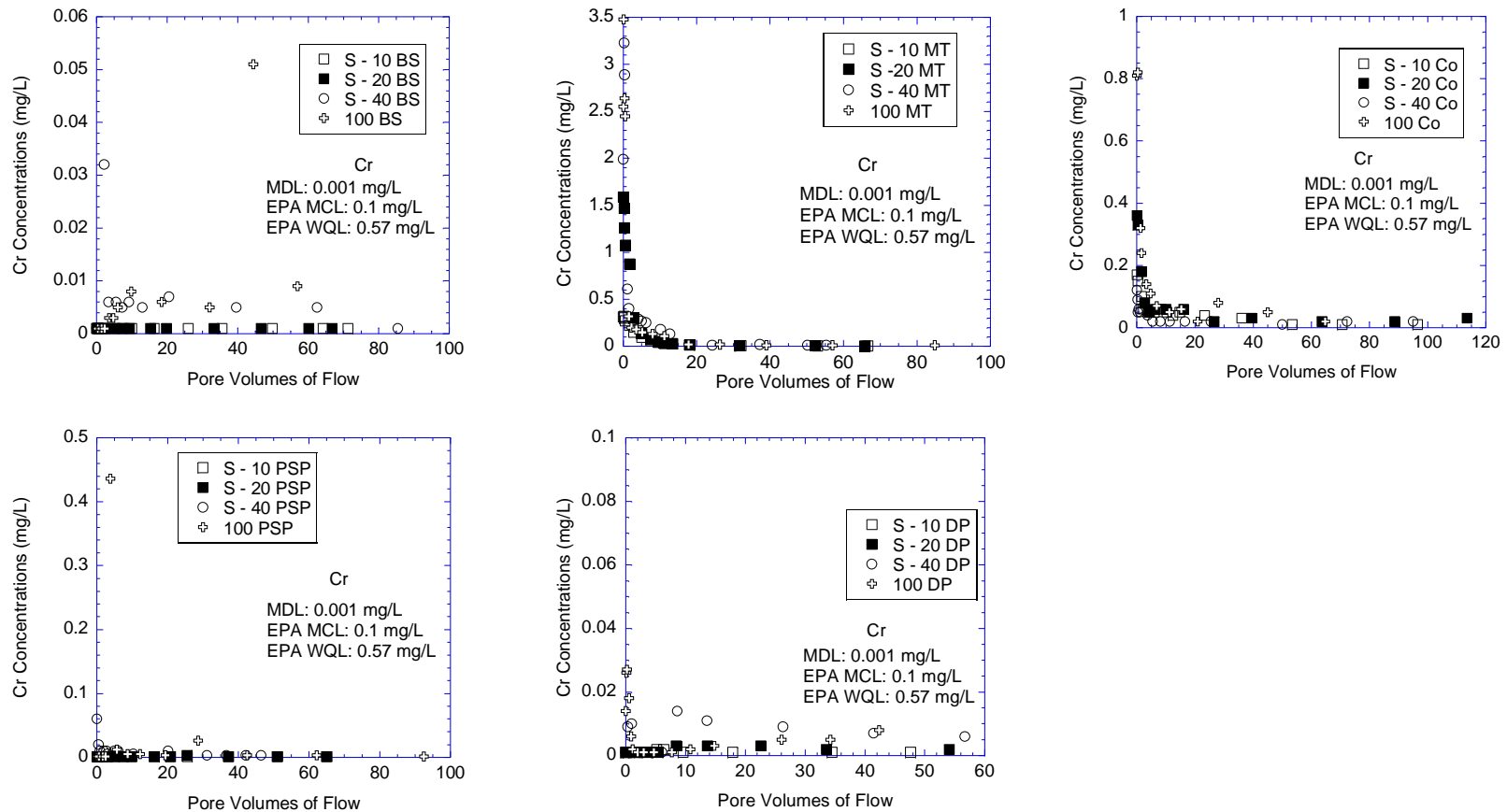


Figure 4.8 Elution curves for chromium metal

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; WQL= water quality limits for protection of aquatic life and human health in fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

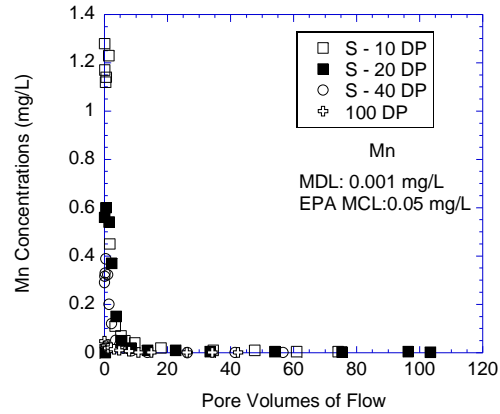
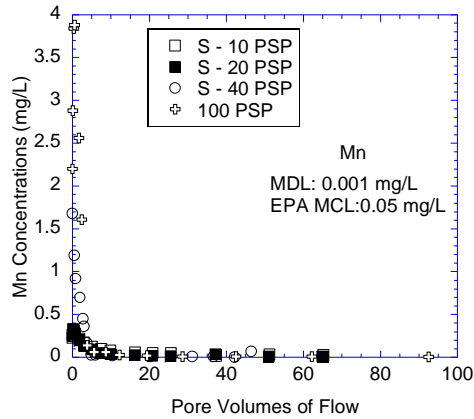
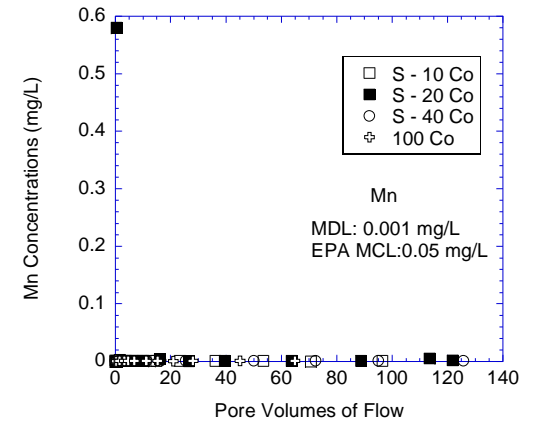
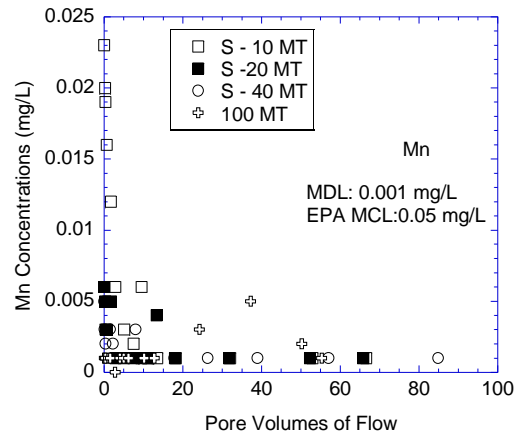
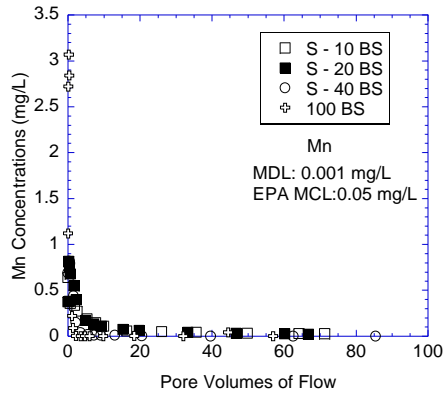


Figure 4.9 Elution curve for Manganese metal.

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.



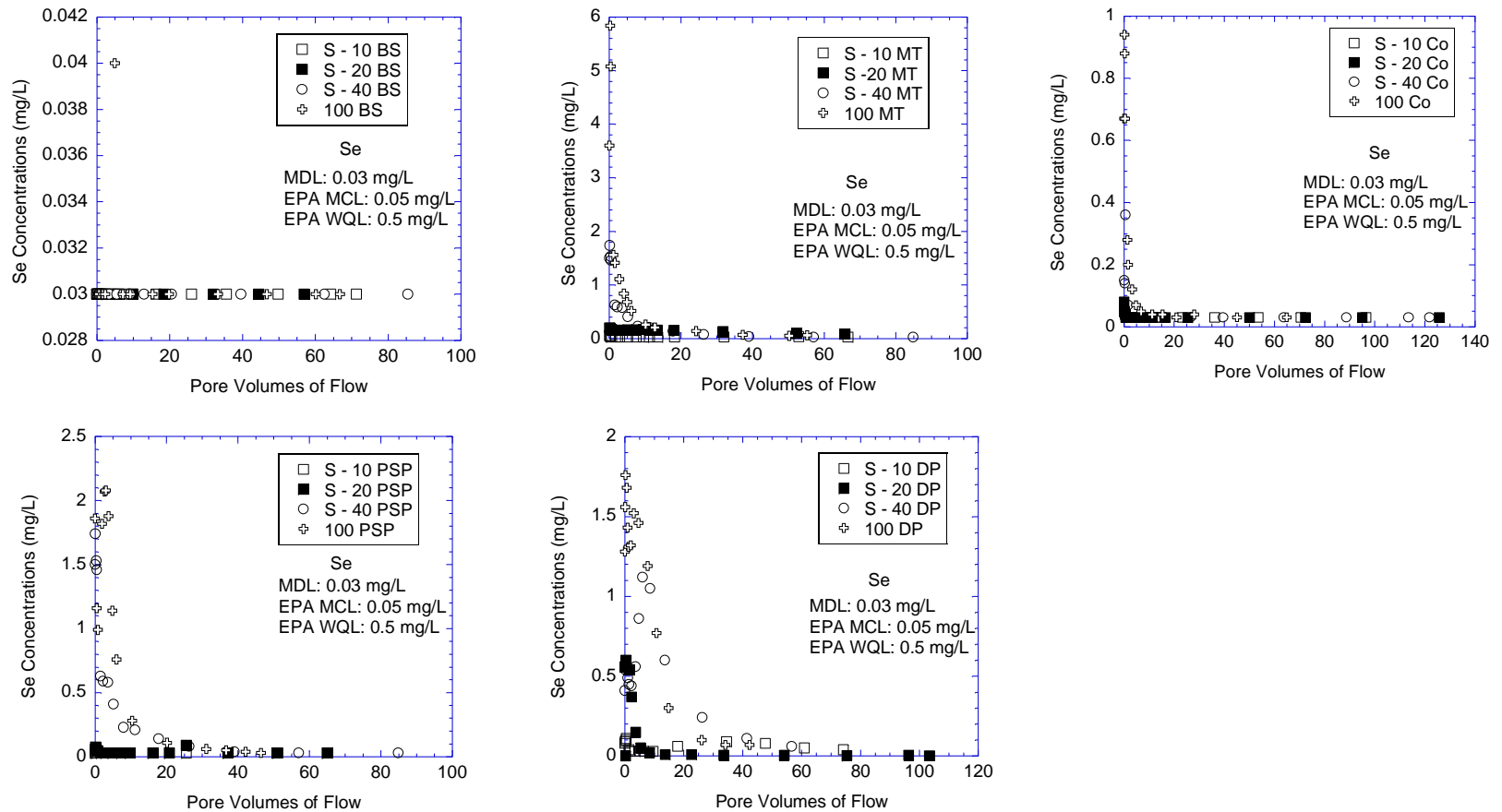


Figure 4.10 Elution curves for selenium metal.

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; WQL= water quality limits for protection of aquatic life and human health in fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

#### *4.4.3 Results Toxicity Characteristic Leaching Procedure Tests*

Toxicity Characteristic Leaching Procedure tests (TCLP) were conducted to determine the leaching of heavy metals under acidic conditions. Duplicate Toxicity Leaching Procedure tests (TCLPs) were conducted on soil alone, fly ash alone and soil-fly ash mixtures. As expected the effluent pH values of the specimens were stabilized at pHs of 4.8 to 5 except the specimens prepared with 100% MT by weight and the soil-fly ash mixtures prepared with Co fly ashes. The pHs of the effluent solutions of these specimens was most probably buffered by the high CaO contents of MT and Co fly ashes (Table 4.2). Therefore, the acetic acid buffer used in TCLP tests was not able to keep the pH values of these specimens between 4.8 and 5.

The pHs of the TCLP effluents of the specimens varied between 4.8 and 5 (Figure 4.1.c). An increase in fly ash content did not affect the pH of the soil-fly ash mixtures but for only specimens prepared with Co fly ash. CaO content of the Co fly ash was 19.4% (Table 4.2) and the release of Ca in high concentrations dominated the pH of the TCLP leachate, consistent with observations made by Mudd et al. (2004).

In general, leached concentrations of six metals (Al, As, B, Cr, Mn, Se) from the soil-fly ash mixtures in the TCLP tests were higher than those from WLTs and were lower than the maximum peak concentrations of metals leached from CLTs. TCLP test results indicated that at extreme pH conditions ( $\text{pH} < 5$ ), the leached metal concentrations exceeded the any environmental health regulation limits (Table 4.7). This was an expected behavior because the leaching of heavy metals is extreme at low (acidic) pHs (Van der Hoek et al. 1994). At acidic pHs, the surfaces of the soil and fly ash particles are

positively charged and cause them to leach significant amounts of cationic metal species into the aqueous solutions (Stumm and Morgan 1995). For Instance, Al metals start precipitating in their oxide forms such as  $\text{Al}(\text{OH})_3(\text{am})$ ,  $\text{Al}(\text{OH})_3(\text{gibbsite})$  at  $\text{pH} > 5.5$ . At  $\text{pH} < 5.5$ , Al is dissolved from these Al-oxides and is available in its free form of  $\text{Al}^{3+}$  (Sparks 2003). Similarly, As metals exist in their reduced form as As(III), the most toxic As species, at  $\text{pH} < 5$  (Pandey et al. 2011). Se behaves similar to As, and anionic species of Se are likely to be adsorbed by soil and fly ash particles at acidic conditions at  $\text{pH} < 5$ , which yields the release of cationic species of these metals into the aqueous solutions (Su et al. 2011). Under natural conditions, Al-oxides and Fe-oxides may provide adequate surface sites for As and Se metals to be sorbed. However, at acidic pHs, these As and Se attached metal oxides dissolve and increase the concentrations of As and Se metals (Apul et al. 2010). This may also have contributed to higher As and Se concentrations observed in the TCLP tests as compared to the WLTs.

The data in Figure 4.11 suggests that, with few exceptions, an increase in fly ash content generally increased the metal concentrations. In TCLP tests, leaching amount of metals is expected to be dependent on the total metal content in the fly ash since the pHs of the effluent solutions were kept nearly constant. Differences in Mn concentrations measured from TCLP tests and WLTs prove that the leaching of Mn was a cationic leaching pattern indicating that leaching of Mn was higher at low pHs. Mn is complexing with free  $\text{OH}^-$  in the aqueous solution at neutral pHs to alkaline pHs and precipitates as Mn-(hydro)oxides.

Table 4.7. Effluent metal concentrations in TCLP tests. Concentrations exceeding EPA MCL are in **bold**.

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (µg/L)	B (µg/L)	Cr (µg/L)	Mn (µg/L)	Se (µg/L)
S – 10 BS	10	4.82	<0.05	<0.01	0.08	0.01	0.04	<0.03
S – 20 BS	20	4.82	<0.05	<0.01	0.1	0.01	<b>0.11</b>	<0.03
S – 40 BS	40	4.82	0.055	<0.01	0.14	0.01	<b>0.14</b>	<0.03
100 BS	100	4.83	0.06	<b>0.045</b>	0.39	0.02	<b>0.21</b>	<0.03
S – 10 PSP	10	4.84	<0.05	<0.01	0.11	<0.001	<b>0.18</b>	<0.03
S – 20 PSP	20	4.85	0.085	<0.01	0.15	<0.001	<b>0.18</b>	<0.03
S – 40 PSP	40	4.85	<b>0.27</b>	<b>0.15</b>	0.35	0.004	<b>0.3</b>	<b>0.075</b>
100 PSP	100	4.86	<b>0.58</b>	<b>0.47</b>	1.03	0.0045	<b>0.48</b>	<b>0.35</b>
S – 10 MT	10	4.87	0.185	<0.01	0.91	0.02	<b>0.15</b>	<0.03
S – 20 MT	20	4.89	<b>0.32</b>	<0.01	1.37	0.03	<b>0.16</b>	<0.03
S – 40 MT	40	4.92	<b>2.37</b>	<0.01	2.44	0.085	<b>0.29</b>	<0.03
100 MT	100	5.12	<b>5.43</b>	<b>0.03</b>	7.3	<b>0.11</b>	<b>0.43</b>	<b>0.085</b>
S – 10 DP	10	4.83	<b>4.83</b>	<b>0.61</b>	0.01	<b>0.25</b>	0.01	<b>0.23</b>
S – 20 DP	20	4.87	<b>4.87</b>	<b>1.25</b>	0.15	<b>0.38</b>	0.02	<b>0.24</b>
S – 40 DP	40	4.92	<b>4.87</b>	<b>2.07</b>	0.46	<b>0.53</b>	0.03	<b>0.24</b>
100 DP	100	4.87	<b>4.87</b>	<b>8.7</b>	0.5	<b>1.65</b>	<b>0.06</b>	<b>0.28</b>
S – 10 Co	10	5.21	<b>3.95</b>	<0.01	1.12	0.02	<b>0.21</b>	<0.03
S – 20 Co	20	5.42	<b>1</b>	<b>0.025</b>	1.73	0.035	<b>0.18</b>	0.045
S – 40 Co	40	7.41	0.05	<b>0.045</b>	3.1	0.07	<b>0.11</b>	<b>0.14</b>
100 Co	100	10.86	14.445	<b>0.06</b>	4.32	0.23	0.04	<b>0.35</b>
Sandy Soil	-	6.74	<0.05	<0.01	<0.02	<0.001	<0.001	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	0.57	NA	NA

Note: MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

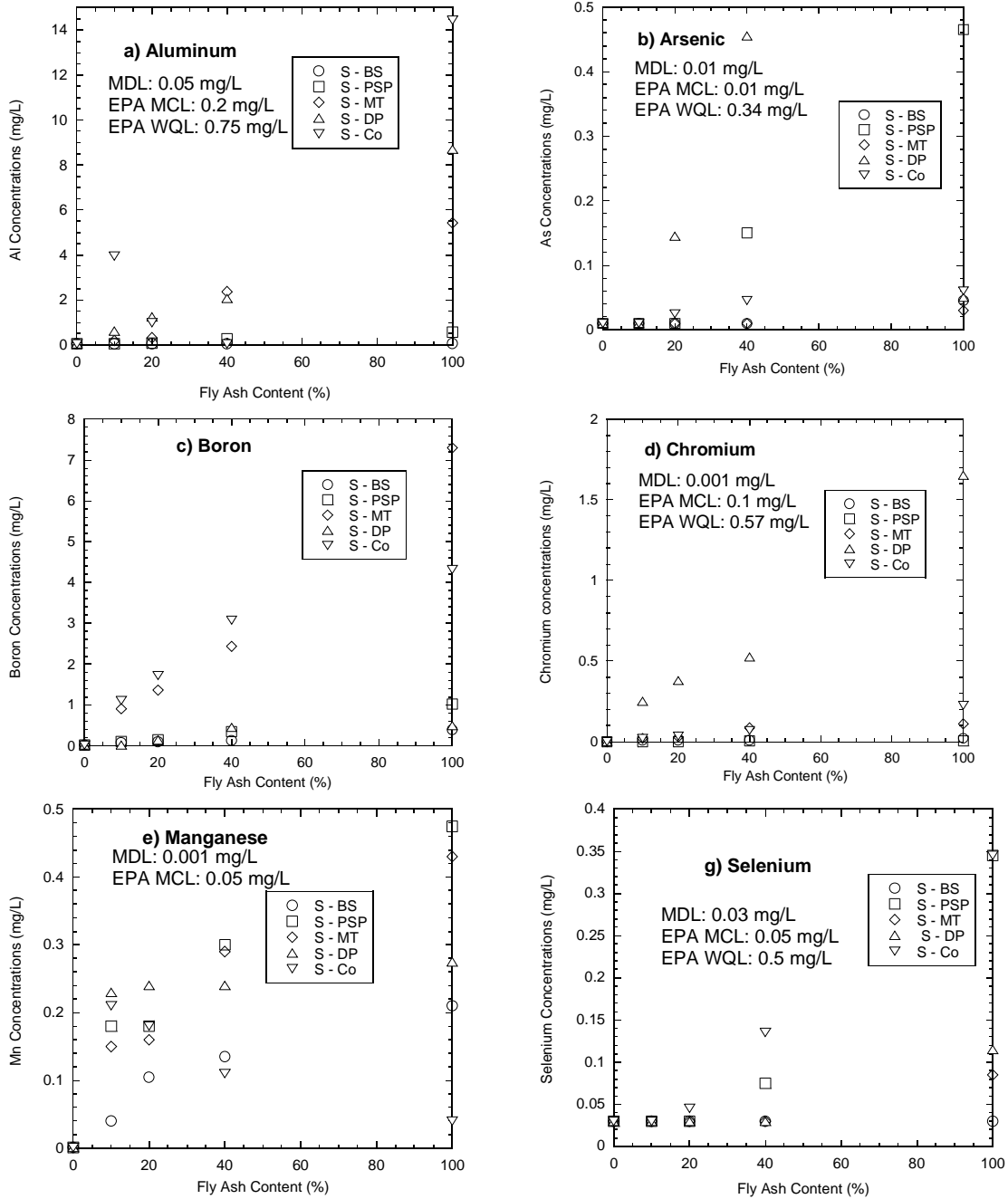


Figure 4.11 Concentrations of six metals in the effluent from TCLPs (Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgantown); MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water.)

These solid Mn-(hydro)oxides minerals are dissolving with an increase in pH due to the hydrolysis reactions and leaving  $Mn^{2+}$  free in the effluent solutions (Gitari et al. 2009).

As mentioned in the previous sections, Cr tends to follow an amphoteric leaching pattern similar to As, Se and Al (Cetin et al. 2012). At neutral pHs, the leaching of Cr is minimal and at  $pH < 7$  the leaching of Cr increases significantly (Karamalidis and Voudrias 2008).

Therefore, it was expected to see higher Cr concentrations leached from the soil-fly ash mixtures in TCLP tests than the Cr concentrations leached from the soil-fly ash mixtures in WLTs. Cr exists mostly in its oxidized form Cr (III) at low pHs ( $pH < 6$ ) due to reduction of Cr(VI) to Cr(III) (Geelhoed et al. 2002, Samaras et al. 2008). Even though specimens released more Cr into the aqueous solutions at acidic conditions, it is not critical from an environmental standpoint since Cr(III) is non-toxic and provides necessary nutrition metal for plants and animals (Quina et al. 2009). Furthermore, Cr(VI) is the anionic form of the Cr metals and it is likely that these Cr(VI) metals are being adsorbed onto the soil and fly ash surfaces with a decrease in pH of the aqueous solutions. Solubility of Cr(III) is generally controlled by  $Cr(OH)_3$  minerals and a decrease in pH will hydrolyze these minerals and release the Cr(III) metals into the effluent solutions (Engelsen et al. 2010). Dissolution of  $Cr(OH)_3$  minerals may have caused the leaching of higher Cr concentrations in TCLP tests than WLTs.

B concentrations in the aqueous solutions were increased with fly ash content (Figure 4.11c). This trend was consistent with the results obtained from both WLTs and CLTs. Leaching of B increased with a decrease in pH and typically remains at its maximum at acidic pHs (Querol et al. 1995). However, the B concentrations leached from soil-Co fly

ash mixtures were the highest, even though the pHs of the effluent solutions of the soil-Co fly ash mixtures were significantly higher than the pHs of the effluent solutions of other soil-fly ash mixtures (Table 4.7). These results could be explained using the comparison of total B contents of the fly ash materials determined via total elemental analysis. Table 4.3 indicates that Co fly ash contains 2.5 to 28 times higher total B content than the other fly ashes used in this study. A similar trend also was observed for the MT fly ash-alone specimen. Higher B concentrations were leached from the MT fly ash alone specimen, even though its pHs was relatively higher than the pH of the other soil-fly ash mixtures.

It was observed that leaching of Al and Mn metals for specimens prepared with Co fly ash was not only dependent on the total metal content of the Co fly ash but also pH of the effluent solutions. TCLP test results indicated that the pH values of the soil-Co fly ash mixtures increase significantly with an increase in fly ash while the pH of other soil-fly ash mixtures were around pH of 5. An increase in Co fly ash content resulted in decrease in the Mn concentrations. Mn leaching is extreme at acidic pHs and increase in pH would decrease the leaching capability of Mn significantly (Goswami and Mahanta 2007, Cetin et al. 2012). Therefore, the concentrations of Mn for the specimens prepared with the Co fly ash were much lower than those prepared with other fly ashes. On the other hand, different leaching trend was observed for the leaching of Al metals from the soil-Co fly ash mixtures. The pHs of the S-10 Co, S-20 Co, S-40 Co, and 100 Co specimens were 5.21, 5.42, 7.41, and 10.86, respectively and the Al concentrations of these specimens with the same order were 4 mg/L, 1mg/L, 0.05 mg/L, and 14.5 mg/L, respectively. Al

shows an amphoteric leaching pattern and is very mobile at acidic pHs and basic pHs; its leaching is minimal at neutral pHs (Komonweeraket et al. 2010, Cetin et al. 2012). The results for Al leaching in this part of the study confirmed that Al leaching is highly dependent on the pH of the effluent solutions and showing amphoteric leaching pattern. An increase in Co fly ash content from 10% to 40% did not increase the Al concentrations but decreased which is due to the precipitation of Al into Al-(hydr)oxide minerals (Mudd et al. 2004). On the other hand, Co fly ash alone samples leached the highest Al concentrations in all the soil-fly ash mixtures, which was due to extreme basic conditions (pH=12.2) and total Al content of the Co fly ash (Table 4.3).

#### *4.4.4 Comparison of the Leaching Test Results*

Attempts were made to compare the TCLP, CLT, and WLTs in Figure 4.12. The peak CLT concentrations are consistently greater than the WLT concentrations. Differences in L:S ratio between the two leaching tests (a ratio of 20:1 in WLTs versus 0.1:1 in CLTs in the initial PVFs) could be responsible for the significant metal concentration differences measured in these two leaching tests. Su et al. (2011) claimed that a decrease in L:S ratio increased the concentrations of leached metals. Figure 4.12 shows that the maximum concentrations of the Al, As, B, Cr, Mn and Se from CLTs is up to 16, 100, 100, 100, 100 and 50 times higher than the metal concentrations obtained from WLTs, respectively. In addition, the peak CLTs are consistently greater than the TCLP test concentrations. Figure 4.13 shows that the maximum concentrations of the As, Al, B, Cr, Mn and Se from CLTs is up to 10, 100, 100, 100, 10, and 10 times higher respectively than the metal concentrations obtained from TCLPs. Figure 4.14 shows that the concentrations of the



As, B, Cr, Mn and Se from TCLPs is up to 20, 20, 10, 50 and 10 times higher respectively than the metal concentrations obtained from WLTs. No relationship can be seen between TCLP and WLT test results for Al metal concentrations since the Al concentrations in the leachates collected in WLTs were below the detection limits which yielded constant Al concentrations values for many specimens. The pHs of the effluent solutions obtained from TCLP tests were more acidic than the pHs of the effluent solution obtained from WLTs. This could be the reason for obtaining higher leached metal concentrations in TCLP tests from the soil-fly ash mixtures since the leaching of metals are the highest at acidic conditions (Komonweeraket et al. 2012).

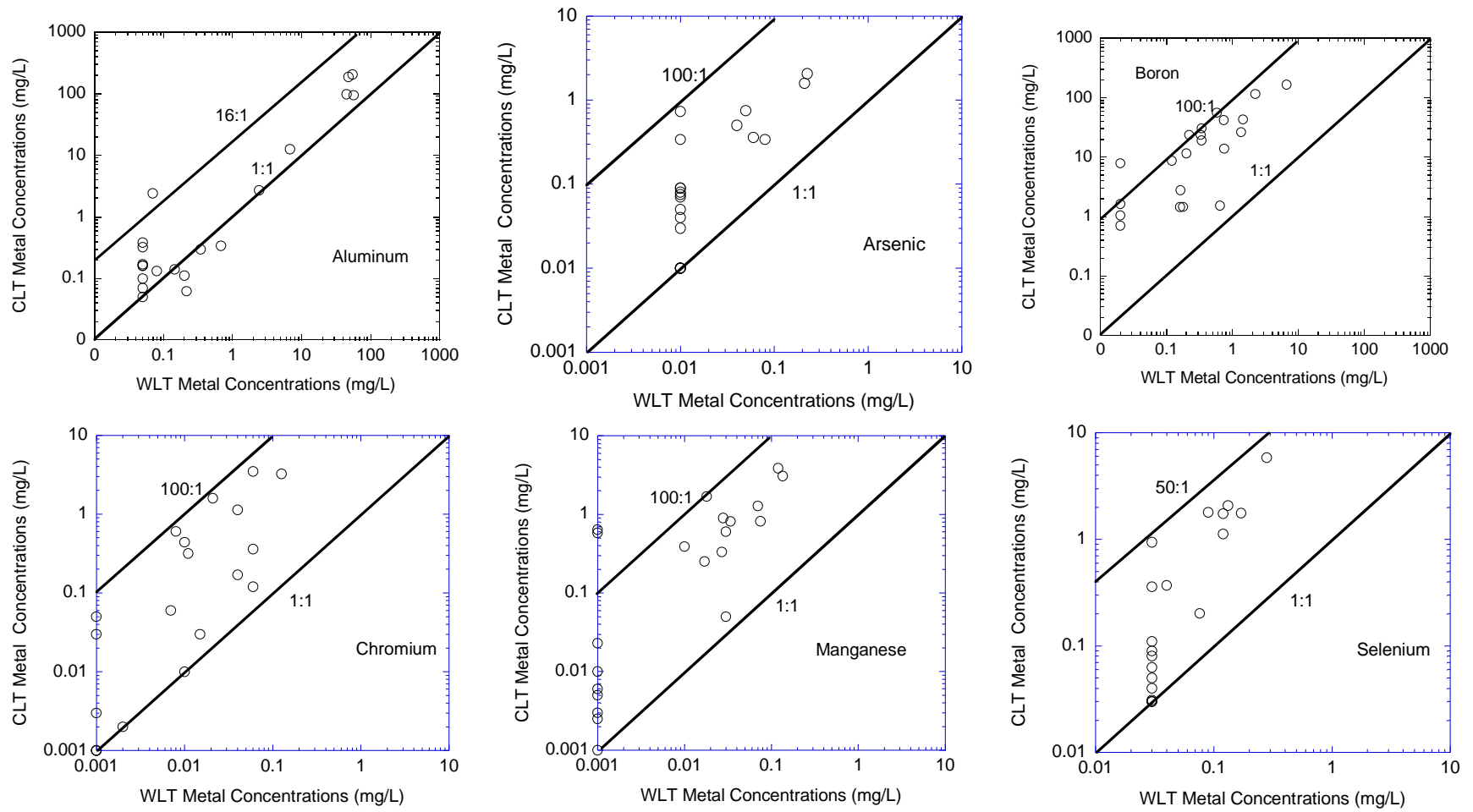


Figure 4.12. Comparison of peak effluent concentrations of six metals from the CLTs and the WLTs

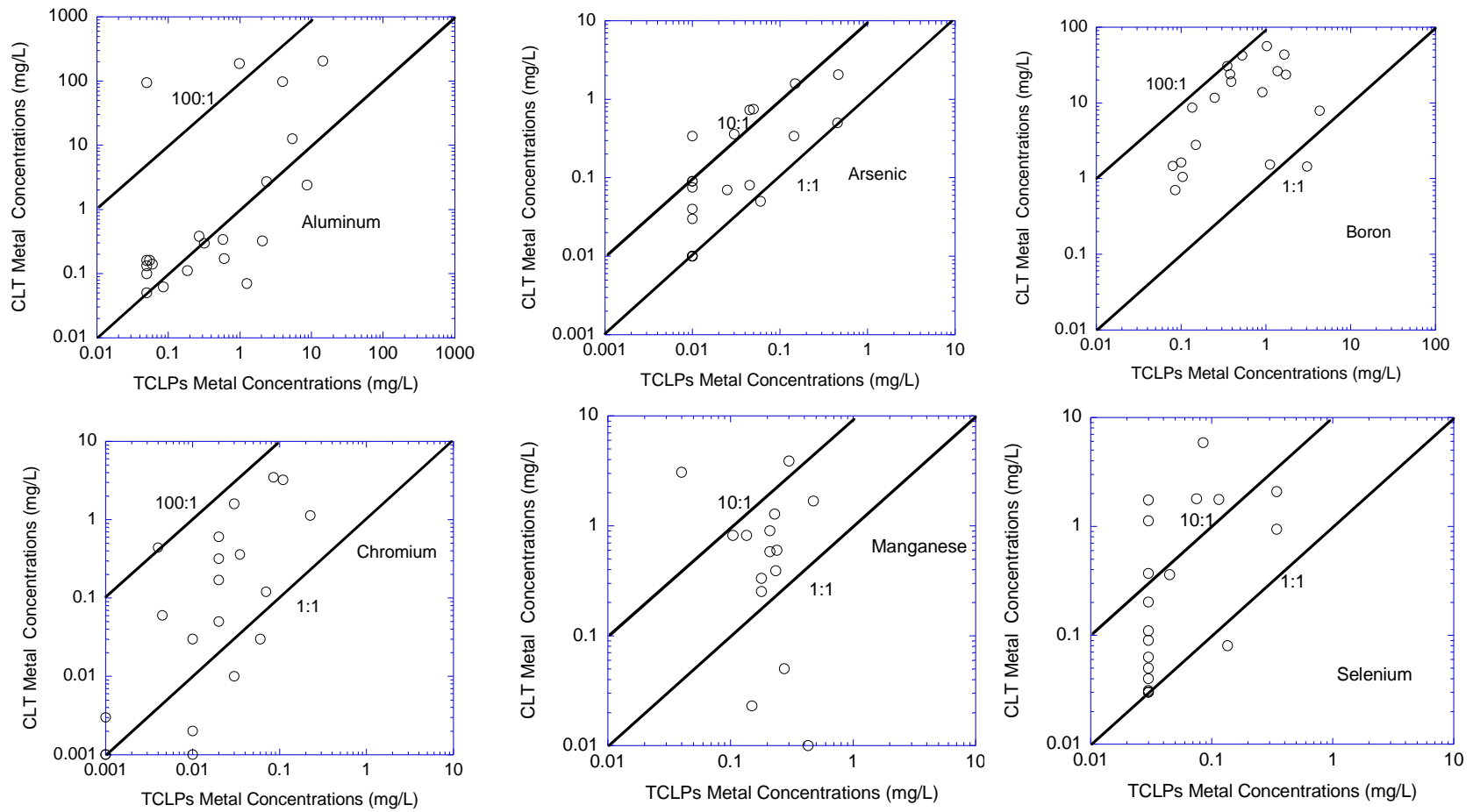


Figure 4.13. Comparison of peak effluent concentrations of six metals from the CLTs and the TCLPs

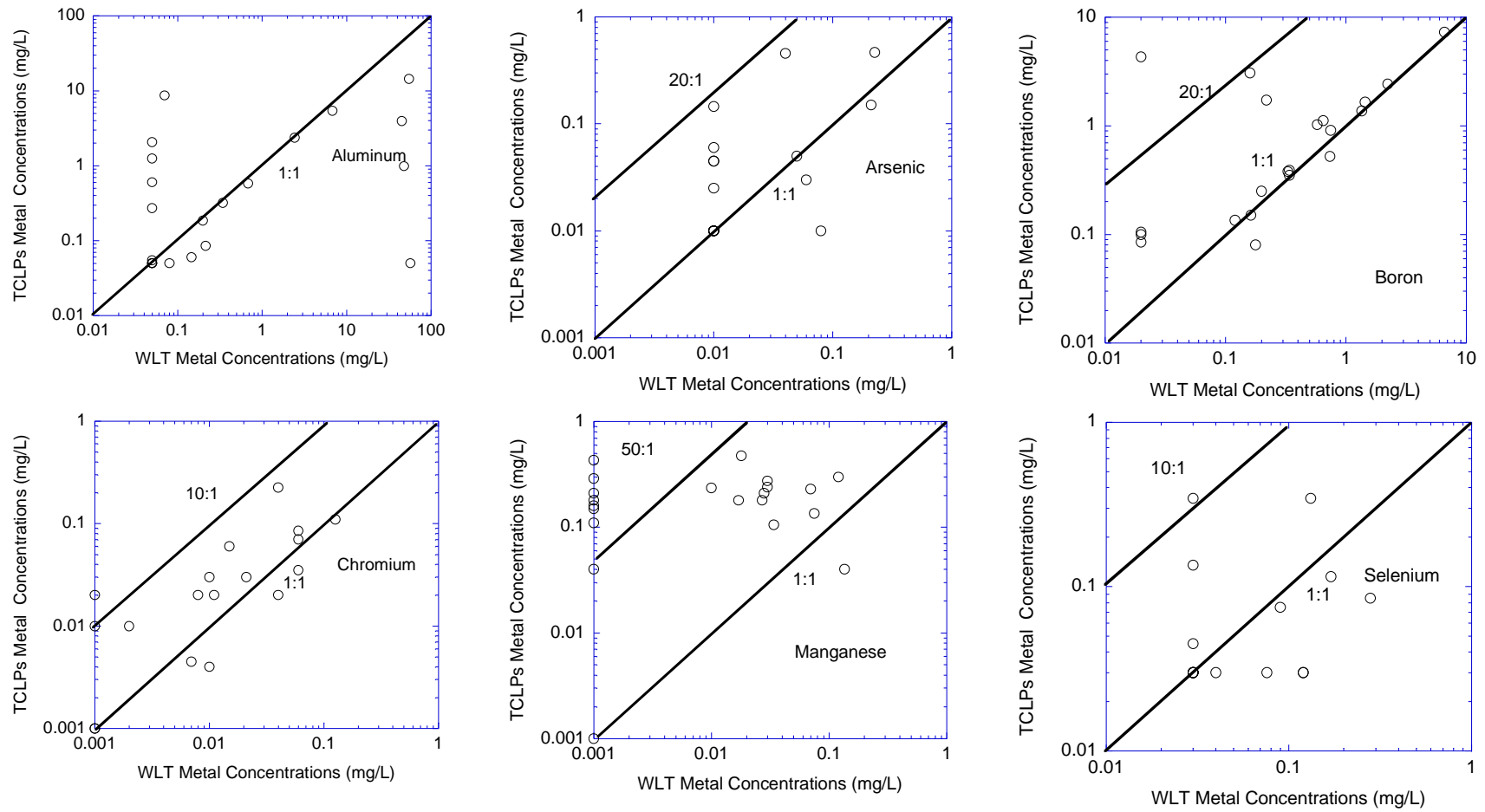


Figure 4.14. Comparison of peak effluent concentrations of six metals from the WLTs and the TCLPs

## 4.5 CHEMICAL TRANSPORT MODELING

### 4.5.1 *Numerical Model*

The flow and transport of metals in fly ash mixed embankment construction was simulated using WiscLEACH, a recent and verified windows-based software package for simulating water and solute movement in two-dimensional variably saturated and unsaturated media. Three analytical solutions to the advection-dispersion-reaction equation are combined in WiscLEACH to develop a method for assessing impacts to groundwater and the soil vadose zone caused by leaching of trace elements from fly ashes used in embankment constructions.

A schematic diagram of WiscLEACH for embankment structures is shown in Figure 4.15. WiscLEACH simulations were conducted to study the locations of maximum soil vadose zone and groundwater concentrations (e.g., at the centerline of the embankment structure, at the vicinity of point of compliance). Contours of trace metals are predicted at different years as a function of depth to groundwater, thickness of the embankment layer, percent fly ash by weight, hydraulic conductivity of the least conductive layer in the vadose zone, hydraulic conductivity of the aquifer material and the initial concentration in the fly ash. Model formulation of embankment version of WiscLEACH was defined before in section 3. Therefore, it will not be repeated here again.

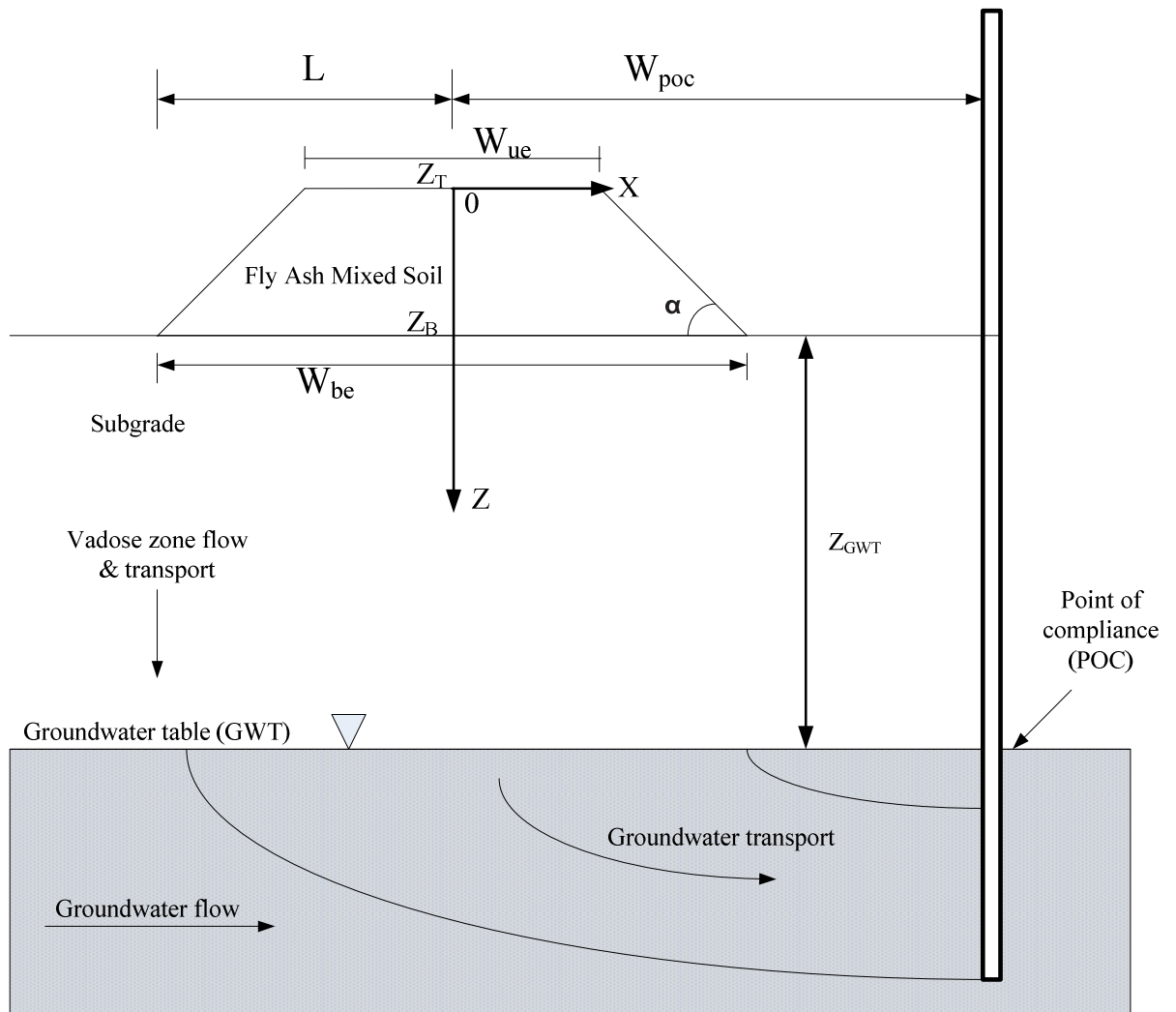


Figure 4.15. Conceptual model for embankment structure

#### *4.5.2 WiscLEACH Results*

WiscLEACH was used to predict the metal concentrations in contour graphs at different years and determine the location of maximum concentrations of the trace metals in the soil vadose zone and groundwater after a period of 50 years. The input data in Tables 4.8 and 4.9 were used for all soil-fly ash mixtures to be consistent. The hydraulic conductivities and transport parameters of the pavement layers and soil mixtures are summarized in Table 4.9. The transport parameters were determined from the laboratory tracer tests, and the pavement and subgrade properties were taken from Li et al. (2007). The retardation factors along with chromium concentrations for four different soil mixtures, S – 20 DP, S – 40 DP, S – 20 PSP, S – 40 PSP (Note: 20 DP, 40 DP, 20 PSP, 40 PSP designate the specimens with 20% and 40% Dickerson Precipitator, 20% and 40% Paul Smith Precipitator fly ash respectively) are shown in Table 4.9. The annual precipitation rate selected in this study was 1 m/year, the average annual rainfall in the State of Maryland according to the U.S. Geological Survey.

Table 4.8 Input site parameters for embankment and soil structures.

	W <sub>poc</sub>	W <sub>p</sub>	W <sub>s</sub>	Z <sub>GWT</sub>	Prcpt	T <sub>max</sub>	T (m)	Side Slope (H:V)
Constant values for all specimens	30	6	2	5	1.00	50	5	2:1

Notes: All measurements are in meter, W<sub>poc</sub>: Point of compliance, W<sub>p</sub>: Pavement width, W<sub>s</sub>: Shoulder width, Z<sub>GWT</sub>: Depth to groundwater table, Prcpt: Annual precipitation rate in m/year, T<sub>max</sub>: 50 years, Thickness of embankment structure,

Table 4.9 Hydraulic and transport parameters or pavement, embankment, soil aquifer structures to be used as an input in WisLeach

Specimen	Hydraulic Conductivity, K <sub>s</sub> (m/year)	n <sub>e</sub>	Hydraulic Gradient	α <sub>L</sub> (m)	α <sub>T</sub> (m)	R <sub>d</sub> for Cr
S – 20 PSP	8.67	0.302	0.001	0.193	0.0193	27
S – 40 PSP	6	0.395	0.001	0.485	0.0485	8
S – 20 DP	25.23	0.42	0.001	0.401	0.0401	1.1
S – 40 DP	20.08	0.489	0.001	0.671	0.0671	15
Pavement	18.29	0.35	0.001	0.1	0.01	1
Subgrade	1.01	0.35	0.001	0.1	0.01	3.5
Aquifer	3784	0.30	0.001	0.1	0.01	1

Notes; α<sub>L</sub> : Longitudinal dispersivity, α<sub>T</sub> : Transverse dispersivity, hydraulic gradients is assumed as 0.001 to simulate the natural conditions, n<sub>e</sub> : effective porosity, Cr: Chromium.



Figures 4.16 through 4.19 show the contour plots of the predicted concentrations of Cr in the soil vadose zone as well as groundwater. The contour plots provide predictions of the metal concentrations after 5, 10, 20 and 50 years of construction. WiscLEACH simulations indicate that Cr concentrations for all specimens were below the EPA MCL of 100 µg/L, except the S – 40 PSP. The results indicated that the maximum Cr concentrations were reached in approximately 10 to 20 years; however, they were far below the EPA MCL at the groundwater table (Figures 4.16- 4.19).

As shown in Figures 4.16 through 4.19 the Cr metal concentrations decreased with distance from HCFA amended embankment's ground surface and groundwater surface which was likely due to the dispersion of the metals in the soil vadose zone. High annual precipitation rate may also have caused an increase in the leaching rate of the metals from HCFA amended embankment and absorbing the metals before reaching to the groundwater.

The WiscLEACH computer model was also redesigned to simulate the leaching of metals from embankment structures built in multiple fly ash alone and soil alone layers. Multiple layer version of WiscLEACH was used to predict the concentrations of four metals of concern (As, Cr, Mn, and Se) at different years and determine the maximum concentrations of the trace metals in the groundwater after a period of 100 years at the point of compliance (POC). The input data used in the analyses of the WiscLEACH is summarized in Table 4.10.

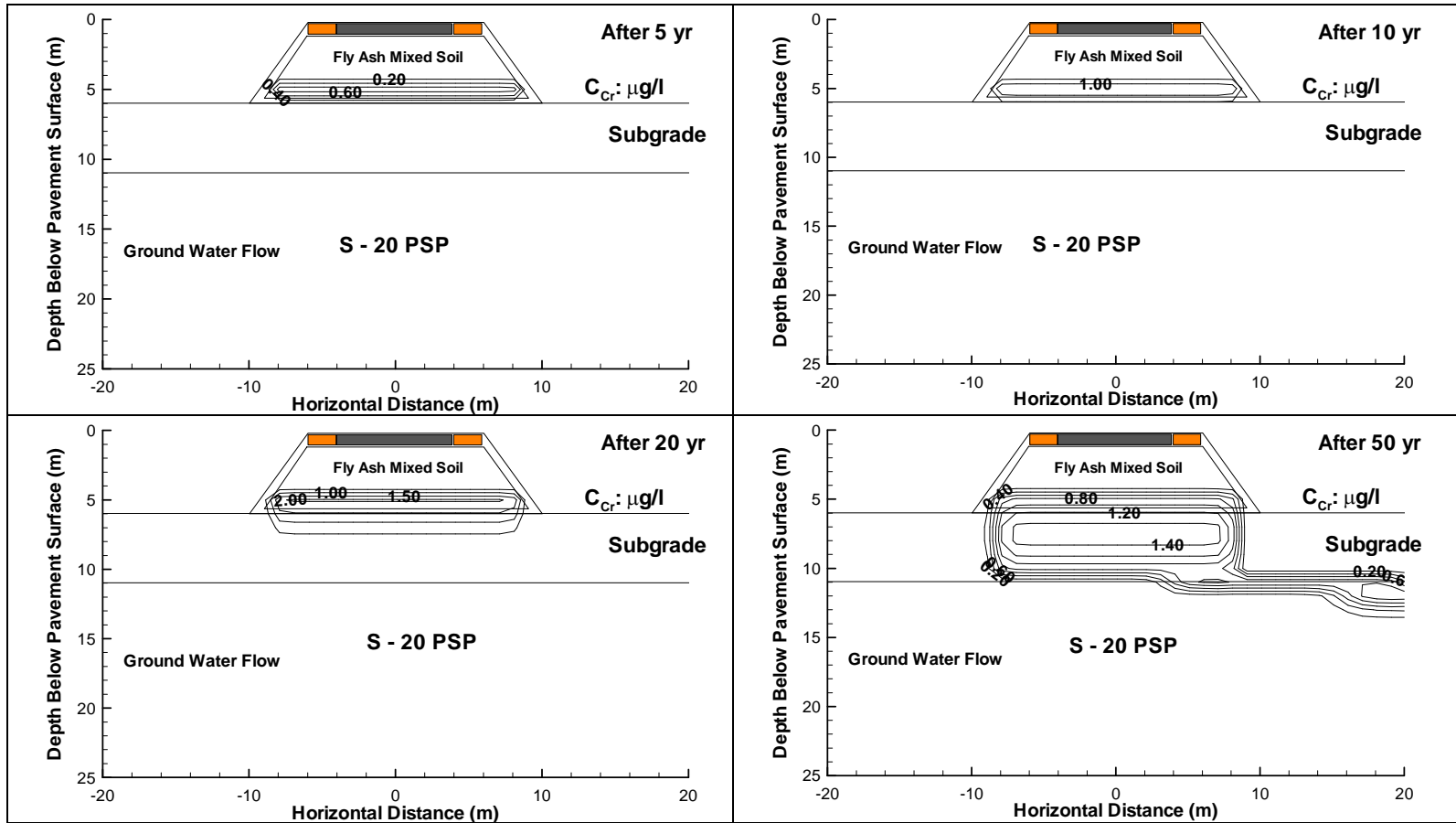


Figure 4.16. Predicted  $C_r$  concentrations in vadose zone and ground water (Note: 20 PSP designate the specimens with 20 % Paul Smith Precipitator fly ash.)

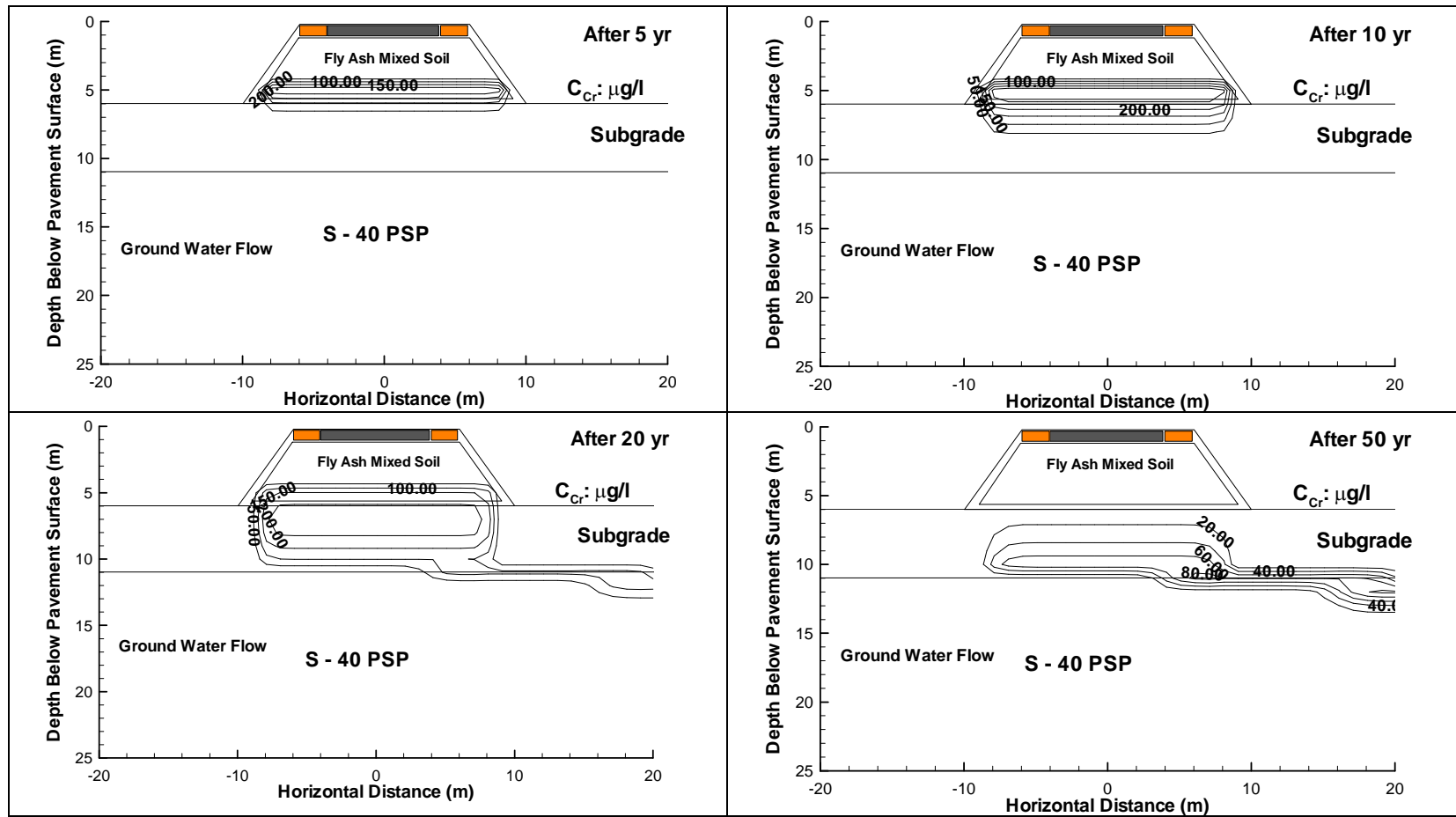


Figure 4.17. Predicted Cr concentrations in vadose zone and ground water (Note: 40 PSP designate the specimens with 40 % Paul Smith Precipitator fly ash.)

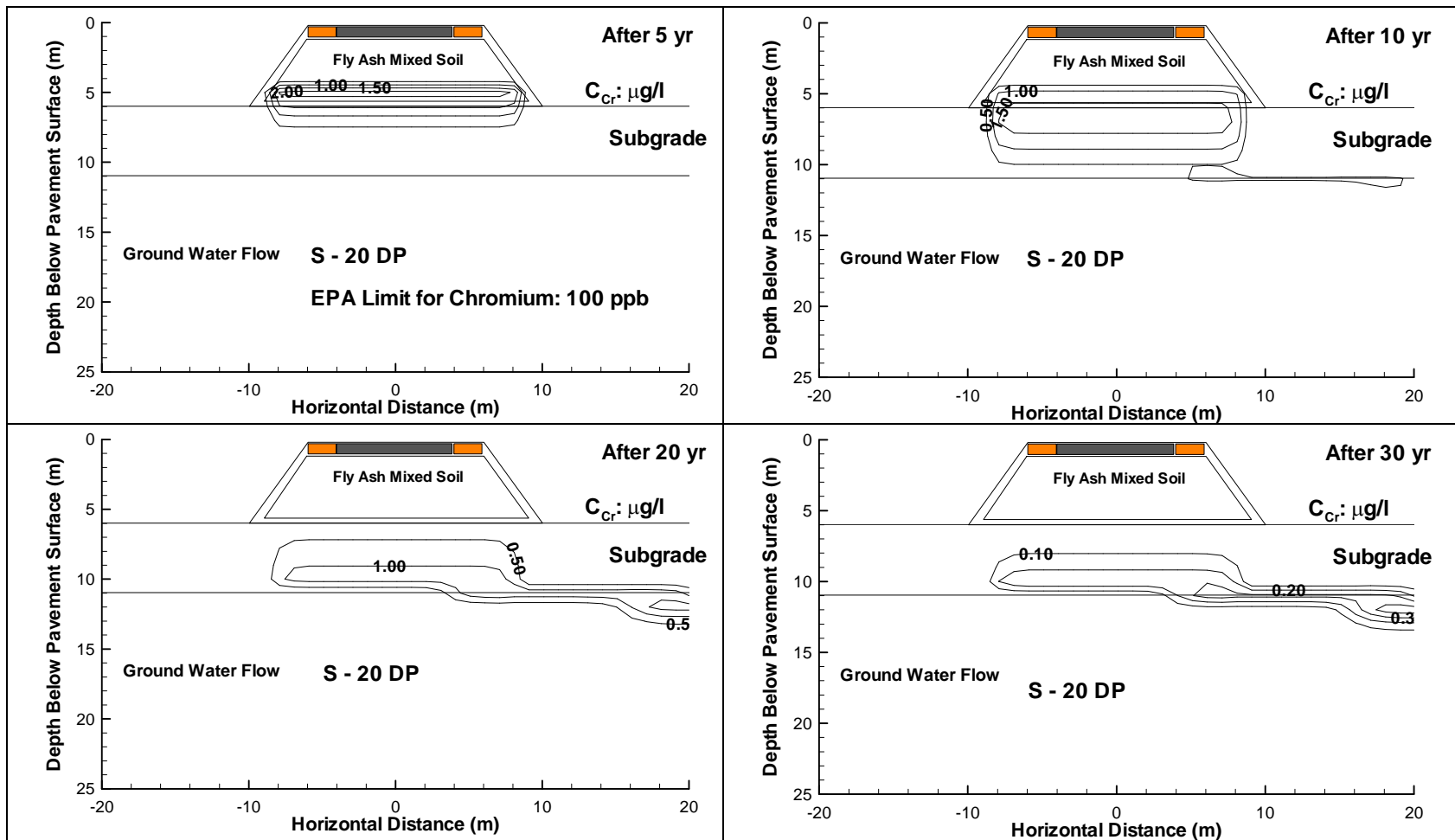


Figure 4.18 Predicted Cr concentrations in vadose zone and ground water (Note: 20 DP designate the specimens with 20 % Dickerson Precipitator fly ash.)

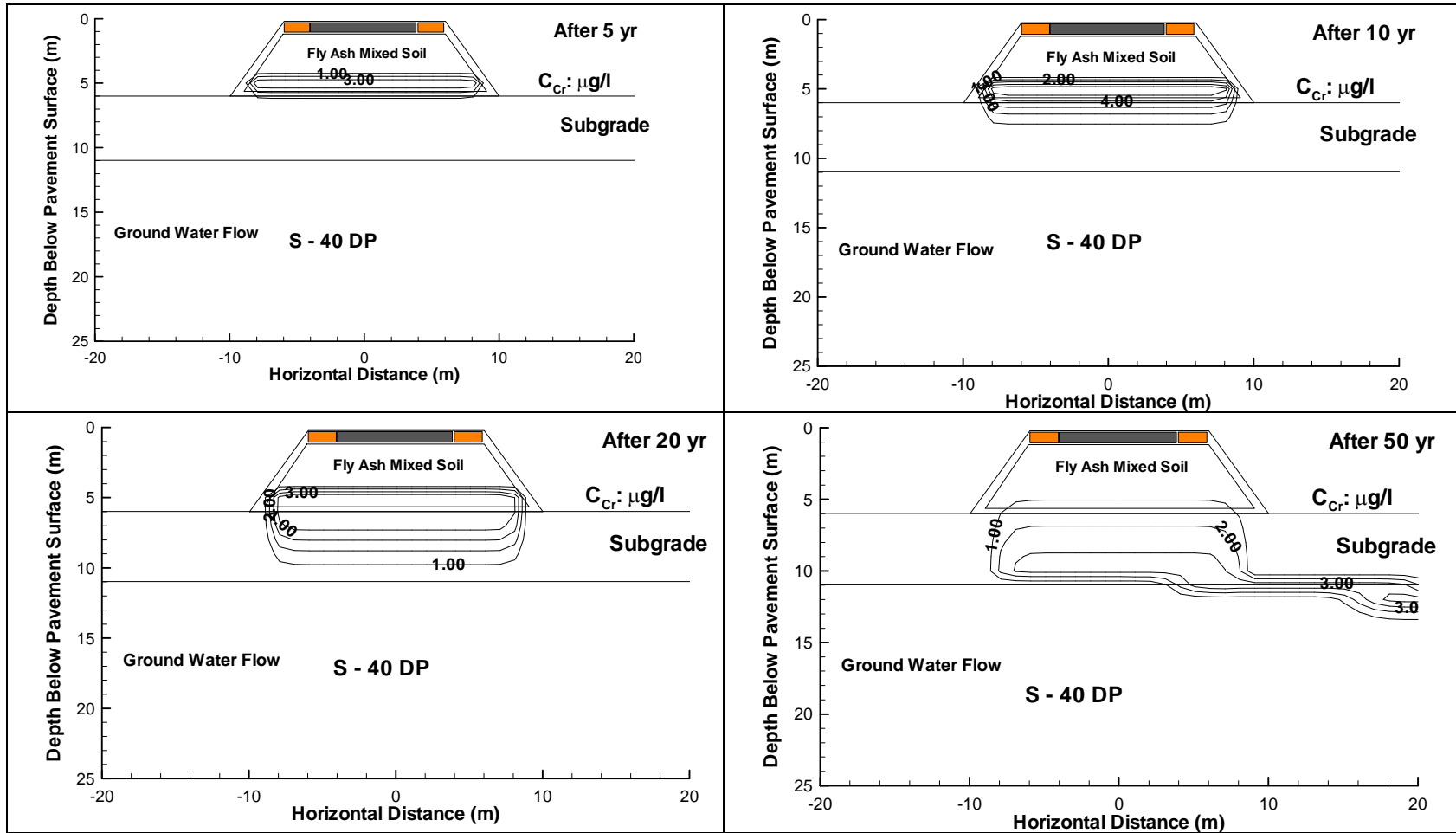


Figure 4.19 Predicted Cr concentrations in vadose zone and ground water (Note: 40 DP designate the specimens with 40 % Dickerson Precipitator fly ash.)

Figure 4.20 shows the schematic diagram of the multiple layer embankment construction. It contains a series of 3 soil layers and 3 fly ash layers placed on top of each other. Each layer is 1-meter (~3-ft) thick. The hydraulic conductivities, transport parameters of the pavement layers and both fly ashes are summarized in Table 1 along with the retardation factors for each of the 4 analyzed trace metals.

Figures 4.21 to 4.28 show the contour plots of the predicted concentrations of As, Cr, Mn, and Se in the soil vadose zone as well as the groundwater. The contour plots provide the predictions of the metal concentrations after 1, 10, 20 and 40 years of construction. WiscLEACH simulations indicated that As, Mn, Se metal concentrations are exceeding the EPA Maximum Concentration Limits for drinking waters (MCLs). However, as mentioned in the previous section, the soils prepared with 20% fly ashes by weight yielded lower metal concentrations that were far below the EPA MCL. This indicates that extra care should be taken when using fly ash in geotechnical applications. Using pure fly ash as an embankment fill may cause serious environmental problems. WiscLEACH simulations showed that the maximum concentrations of all 4 metals are reached in approximately 10 to 20 years. After the maximum concentrations are reached, metal concentrations in the vadose zone start to decrease with time. Furthermore, Figures 4.23 and 4.27 indicate that the Cr concentrations are far below the MCL when it reaches to the groundwater.

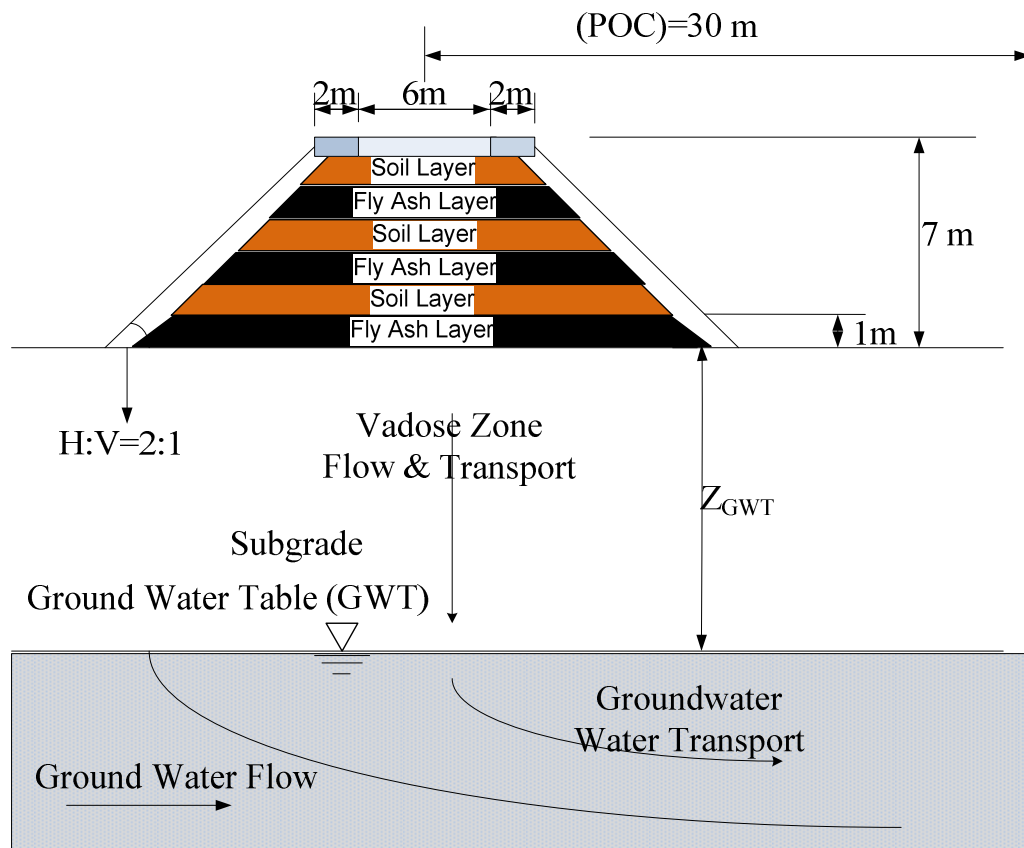


Figure 4.20. Conceptual model of WiscLEACH for multiple layer fly ashes. Note: POC = Point of compliance

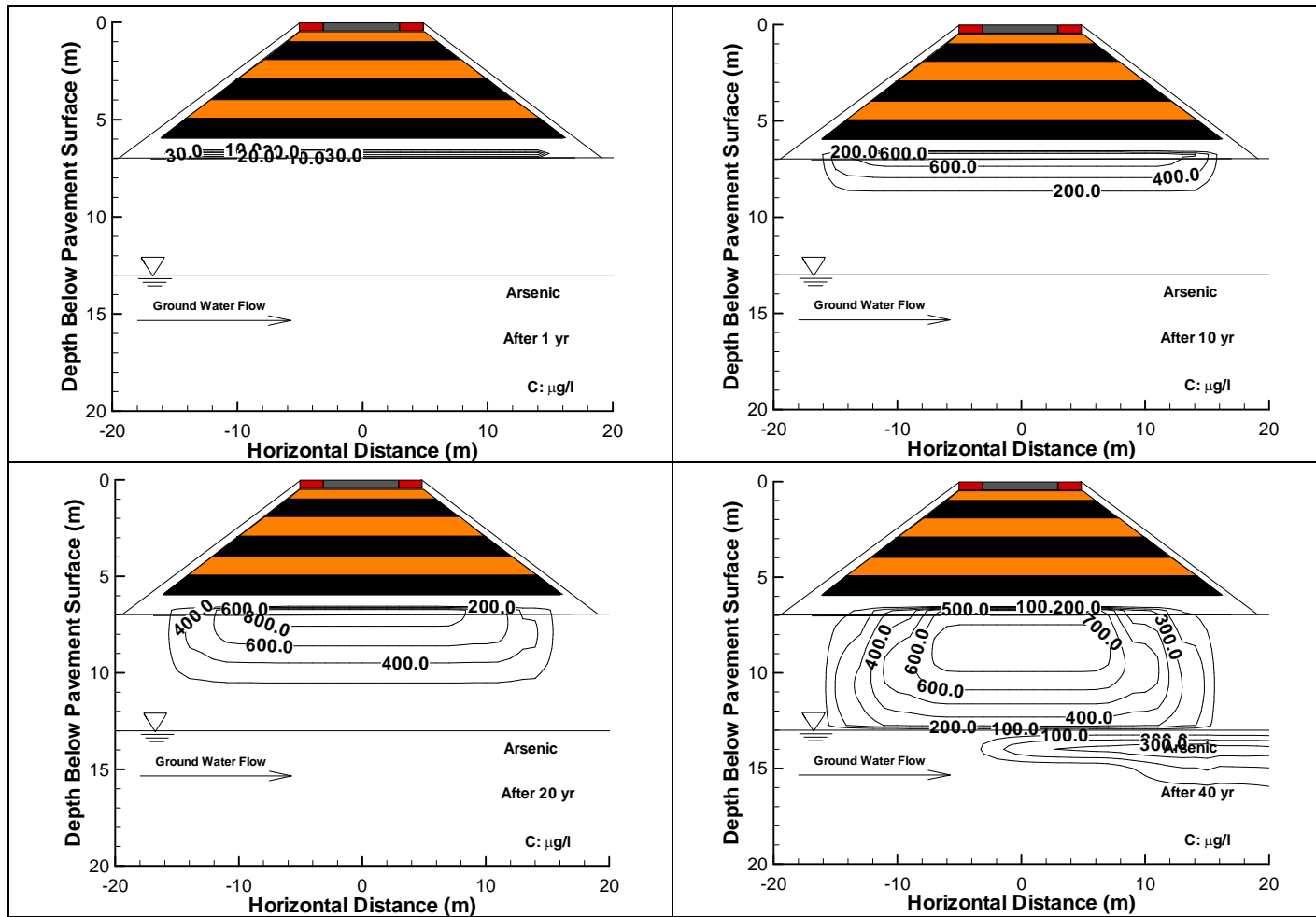


Figure 4.21. Predictions of As concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash.



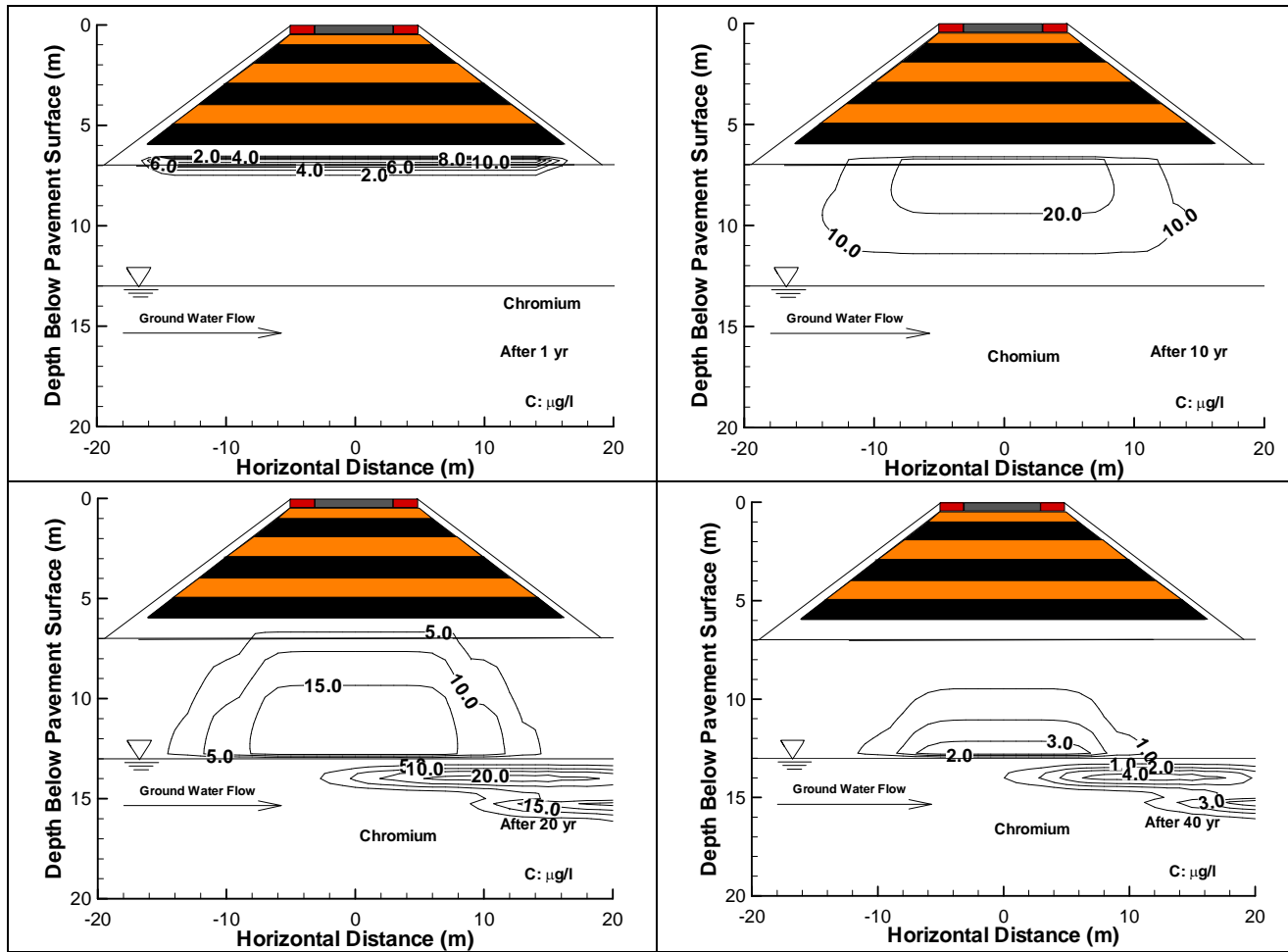


Figure 4.22 Predictions of Cr concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash.

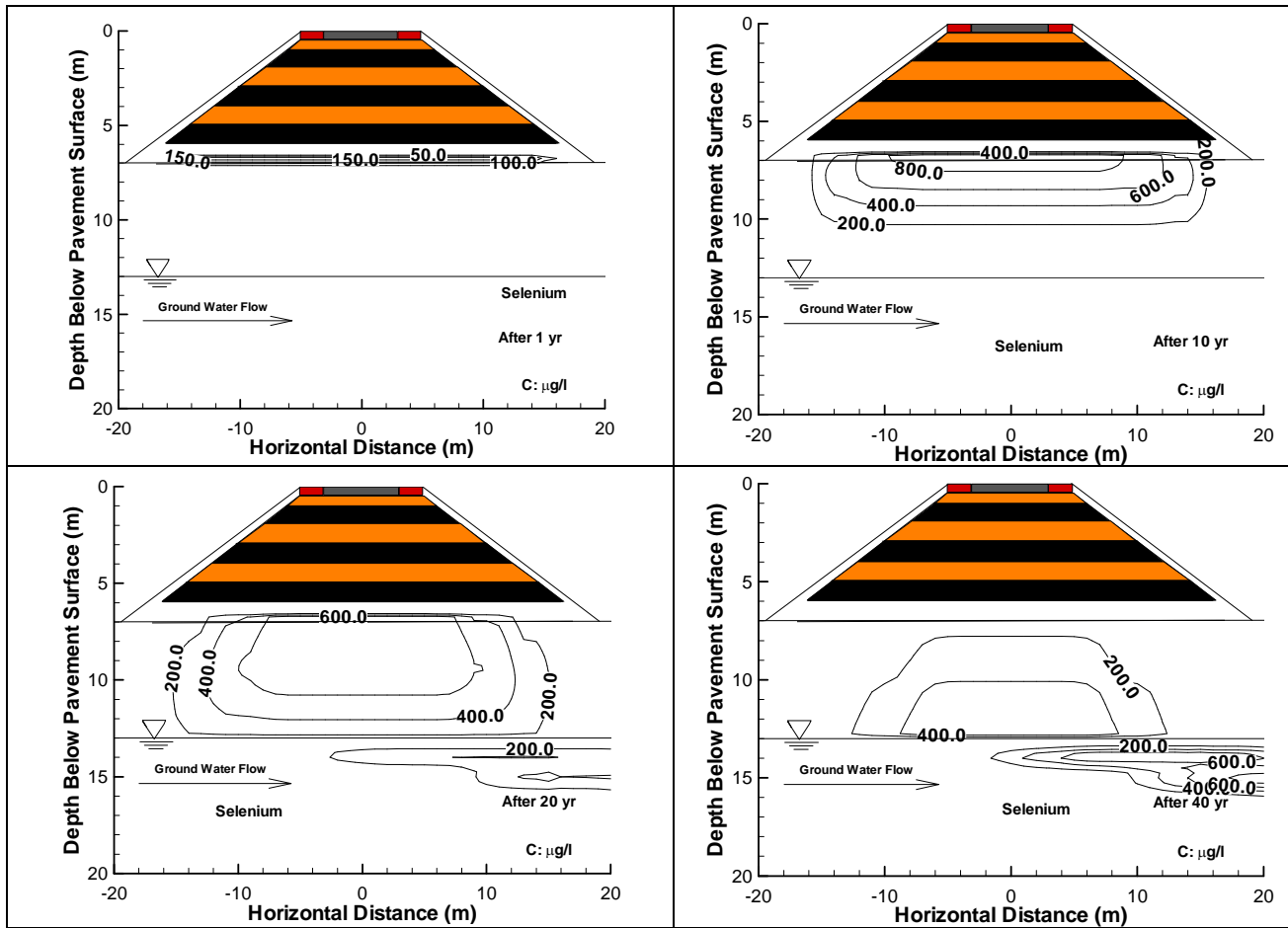


Figure 4.23 Predictions of Se concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash.

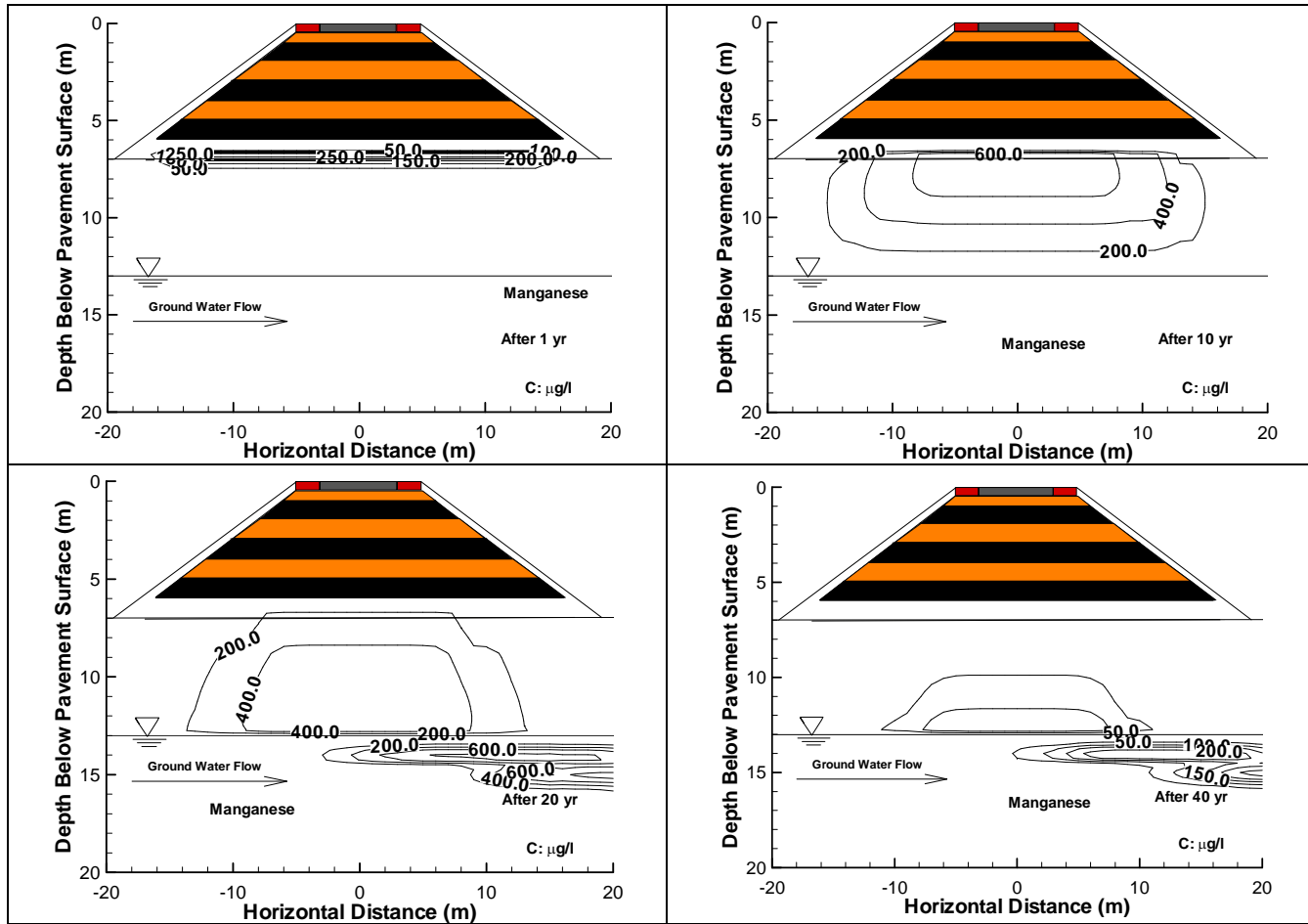


Figure 4.24 Predictions of Mn concentrations in soil and groundwater for 100 PSP fly ash. PSP: Paul Smith Precipitator fly ash

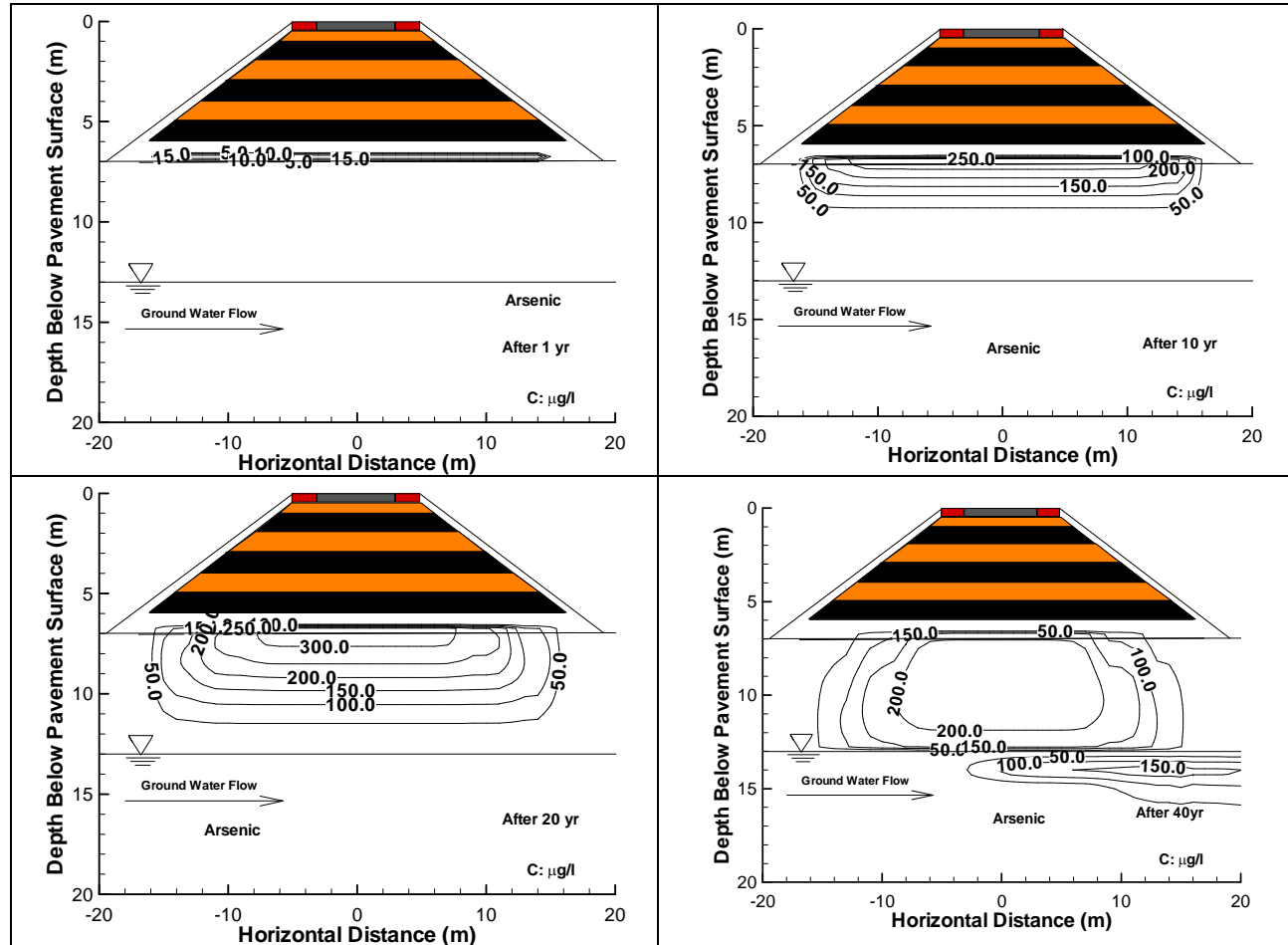


Figure 4.25 Predictions of As concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash.

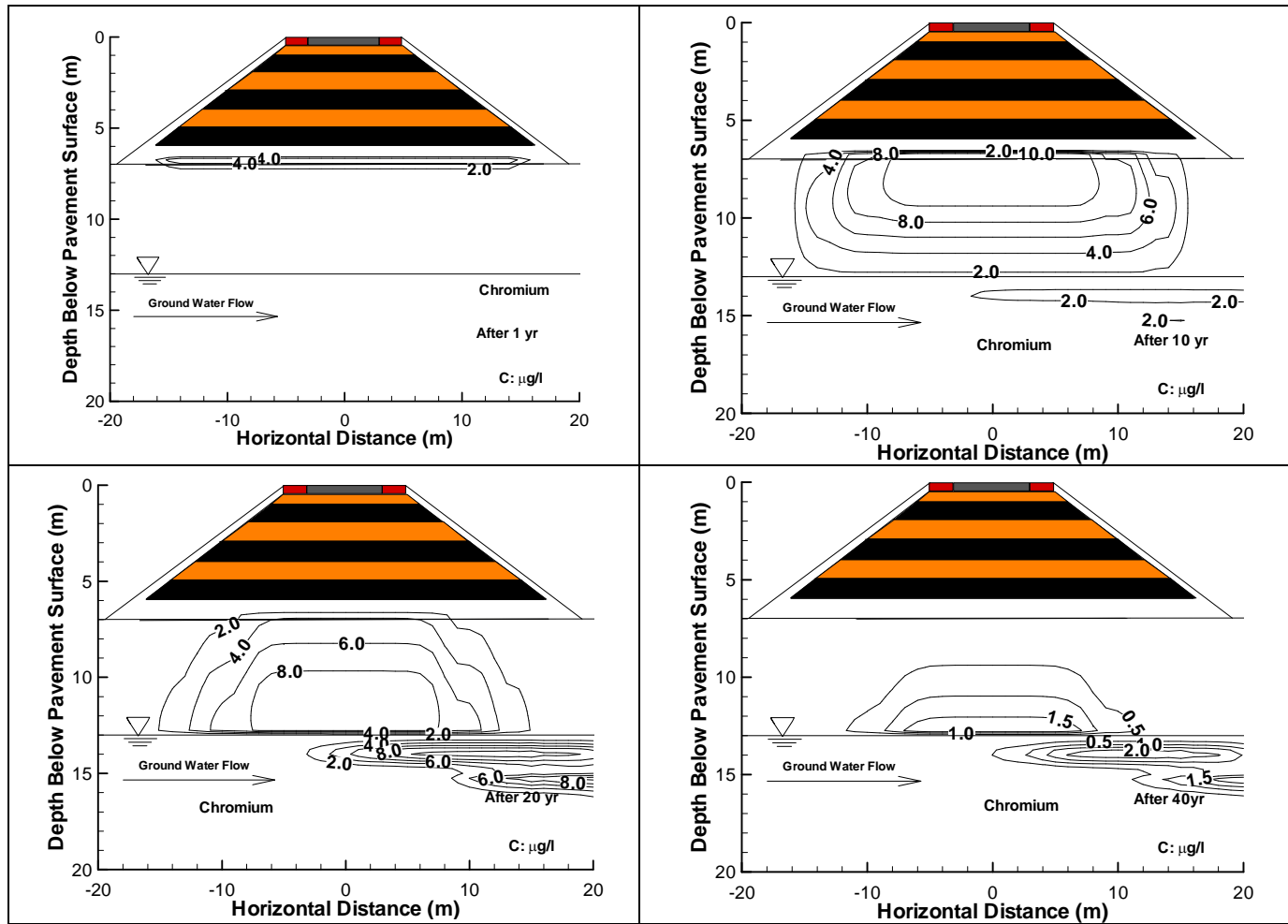


Figure 4.26. Predictions of Cr concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash

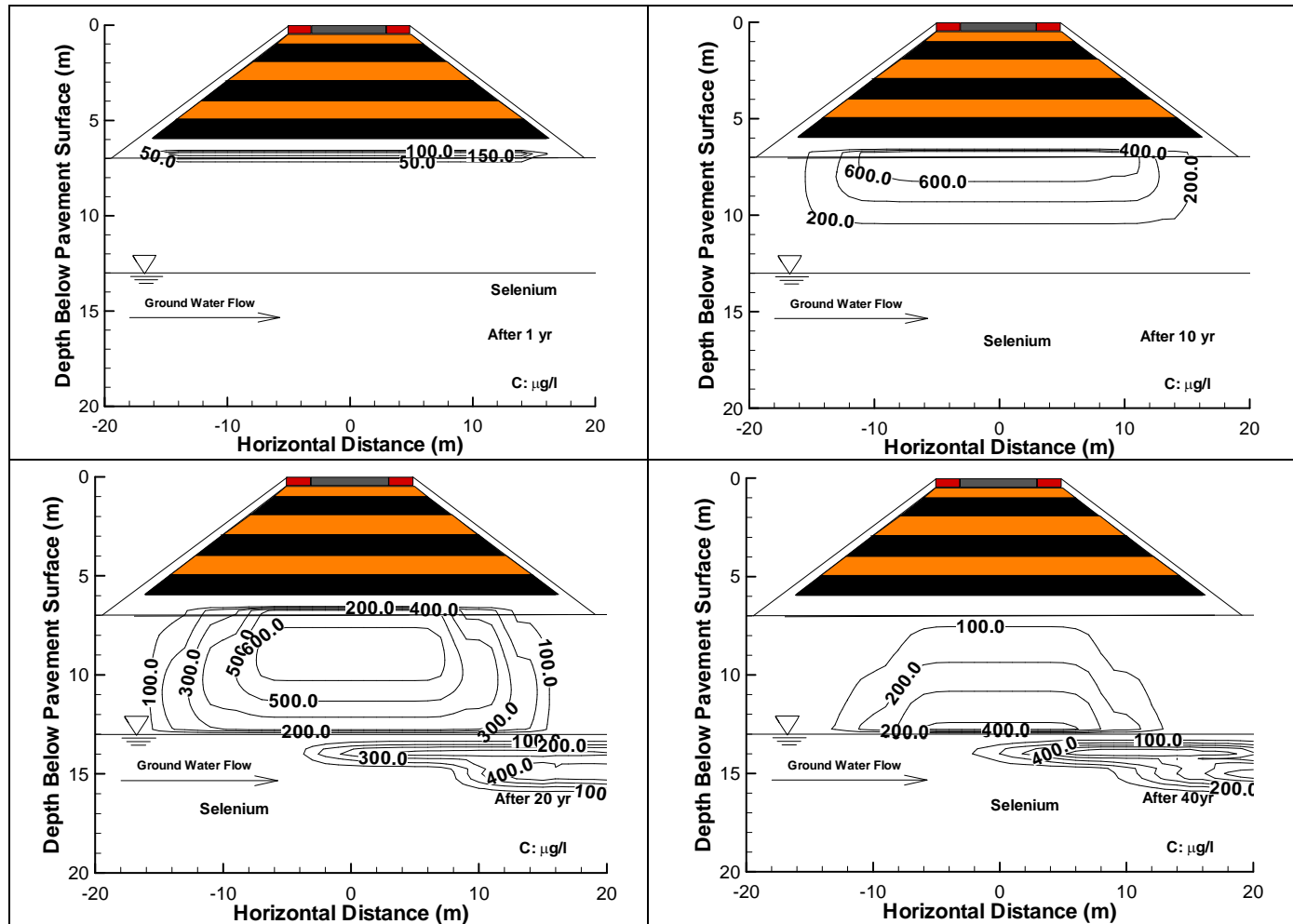


Figure 4.27 Predictions of Se concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash

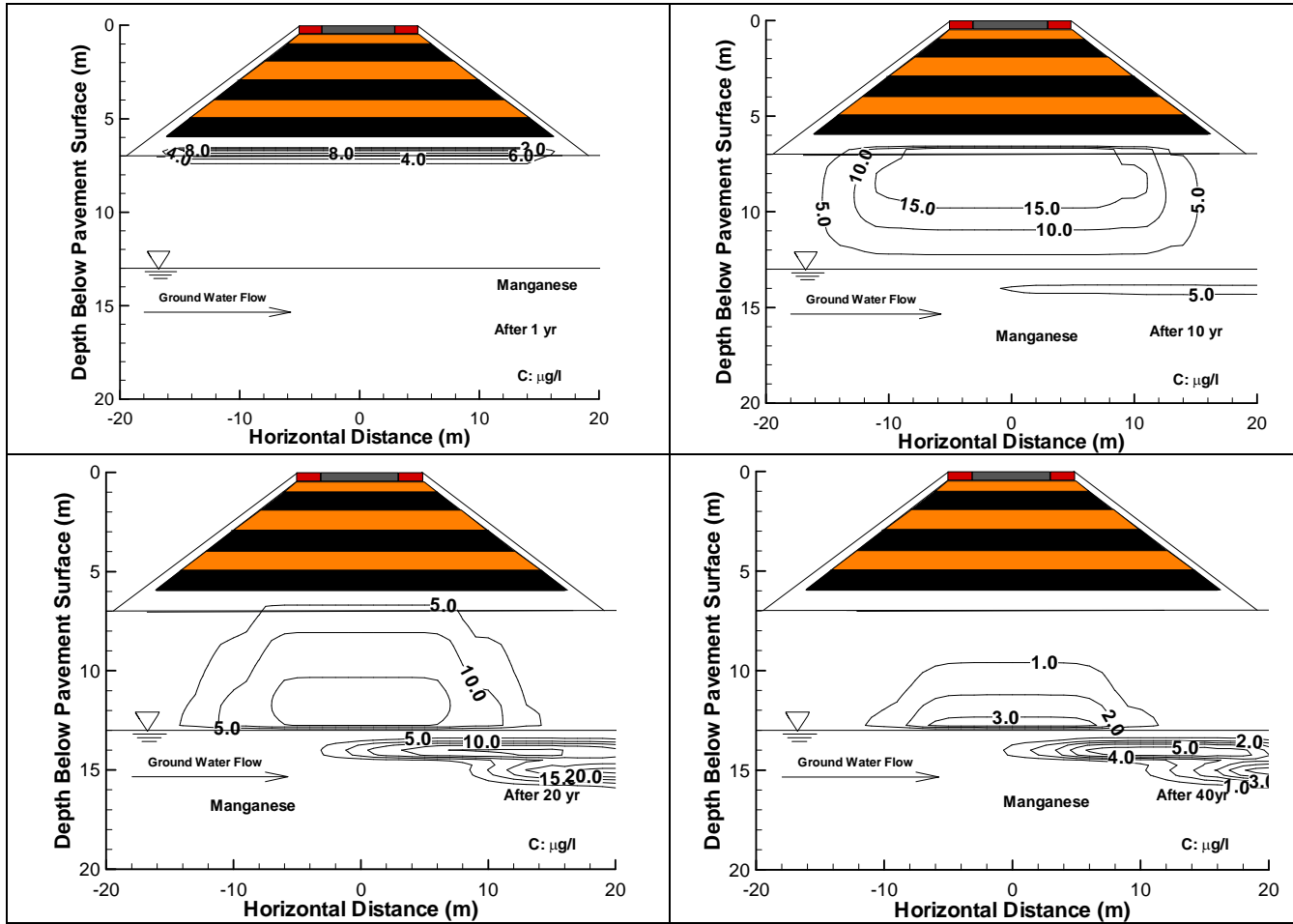


Figure 4.28 Predictions of Mn concentrations in soil and groundwater for 100 DP fly ash. DP: Dickerson Precipitator fly ash

Table 4.11 summarizes the maximum concentrations of the four metals at 1, 10, 20 and 40 years for multiple layer embankments built with 100% PSP and 100% DP fly ashes respectively. Table 4.11 indicates that for the embankments with PSP and DP fly ashes, As metals do not reach the groundwater table before 40 years. However, at 40 years the As concentrations were approximately 400 µg/L, which exceeded the EPA MCL (10µg/L). High retardation factors of these two fly ashes for As metals could be the reason for delaying the leaching of As metals to ground water as fast as the leaching of other metals (Table 4.10). On the other hand, Cr, Mn, and Se metals reach the groundwater table after 20 years. Relatively low retardation factors of the fly ashes for these three metals may have caused these heavy metals to the groundwater earlier than the As metals. Table 4.11 shows that in both cases the leached concentrations of Cr metal were far below the EPA MCL.

The embankment designed with 100 PSP fly ash yielded leaching of Mn and Se concentrations that exceeded the EPA MCL significantly. Furthermore, after 20 years, the Se concentrations from the embankment constructed with 100 DP fly ash were above the EPA MCL, but the Mn concentrations remained below the EPA MCLs. These results indicate that extra care should be taken especially for the leaching of As and Se metals from the multiple layer embankments.

Maximum concentrations of these four trace metals at the point of compliance (POC) with groundwater depths over a 100-year period were also observed. From an environmental perspective, the metal concentrations in groundwater at the POC are much



more important than the metal concentrations in groundwater located directly under the embankment construction. A POC of 30 m was selected in the current study. Figures 4.29 and Figure 4.30 show the concentrations of leached metals at the POC for the fly ash layered embankments designed with two different covers. Two different cover materials, a sandy borrow material typically used for embankments in Maryland, and a clayey soil material were used to encapsulate the multiple soil-fly ash layers in the embankment. Figure 4.29 and Figure 4.30 show the variation of metal concentrations at the POC for a 100-year period. The results indicate that using clayey material in embankments to encapsulate the fly ashes decreased the leached metal concentrations in the groundwater at the POC significantly. Low hydraulic conductivity ( $k \sim 1 \times 10^{-7}$  cm/sec), and relatively higher retardation factor ( $R_d$ ) of the clayey soil were most likely the reason for these results. Relatively lower  $k$  values prevented the leaching of metals from embankment to the soil vadose zone for short period of time and high  $R_d$  values yielded adsorption of metals by the clay particles. It is well known that, clay particles have a much higher surface area than sandy soil grains, which increase the adsorption potential of the trace metals by this type of soils (Sparks 2003).

Table 4.10. Input parameters for specific soil-fly ash mixtures analyzed in WiscLEACH.

	Pavement	Subgrade	Sand Borrow Material for embankment cover	Clay Material for embankment cover	100 DP				100 PSP			
					As	Cr	Mn	Se	As	Cr	Mn	Se
$R_d$	-	3.5	1	7.2	15	1.15	1.24	5	18	1.1	1.61	6.35
Metal Conc. ( $\mu\text{g/L}$ )	-	-	-	-	2060	60	1680	2080	750	30	50	1760
k (m/year)	18.25	3	4	0.0315	1.57				1.58			
$n_e$	0.33	0.3	0.33	0.25	0.59				0.61			
$\alpha_L$ (m)	-	-	-	-	0.74				0.6			
$\alpha_T$ (m)	-	-	-	-	0.074				0.06			

Note:  $\alpha_L$  (m)= Longitudinal dispersivity,  $\alpha_T$  (m)= Transverse dispersivity

Table 4.11 Predicted maximum metal concentrations in groundwater at 1, 10, 20, and 40 years for specimens prepared with 100% PSP and DP fly ashes. Concentrations exceeding MCLs in **bold**.

Time (years)	Metal Concentrations leached from PSP fly ash ( $\mu\text{g/L}$ )				Metal Concentrations leached from DP fly ash ( $\mu\text{g/L}$ )			
	As	Cr	Mn	Se	As	Cr	Mn	Se
10	-	20	-	-	-	-	-	-
20	-	4	<b>600</b>	<b>200</b>	-	8	20	<b>400</b>
40	<b>300</b>	-	<b>200</b>	<b>600</b>	<b>150</b>	2	5	<b>400</b>
EPA MCL ( $\mu\text{g/L}$ )	10	100	50	30	10	100	50	30

Notes; MCL = Maximum contaminant levels for drinking water; PSP=Paul Smith precipitator fly ash, DP=Dickerson precipitator fly ash.

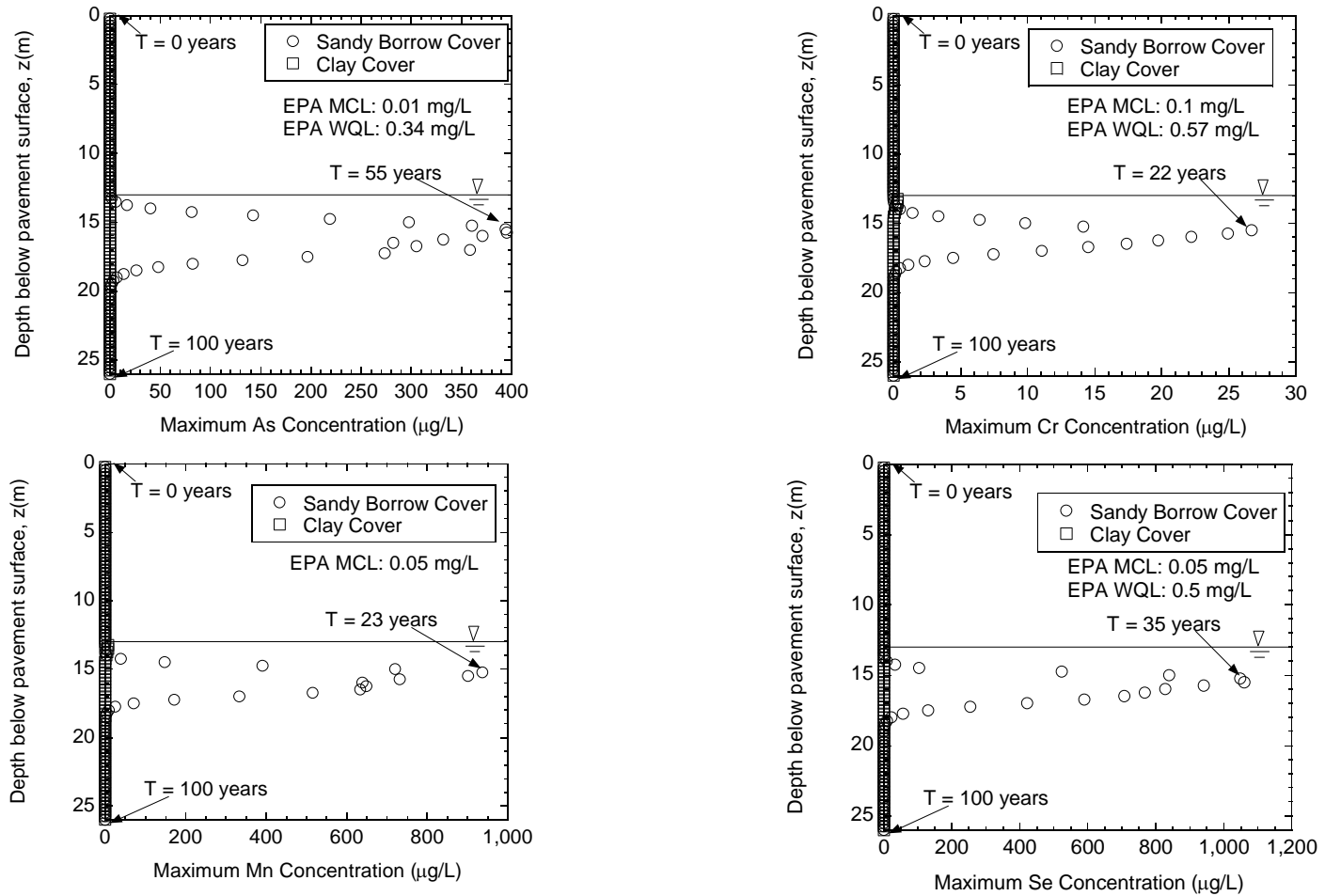


Figure 4.29 Maximum metal concentrations within 100 years at point of compliance for specimens prepared with 100% PSP. Note: PSP= Paul Smith Precipitator fly ash. MCL= maximum contaminant levels for drinking water; WQL= water quality limits for protection of aquatic life and human health in fresh water.

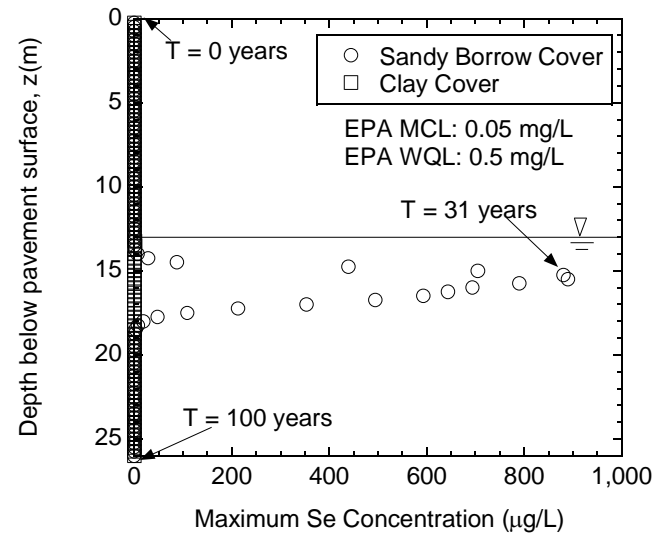
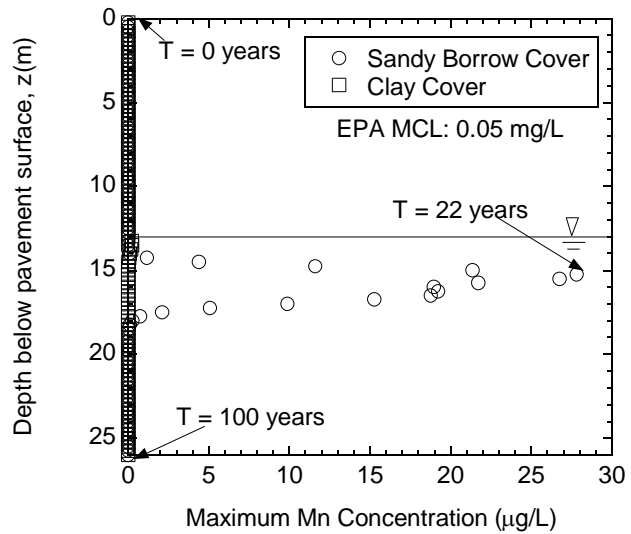
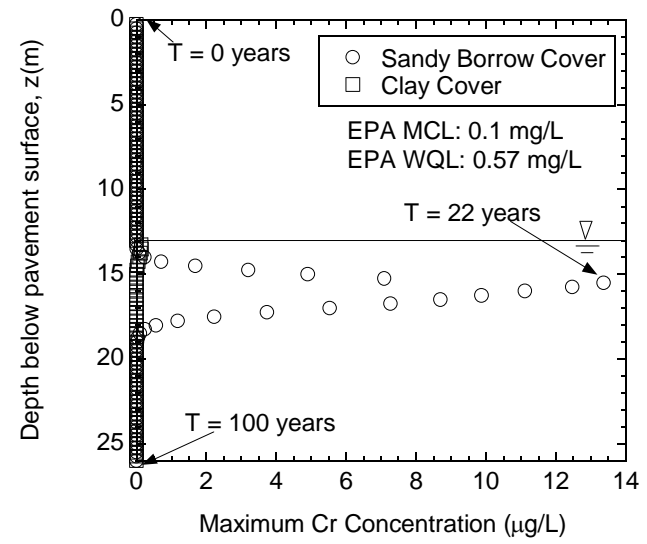
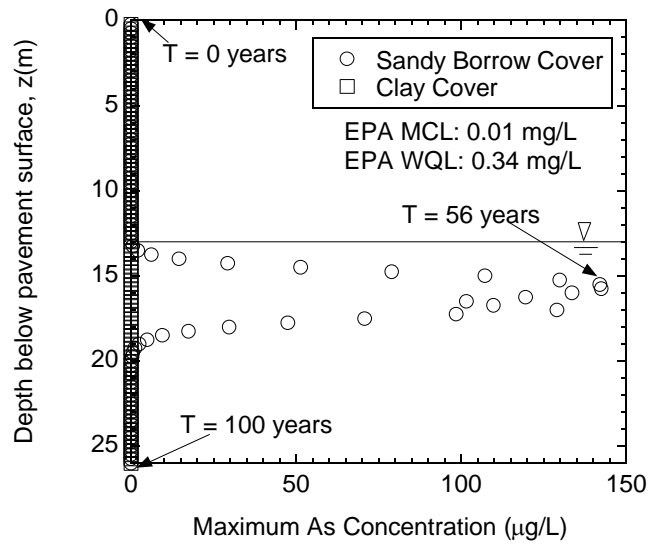


Figure 4.30 Maximum metal concentrations within 100 years at point of compliance, for specimens prepared with 100% DP. Note: DP=Dickerson Precipitator fly ash. MCL= maximum contaminant levels for drinking water WQL= water quality limits for protection of aquatic life and human health in fresh water.

## 4.6 CONCLUSIONS

The primary objective of this study was to investigate the leaching behavior of the heavy metals from fly ash-amended soils used in embankment constructions. The effect of fly ash addition and the feasibility of its use in geotechnical applications are studied. To achieve these objectives, a series of batch water leach test (WLTs) and column leach test (CLTs) were conducted to evaluate the leaching pattern of the metals from fly ash mixed soils. The conclusions from the current study are summarized as follows:

- 1) An increase in fly ash content increased the pH values of the soil – fly ash mixtures significantly due to the release of CaO, and MgO minerals. An increase in fly ash content from 0 to 40% by weight had greater influence on pH increase than an increase in fly ash content from 40 to 100%.
- 2) Arsenic, aluminum, chromium, boron, and selenium concentrations increased with increasing fly ash content. The solubility of Mn, on the other hand, is highly dependent on the effluent pH, and at  $\text{pH} > 6$  the Mn metals precipitate with Al – oxides and Fe – oxides.
- 3) The CLT elution curves for all but As exhibit a first flush leaching pattern that occurs due to the release of metals from the water soluble fraction as well as from the sites with low adsorption energies. The concentrations of Al, B, Cr, Mn and Se begin to stabilize after 10- 15 pore volumes of flow. Only the leaching curves for As metals showed a lagged flush response. The leaching of As metals continued to increase until 10 – 20 pore volumes of flow was reached, after which

the concentrations started to decrease dramatically.

- 4) The concentrations of the six metals are influenced by the pH of the effluent solution significantly which suggest that the leaching pattern is highly dependent on the pH of the aqueous solutions.
- 5) The concentrations of the Al, As, Se and Cr metals exceeded the EPA MCLs beyond the addition of 20% of MT and Co fly ashes. The reason for this is the high pH of the MT and Co fly ashes. Addition of these fly ashes increase the pH of the effluent solutions and cause an additional increase in metal concentrations since these metals generally exhibit an amphoteric leaching pattern.
- 6) The WiscLEACH results indicated that the maximum Cr concentrations are reached in approximately 10 to 20 years. Cr concentrations in the vadose zone decrease significantly with time, and are far below the EPA MCL at the groundwater table. Therefore, according to the WiscLEACH results, using fly ash as a soil amendment in embankment construction is safe when used at 10 – 20%.
- 7) Based on WiscLEACH simulations, metal concentrations decrease with distance from the embankment and groundwater surface, most probably due to the dispersion of the metals in the soil vadose zone. High annual precipitation rate may also have caused an increase in the leaching of the metals from the HCFA amended embankment..
- 8) Simulations using the multiple layer version of WiscLEACH indicated that As, Cr, Se metals concentrations exceeded the EPA MCL. However, as mentioned in the single version of WiscLEACH results, the soils prepared with 20% fly ash by

weight yielded lower metal concentrations that were far below the EPA MCLs.

This indicates that extra care should be taken when using fly ash in this geotechnical application.

- 9) All metal concentrations reached the groundwater between 10 and 20 years except As metals. As metals reached the ground water after 40 years. High retardation factors of both fly ashes for As metal could cause the delay in leaching of As metals through the embankment and soil vadose zone.
- 10) Using clayey material instead of a common sandy borrow material as an encapsulation (protection) layer around the embankment reduced the leached metal concentrations to 25 times to 1000 times lower in the groundwater at the point of compliance significantly due to very high retardation factor of clay material compared to sandy borrow material.

## 5 GEOCHEMICAL MODELING

### 5.1 INTRODUCTION

Metals can exist in different species in aqueous solutions which means they can have different oxidation states (e.g. Cr(VI), Cr(III) ). Leaching of metals and metal transportation processes are highly dependent on the oxidation states of the metals (Dijkstra et al.2004), and such states may affect the toxicity of metals (Shah et al 2007). For instance, Cr (III) is needed by living organisms (humans, animals etc.), however, Cr (VI) is very toxic and can threaten the human health (Geelhoed et al. 2002). Similarly, As(III) is most toxic arsenic species and As(V) is not known as a toxic metal (Pandey et al. 2011). The most common selenium species are Se(IV) and Se(VI), however, are both very toxic (Narukawa et al. 2005).

Previous studies showed that the two main equilibrium mechanisms that control the leaching of metals from coal combustion byproducts are solubility (dissolution-precipitation) and sorption (Komonweeraket et al. 2010, Mudd et al. 2004, and Wang et al. 2004). In the case that dissolution-precipitation reactions control the leaching of metals, geochemical equilibria models based on thermodynamic data have been shown to predict aqueous concentrations, assuming equilibrium between the leachate and the solubility-controlling solids. A more complex model that incorporates sorption of kinetic algorithms is required to predict solute concentrations if sorption reactions or dissolution kinetics control the leaching of metals( Fruchter et al. (1990).



The objective of this part of the research was to determine the predominant oxidation states of each metals that are released from fly ash alone, soil-fly ash and soil-fly ash-LKD mixtures, and examine whether the leaching of these metals from fly ash amended soils are solubility (dissolution-precipitation) controlled or sorption controlled. MINTEQA2, a numerical model developed by U.S. EPA and aims to simulate equilibria and speciation of inorganic solutes in aqueous solutions, was used to determine the predominant oxidation states and leachate controlling mechanisms of these leached constituents. Total peak metal concentrations from column leach tests, leachate pH, electrical conductivity (EC) and leachate Eh, were used as an input in the MINTEQA2 geochemical modeling program. This study was conducted on the mixture of two type of soils and 8 different fly ashes and LKDs. It should be noted that no laboratory metal speciation tests were not conducted to determine the dominant metal species directly.

In this part of the study, the results obtained from part 2, part 3 and part 4 were used as an input data into the geochemical numerical computer modeling program (MINTEQA2). These data are summarized in Appendix C and it includes effluent pH, EC, Eh and aqueous metal concentrations corresponding to soil alone, fly ash alone, soil-fly ash mixtures and soil-fly ash-LKD mixtures.

## 5.2 GEOCHEMICAL ANALYSIS

MINTEQA2 was run in two phases. In the first phase, speciation analyses were conducted on all CLT leachates to identify the predominant oxidation states of the leached metals that are redox sensitive. In the second phase, aqueous concentrations of all

metals species in the effluent solutions and saturation indices of the leachates with respect to solids or minerals were calculated.

### *5.2.1 Speciation Analysis*

Aqueous concentrations of metals, EC, pH and Eh data from previously conducted column leach tests were used to determine speciation analyses. Speciation analysis to determine the dominant oxidation state of the leached metals were determined as explained follow.. Eh and redox couple are specified as equilibrium constraints in MINTEQA2 to calculate the amount of the metals in each of the two oxidation states corresponding to the specified equilibrium Eh (Allison et al. 1991). Thus, the metal species that had the highest concentrations were assumed as the dominant oxidation state of leached metals. Speciation analyses were conducted only on the redox sensitive metals, i.e., As, Cr, Cu, Fe, Mn, Sb, V, Se. List of all species determined by MINTEQA2 of the redox sensitive metals are summarized in Appendix C. The analyses indicated that the predominant oxidation states of As was As(V), Cu was Cu(II), Fe was Fe(III), Mn was Mn(II), Sb was Sb(V), Se was Se(IV), and , V was (IV) for all specimens. However, the predominant oxidation states of Cr varied depending on the type of mixtures. Based on the predictions from MINTEQA2, Cr(III) is the predominant oxidations states for the fly ash alone and soil-fly ash mixtures. Conversely, Cr(VI) was the predominant oxidation state for the specimens activated with lime kiln dust (LKD).

Under alkaline conditions As exists in its anionic and oxidized forms, such as  $\text{AsO}_4^{3-}$  and  $\text{HAsO}_4^{2-}$  (Ettler et al. 2010), and leaching of As increases with an increase in pH under alkaline conditions (Su et al. 2011). Speciation analyses indicated that As(V) is the most

dominant oxidation state of the leached As metals from soil-fly ash mixtures which is less toxic As species than As(III) species (Shah et al. 2007). This finding is consistent with the previous studies which focused on speciation of As metals from similar waste materials (Pandey et al. 2011, Ettler et al. 2010). Small amounts of As(III) may have leached from the fly ash amended soils; however, the oxidation of As(III) occurs quickly in alkaline and aerobic conditions (Turner 1981, Su et al. 2011). Since the effluent solutions were collected in a beaker that was exposed to atmosphere in the current study it was also speculated that these As(III) species to be oxidized to As(V) and that all leached As metals were present in their oxidized forms as  $\text{AsO}_4^{3-}$ .

Cr leaching is highly dependent on pH of the aqueous solutions (Karamalidis and Voudrias 2009). Therefore, different oxidation states of Cr were observed for the specimens prepared with different materials. For instance, Cr(III) was the dominant oxidation state of Cr leached from specimens prepared with soil and fly ash. The pH of the soil-fly ash mixtures was between 6 and 10, which explains why Cr(III) was the dominant Cr species in the aqueous solutions. At neutral and low pHs, Cr(VI) is reduced to Cr(III) and results in elevated concentrations of Cr(III) in the aqueous solutions (Geelhoed et al. 2002). In contrast, the Cr metals leached from URM-fly ash-LKD mixtures were in oxidized forms (Cr(VI)) as  $\text{CrO}_4^{2-}$  due to high pHs ( $\text{pH} > 10$ ), consistent with the findings of Karamalidis and Voudrias (2008), Engelsen et al. (2010), and Izquierdo et al. (2011). Cr(III) was used as the dominant oxidation state for soil-fly ash mixtures while, Cr(VI) was used as dominant oxidation states for URM-fly ash-LKD mixtures in the geochemical modeling study.

To verify the dominant oxidation states of leached Cr metals produced by MINTEQA2 in soil-fly ash mixtures and URM-fly ash-LKD mixtures, chromium oxidation quick test was conducted (Barret and James 1979). This test was performed on the specimens that released Cr concentrations exceeding the EPA Cr MCLimits (100 µg/L). The dominant oxidations states of the Cr metals were determined by observing the color change in the effluent solutions with addition of s-diphenyl carbazide reagent into the leachate. The Cr oxidation quick test indicates that if the color of the effluent solutions turns pink (magenta) after addition of s-diphenyl carbazide reagent into leachate, it indicates that Cr Cr(VI) species also present in the leachates. As shown in Table 5.1 the predicted dominant Cr species by MINTEQA2 and speciation laboratory test provided contradicting results. For instance, based on MINTEQA2 analysis the dominant oxidation states of Cr for the specimens prepared with 40%, 100% Morgantown fly ashes and all specimens prepared with Columbia fly ashes were Cr(III). However, based on the laboratory speciation analysis these soil-fly ash mixtures leached Cr(VI) along with Cr(III) species. This was an expected behavior since the pH of the specimens prepared with 40%-100% MT and Co fly ashes had very high pHs and at basic conditions Cr typically oxidized to its Cr(VI) form. These results indicated that conducting laboratory speciation tests besides MINTEQA2 analysis is critical in determination of the dominant oxidation states of the leached metals.

The dominant species of the metals were estimated with MINTEQA2 by using the measured Eh, EC, pH and total leached metal concentrations. Based on the MINTEQA2 results, the leached Se metals existed in their reduced form, Se(IV) in the effluent

solutions which is consistent with the literature (Narukawa et al. 2005, Su et al. 2011). In the current study, Se(IV) was used as the dominant oxidation states of Se in the effluent solutions but it should be kept in mind that there may still be some oxidized forms of Se(VI) and this form may have reduced to Se(IV) over time.

Table 5.1 Comparisons of Cr speciation laboratory test results to MINTEQA2 results

Specimens	pH	Color	Cr Oxidation Quick Test Results	MINTEQA2 Results
10 BS + 5 LKD	11.8	Pink	Cr(VI)	Cr(VI)
20 BS + 5 LKD	11.9	Pink	Cr(VI)	Cr(VI)
10 DP + 5 LKD	12	Pink	Cr(VI)	Cr(VI)
20 DP + 5 LKD	12.1	Pink	Cr(VI)	Cr(VI)
S – 10 MT	7.2	Yellow	Cr(III)	Cr(III)
S – 20 MT	8.7	Yellow	Cr(III)	Cr(III)
S – 40 MT	9.6	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
100 MT	9.8	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
S – 10 Co	11.8	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
S – 20 Co	11.9	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
S – 40 Co	12.1	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
100 Co	12.15	Pink	<b>Cr(VI)</b>	<b>Cr(III)</b>
100 DP	8	Yellow	Cr(III)	Cr(III)
100 PSP	7.7	Yellow	Cr(III)	Cr(III)

Notes:BS: Brandonshores fly ash, DP: Dickerson Precipitator fly ash, MT: Morgantown fly ash, Co: Columbia fly ash, PSP: Paul Smith Precipitator fly ash. The Cr species has contradict results between speciation tests and MINTEQA2 are in **bold**.

### 5.2.2 Analysis of Controlling Mechanisms

The main objective of this part of the study is to determine if the leaching of metal concentrations are controlled by solubility reactions. To achieve this goal, laboratory data obtained from column leaching tests was used as input into the MINTEQA2 numerical geochemical modeling program. Leaching behavior of metals that could not be defined by solubility reactions was then considered to be sorption controlled without conducting any further modeling to simulate the sorption reactions in the aqueous solutions. This is out of the scope of the current study and can be considered in future research.

In MINTEQA2 analyses the aqueous phase equilibrium composition and saturation indexes (SI) of all effluent solutions, with respect to solids or minerals, were computed by allowing aqueous complexation reactions and oversaturated solids to precipitate at given laboratory test conditions. Electrical conductivity (EC), pH, redox potential (Eh), and aqueous metal concentrations of each metal leached from the different specimens were used as an input in the geochemical analyses. It was assumed total leached metal concentrations were leached in their dominant oxidations states as determined above. These metals include  $\text{Al}^{3+}$ , As(V) as  $\text{AsO}_4^{3-}$ ,  $\text{Cu}^{2+}$ , B(III) as  $\text{B(OH)}_4^-$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , Cr(III) as  $\text{Cr(OH)}_2^+$ , Cr(VI) as  $\text{CrO}_4^{2-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , Sb(V) as  $\text{Sb(OH)}_6^-$ , Se(IV) as  $\text{HSeO}_3^-$ , V(IV) as  $\text{VO}^{2+}$ , and  $\text{Zn}^{2+}$ . The aqueous phase concentration analyses and the SI calculation were performed assuming equilibrium between the effluent solution and potential solubility-controlling minerals in the solid in an open system at 25°C under the influence of atmospheric  $\text{CO}_2$ .

The leachates of the specimens in the column leaching tests were collected in beakers exposed to atmosphere. Thus, the aqueous solutions were assumed to be in equilibrium with the partial pressure of atmospheric CO<sub>2</sub> at  $3.16 \times 10^{-4}$  atm. (Langmuir 1997).

MINTEQA2 provides the activities of metals in the leachates rather than the concentrations. To calculate the single ion activities for each of the leached metal species, the Davies equation was used in these geochemical analyses. In this process MINTEQA2 required the ionic strength of the each difference effluent solutions. This was computed using the EC values of the leachates, multiplied by a factor of 0.013, which is a number that were empirically developed from a large number of river water samples to determine the ionic strength of aqueous solutions (Griffin and Jurinak 1973).

Next MINTEQA2 computes the saturation indexes of the metal species with respect to minerals and solid phases in the MINTEQA2 database via calculated single ion activities. Saturation index is the parameter that is used in the determination of whether or not the leaching of metal is solubility controlled with respect to a mineral or solid phase (Johnson et al. 1999). High negative or positive SI values are indications of that leached metals are under saturated and over saturated, respectively, suggesting that leaching of this particular metal could be controlled by other minerals or solid phases, or its leaching could be sorption controlled. If the leaching of metals is solubility controlled, the computed metal activities should be close to the solubility line that represents the dissolution/precipitation reactions of the minerals at equilibrium (Komonweeraket et al. 2010). If the activities of these metals are far from these solubility lines, it is typically claimed that the leaching of these metals are not solubility controlled.



Log-activity diagrams were developed by plotting the MINTEQA2-based log activities of each metal versus the corresponding CLTbased pH values. These diagrams were used to determine whether the leached metals are controlled by minerals or solid phases that were included in the MINTEQA2 database.

### 5.2.3 Speciation of Al

The solubility of Al is mainly controlled by the dissolution or precipitation of the Al hydroxides including Al(OH)<sub>3</sub> amorphous, Al(OH)<sub>3</sub> gibbsite, Al<sub>2</sub>O<sub>3</sub> (s), diaspore- $\alpha$ -AlO(OH), and boehmite- $\alpha$ -AlO(OH) (Astrup et al. 2006, Gitari et al. 2009). Figure 5.1 indicates that the Al<sup>3+</sup> metals are controlled by Al(OH)<sub>3</sub> gibbsite, a crystalline form of the Al(OH)<sub>3</sub> mineral at a pH range of 6 to 12.4, consistent with the findings of Murarka et al. (1992), Astrup et al. 2006, and Komonweeraket et al. (2010) during testing of coal and municipal waste combustion by-products.

Johnson et al. (1999) and Gitari et al. (2009) claimed that solubility of Al<sup>3+</sup> is controlled by Al(OH)<sub>3</sub> amorphous for pH =6 - 9 and by gibbsite for pH > 9. However, Geelhoed et al. (2002) and Mudd et al. (2004) indicated that at pH > 5.5, the activity of Al<sup>3+</sup> could be controlled both by crystalline and amorphous forms of Al(OH)<sub>3</sub>, consistent with the results of the current study. Further, Roy and Griffin (1984) showed that amorphous and crystalline forms of Al hydroxides could be controlling the solubility of Al under slightly acidic conditions. Mullite (Al<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>) could also be one of the main sources of Al<sup>3+</sup> cations in the aqueous solution that may be hydrolyzed to Al(OH)<sub>3</sub> and precipitates (Komonweeraket et al. 2010, Medina et al. 2010), and could possibly be another controlling solid phase in this system. However, due to the lack of mineralogical

data in the MINTEQA2, it was not possible to study the effect of mullite mineral on the solubility of  $\text{Al}^{3+}$  cations.

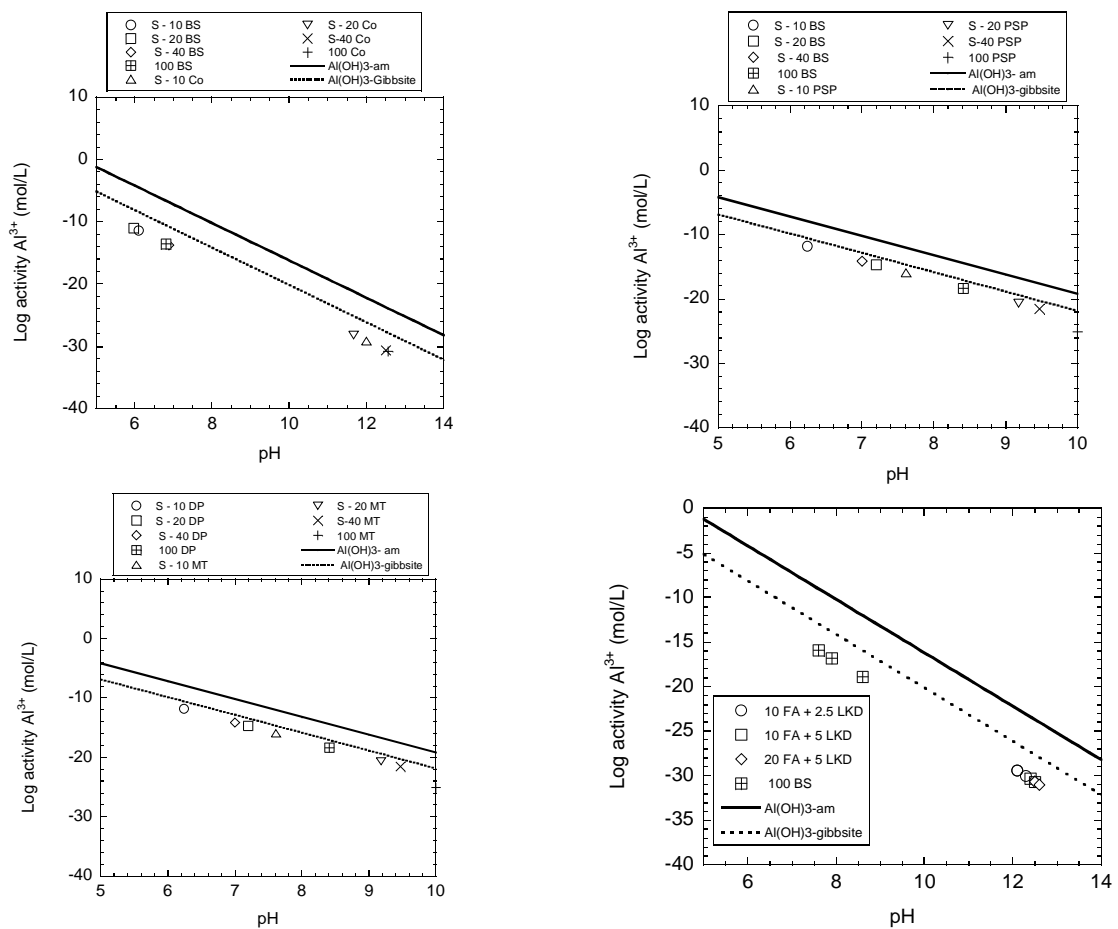


Figure 5.1 Log activity of  $Al^{3+}$  vs. pH in leachates (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures

#### 5.2.4 Speciation of As

As mentioned in the previous section, As(V) is the predominant arsenic species in the aqueous solutions of fly ash which is consistent with the findings of Shah et al. (2007), Gitari et al. (2009), , Pandey et al. (2011), and Su et al. (2011).

Figure 5.2 shows the variation of As(V) as  $\text{AsO}_4^{3-}$  with pH of the effluent solutions of soil-fly ash mixtures. Even though there exists a correlation between  $\text{AsO}_4^{3-}$  and pH of the aqueous solutions, it is certain that the leaching of As metals is not controlled by  $\text{As}_2\text{O}_5(\text{s})$  solid phase since As(V) concentrations are under-saturated with respect to  $\text{As}_2\text{O}_5(\text{s})$  line. These observations are consistent with those obtained by Kim et al. (2009). It is well known that As(V) can react with Al metals and form solid complexes with very low solubility products (Apul et al. 2005, Komonweeraket et al. 2010). Figure 5.3 shows the activity of  $\text{AsO}_4^{3-}$  corresponding to activity of  $\text{Al}^{3+}$  along with the  $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$  solid phase which was created by MINTEQA2 database. The concentrations of  $\text{Al}^{3+}$  compared to As(V) in the aqueous solutions were generally 1 to 6 orders of magnitude lower. However, an increase in  $\text{Al}^{3+}$  concentrations moved species toward the solid line and made them closer to the  $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$  solid phase. This indicates that with an adequate amount of  $\text{Al}^{3+}$  and  $\text{AsO}_4^{3-}$ ,  $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$  may form and control the solubility of As(V) species in the effluent solutions.

Based on the results obtained from MINTEQA2 regarding to speciation of As(V) and  $\text{Mn}^{2+}$ , these two species can form  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  solid solution which appears to be the main leaching controlling mechanisms of the solubility of As(V) in the aqueous

solutions of all soil-fly ash mixtures used in the current study Figure 5.4 shows that the solubility of As(V) is generally controlled by the  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  compound, and in the presence of adequate As(V) concentrations, the complexation of  $\text{AsO}_4^{3-}$  with  $\text{Mn}^{2+}$  is likely to occur. An increase in the concentrations of  $\text{AsO}_4^{3-}$  and  $\text{Mn}^{2+}$  yields the possibility of the reaction between  $\text{AsO}_4^{3-}$  and  $\text{Mn}^{2+}$  and this would produce the  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , the solid phase that controls the leaching of  $\text{AsO}_4^{3-}$ . Cherry et al. (1979) and Turner (1981) claimed that the oxidation of As(III) to As(V) increases significantly in the presence of  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ , resulting in elevated concentrations of As(V) in the aqueous phase. The formation of soluble complexes with Fe and As(V) in neutral to slightly acidic pHs was observed by Sadiq et al. (2002).

Arsenate can also form slightly soluble precipitates with metals such as Ba, Cd, Cu, Mn and Zn (Komonweerakter et al. 2010). Turner (1981) and Ettler et al. (2010) showed that  $\text{Ca}_3(\text{AsO}_4)_2$ ,  $\text{Ba}_3(\text{AsO}_4)_2$  are the main solid phases that may control the solubility of As(V) (). However, no Ca or Ba concentrations were measured in the effluent solutions collected from the soil-fly ash mixtures in the current study, and, thus, was not possible to conclude that if the leaching of As(V) was controlled by  $\text{Ca}_3(\text{AsO}_4)_2$ ,  $\text{Ba}_3(\text{AsO}_4)_2$ .

Kim et al. (2009) claimed that iron oxides could be the oxide minerals that control the solubility of As metals. Ettler et al. (2010) and Pandey et al. (2011) also mentioned that the adsorption of As(V) by iron-oxides and aluminum-oxides is very likely to occur. The sorption of metals to minimize their contamination risks is generally achieved by hydrous ferric oxides and hydrous aluminum oxides (Ettler et al. 2010). Cornelis et al. (2008) claimed that the complexation of metals such as As(V) is possible with ettringite

minerals, i.e.,  $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ . In addition, the precipitation and dissolution of  $\text{CO}_3$  minerals may have an impact on the controlling the leaching of As(V) (Kim et al. 2009). Previous literature indicated that  $\text{CO}_3$  carrier minerals such as  $\text{CaCO}_3$ , is providing surfaces for As(V) metals to be adsorbed (Benedetto et al. 2006). An increase in  $\text{CO}_3$  concentrations increases the sorption of As(V) metals. However, in the current study,  $\text{CO}_3^{2-}$  anion concentrations were not measured from the effluent solutions of the soil-fly ash mixtures, therefore it is not possible to conclude that leaching of As(V) was  $\text{CO}_3^{2-}$  sorption controlled.

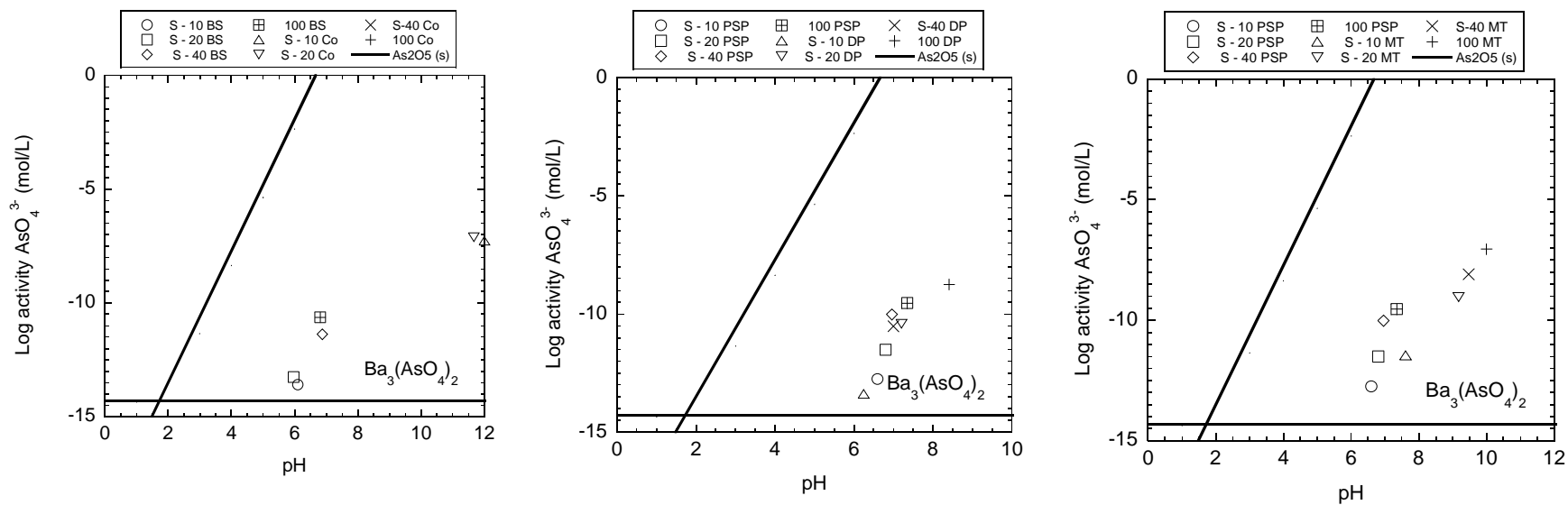


Figure 5.2 Log activity of  $\text{AsO}_4^{3-}$  vs. pH in leachates from fly ashes, soil-fly ash mixtures. (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes.

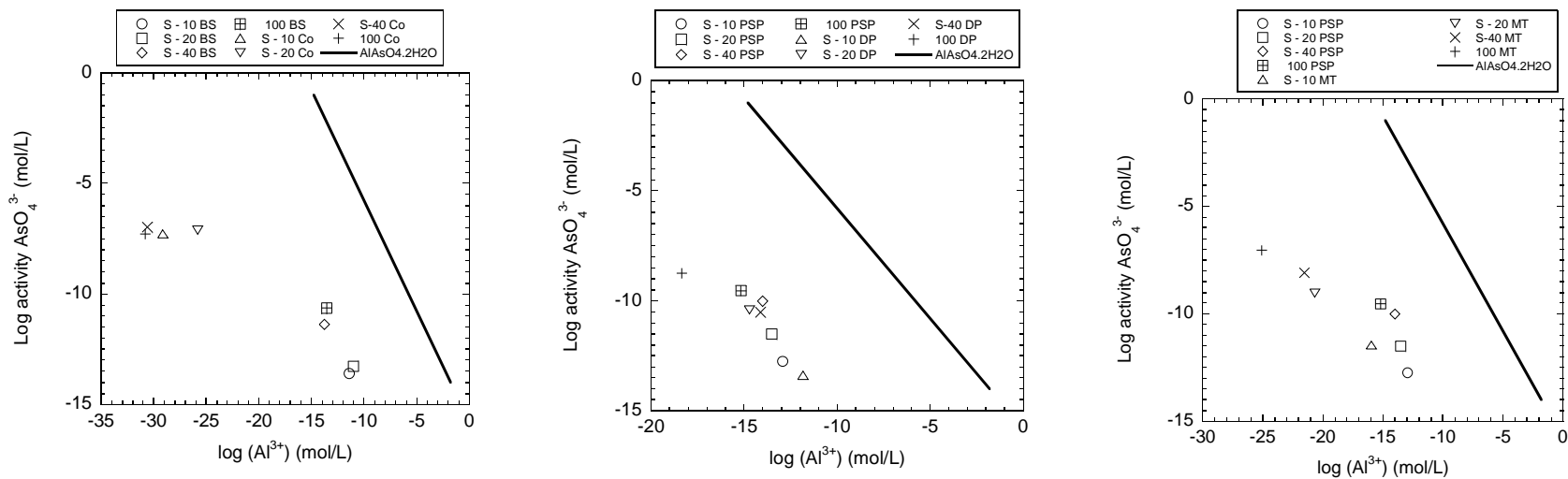


Figure 5.3 Log activity of  $\text{AsO}_4^{3-}$  vs.  $\text{Al}^{3+}$  in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes.



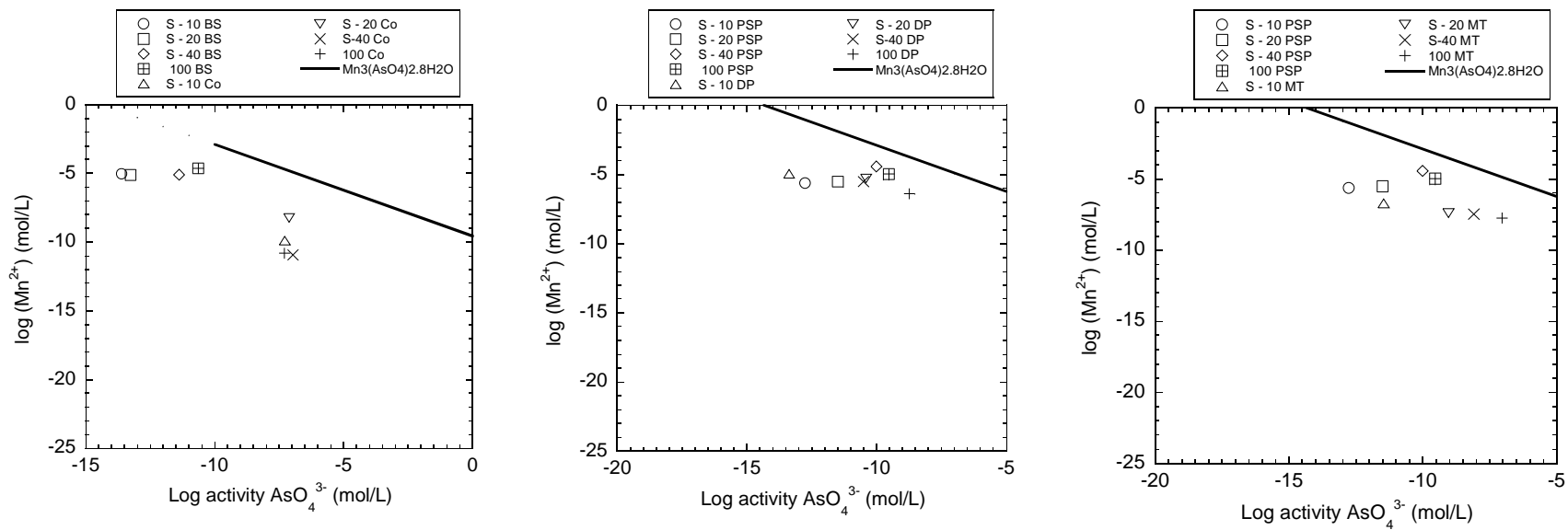


Figure 5.4 Log activity of  $\text{AsO}_4^{3-}$  vs.  $\text{Mn}^{2+}$  in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes.

### 5.2.5 Speciation of Cr

The speciation analysis showed that Cr (III) as  $\text{Cr(OH)}_2^+$  is the dominant oxidation state for the specimens prepared with fly ash-soil mixtures and Cr(VI) as  $\text{CrO}_4^{2-}$  is the dominant oxidation state for the specimens prepared with fly ash-soil-LKD mixtures. Therefore, these specimens will be discussed separately.

Figure 5.5 shows that the solubility of Cr is controlled by  $\text{Cr(OH)}_3$  amorphous,  $\text{Cr(OH)}_3$  and  $\text{Cr}_2\text{O}_3(\text{s})$ . However, it could be said that most of the controlling species was  $\text{Cr(OH)}_3$  and  $\text{Cr}_2\text{O}_3(\text{s})$  rather than amorphous  $\text{Cr(OH)}_3$ .  $\text{Cr}_2\text{O}_3$  is a species present in all fly ashes at % to 5% by weight in the fly ashes used in the current study. It is expected to see the solubility of Cr metals controlled by this chromium oxide mineral (Gitari et al. 2009). Mulugeta et al. (2010) indicated that the release of Cr(III) at neutral pHs is due to the dissolution of mineral phases that Cr(III) is bounded with.  $\text{Cr}_2\text{O}_3(\text{s})$  and ferrihydrites are some of these minerals that Cr(III) could be complexed with ferrihydrites and released at neutral pH conditions (Engelsen et al. 2010). Geelhoed et al. (2002) and Karamadis and Voudrias (2008) also determined that leaching of Cr from fly ashes is controlled by  $\text{Cr(OH)}_3(\text{s})$ . Fruchter et al. (1990) and Johnson et al. (1999) indicated that  $\text{Cr}^{3+}$  may form solid solutions with Fe hydroxides such as  $(\text{Fe,Cr})(\text{OH}_3)(\text{s})$ . The solubility of this solid solution is very low at pHs between 6 and 10 and the pHs of the effluent solutions in the current study were at a range of 5.8 to 10 indicating that it is possible that  $\text{Cr}^{3+}$  solubility may have been dependent on the  $(\text{Fe,Cr})(\text{OH}_3)(\text{s})$  in addition to  $\text{Cr(OH)}_3$  and  $\text{Cr}_2\text{O}_3$ .

Cr(VI) as chromate ( $\text{CrO}_4^{2-}$ ) was the predominant oxidation state of the Cr metal in the aqueous solutions of the specimens prepared with soil-fly ash-LKD materials. Figure 5.5d indicates that the leaching of Cr(VI) in this effluent solutions are not controlled by chromium (hydr)oxides. This is an expected behavior since it is very well known that at very alkaline pHs metal hydroxides begin dissolving and do not have significant impact on the leaching of Cr (VI) (Engelsen et al. 2010).  $\text{BaCrO}_4$  could be the solid phase that may control the leaching of Cr(VI) at high pHs such as  $\text{pH} > 12$  (Astrup et al. 2006). The solubility product of  $\text{BaCrO}_4$  is very low and its precipitation could be very fast (Fruchter et al. 1990). As shown in Figure 5.6a, the comparison of  $\text{Ba}^{2+}$  and  $\text{CrO}_4^{2-}$  concentrations are very close to the solid  $\text{BaCrO}_4$  line, indicating that the solubility of Cr(VI) could be controlled by this solid phase not by chromium (hydr)oxides. However; the Cr (VI) metals leached from specimens prepared with URM-fly ash-LKD materials, are slightly under-saturated with respect to the  $\text{BaCrO}_4(\text{s})$  solid phase line. This also indicates that  $\text{BaCrO}_4(\text{s})$  may not be the solid phase controlling the leaching of Cr(VI). In addition,  $\text{Ba}(\text{S,Cr})\text{O}_4$  could be one of the main solid phases that may control the leaching of Cr (VI) (Apul et al. 2005, Astrup et al. 2006). However, due to lack of measurements of the  $\text{SO}_4^{2-}$  anion concentrations in the effluent solutions, it was not possible to prove this conclusion in the current study. On the other hand, it is well known that leachates from almost all type of fly ashes contain significant amount of  $\text{SO}_4^{2-}$  anions (Komonweeraket et al. 2010) and it could be suggested that the solubility of Cr (VI) may have been controlled by  $\text{Ba}(\text{S,Cr})\text{O}_4 (\text{s})$ . In addition, Mn-(hydro)oxides may have an important effects on leaching of Cr(VI) species at basic conditions ( $\text{pH} > 8$ ). It is

very well known that  $\text{MnO}_2(\text{s})$  and  $\text{MnOOH}(\text{s})$  may tend to create extra adsorption sites for  $\text{Cr}(\text{VI})$  and have impact on control of the leaching of  $\text{Cr}(\text{VI})$ . However, the sorption reaction was not the scope of this study. Therefore, it was not determined whether the sorption of  $\text{Cr}(\text{VI})$  was controlled by  $\text{Mn}(\text{hydro})\text{oxides}$  or not. In the future studies the measurements of  $\text{SO}_4^{2-}$  should be measured, as it plays very important factor on the solubility of  $\text{Cr}(\text{VI})$  (Engelsen et al. 2010).

It has also been claimed that  $\text{CaCrO}_4$  and  $\text{Cr}(\text{VI})$ -ettringite minerals may control the leaching of  $\text{Cr}(\text{VI})$  metal species at highly alkaline conditions ( $\text{pH} > 10$ ) (Johnson et al. 1999, Astrup et al. 2006, Karamadis and Voudrias 2008). Figure 12b shows the variation of  $\log \text{Ca}$  values corresponding to  $\log \text{CrO}_4^{2-}$  values and according to the solid line that represents the  $\text{CaCrO}_4(\text{s})$  is approximately 2 orders of magnitude above the  $\log \text{Ca}$  and  $\log \text{CrO}_4$  values. This indicates that the solubility is  $\text{CrO}_4^{2-}$ , not  $\text{CaCrO}_4(\text{s})$  controlled. In general, the solubility of  $\text{Cr}(\text{VI})$  at high  $\text{pHs}$  is controlled by  $\text{Cr}(\text{VI})$ -ettringite minerals (Astrup et al. 2006, Karamadis and Voudrias 2008, Engelsen et al. 2010). At  $\text{pHs}$  greater than 10 the  $\text{Cr}(\text{VI})$  replaces  $\text{SO}_4^{2-}$  in ettringite minerals. This substitution of  $\text{SO}_4^{2-}$  anion is dependent on the amount of  $\text{Cr}(\text{VI})$  concentrations in the effluent solutions (Engelsen et al. 2010). Figure 5d shows that the leaching of  $\text{Cr}(\text{VI})$  from the specimens prepared with URM-fly ash-LKD materials is not  $\text{Cr}(\text{VI})$ -ettringite controlled. The  $\text{CrO}_4^{2-}$  concentrations are far above the  $\text{Cr}(\text{VI})$ -ettringite solid phase line, indicating that this solid phase does not control the solubility of  $\text{Cr}(\text{VI})$  in this study.

$\text{Fe}(\text{hydro})\text{oxides}$ ,  $\text{Al}(\text{hydro})\text{oxides}$  and  $\text{Mn}(\text{hydro})\text{oxides}$  are possible sorption sites that may adsorb the trace metals such as  $\text{Cr}(\text{VI})$  (Geelhoed et al. 2002). However;

Apul et al. (2005) claimed that leaching of Cr(VI) is not adsorption controlled, especially in the presence of high amount of  $\text{SO}_4^{2-}$  anion in the effluent solutions. Adsorption of Cr(VI) on the iron and aluminum oxides is weak at high pHs and in the presence of high amounts of  $\text{SO}_4^{2-}$  (Apul et al. 2005). Even though previous studies claimed that the leaching of Cr(VI) is not adsorption controlled, it seems adsorption of Cr(VI) on the minerals or (hydro)oxides is the main leaching controlling mechanisms of this chromium species in this study. The scope of this study was focused on the leaching of solubility controlling mechanisms of the heavy metals. Therefore, no further geochemical analysis has been conducted to determine the adsorption properties of Cr(VI). However, future studies should take these possibilities into account.

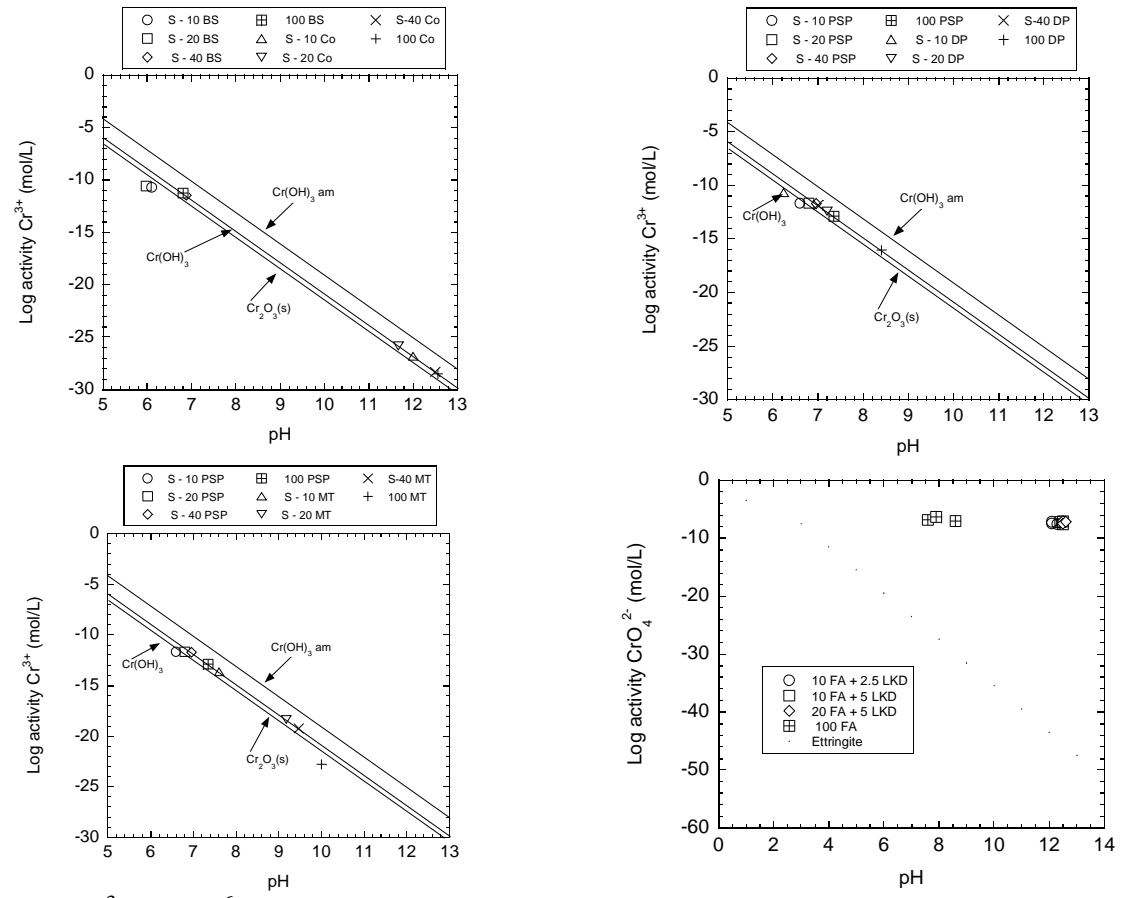


Figure 5.5 Log activity of Cr<sup>3+</sup> and Cr<sup>6+</sup> in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures

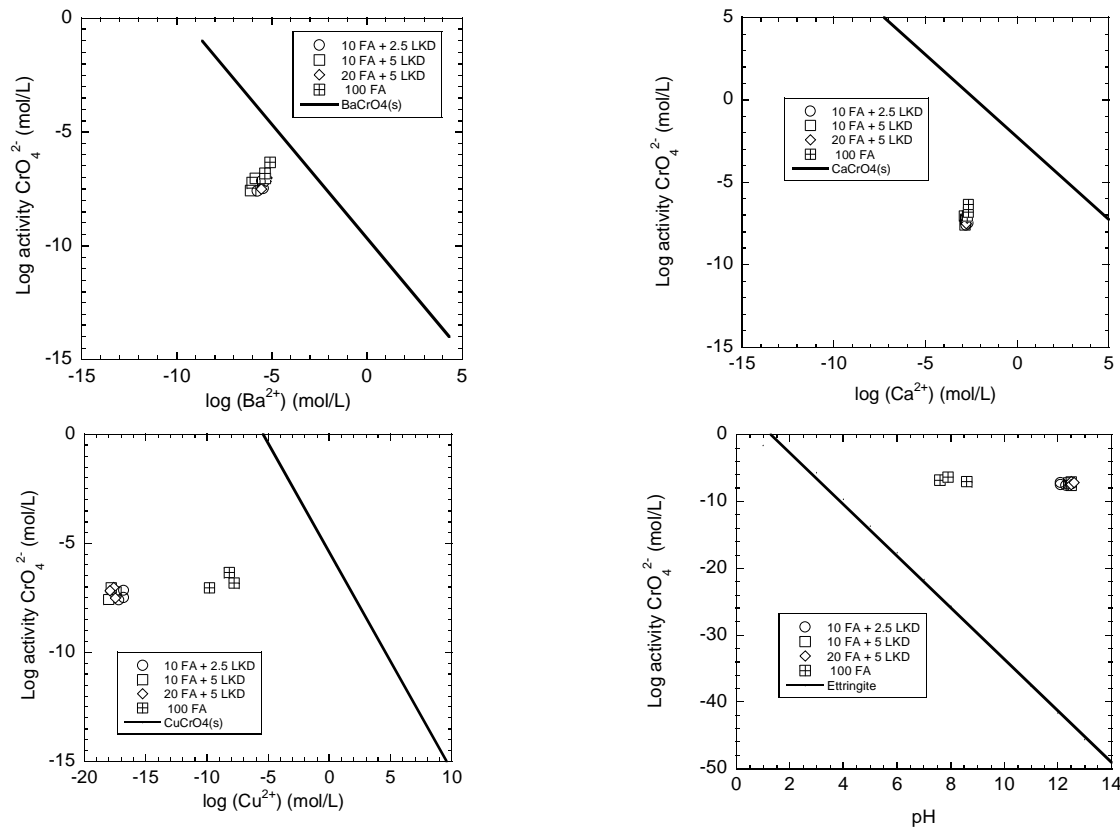


Figure 5.6 Log activity of (a)  $\text{CrO}_4^{2-}$  vs.  $\text{Ba}^{2+}$ , (b)  $\text{CrO}_4^{2-}$  vs  $\text{Ca}^{2+}$  (c)  $\text{CrO}_4^{2-}$  vs  $\text{Cu}^{2+}$ , and (d)  $\text{CrO}_4^{2-}$  vs ettringite leachates from fly ashes and URM-fly ash-LKD mixtures.

### 5.2.6 Speciation of Mn

The speciation analysis showed that Mn(II) as  $Mn^{2+}$  is the dominant oxidation state for both the specimens prepared with fly ash-soil mixtures and the specimens prepared with fly ash-soil-LKD mixtures.

An increase in pH decreases the leaching concentrations of Mn metal species in general due to the precipitation or dissolution of manganese (hydro)oxides (Su et al. (2011), Cetin et al.(2012)). Figure 5.7 indicated that at a pH >10 the solubility of Mn(II) is controlled by pyrochroite ( $Mn(OH)_2$ ). At neutral pH conditions ( $5 < pH < 10$ )  $Mn^{2+}$  cations are more freely available and increasingly precipitate as  $Mn(OH)_2$  as the pH of the aqueous solutions increases (Gitari et al. 2009, Komonweeraket et al. 2010). This explains that how the  $Mn(OH)_2(s)$  minerals control the solubility of Mn(II) metal species in the effluent solutions of the specimens prepared with URM-fly ash-LKD mixtures while  $Mn(OH)_2(s)$  minerals do not control the solubility of Mn(II) metal species in the effluent solutions of specimens prepared with soil-fly ash mixtures (Gitari et al. 2009). The pH values of the effluent solution of specimens prepared with soil-fly ash mixtures ranged from 6 to 10 (Table 4.5) while the pH values of the effluent solutions of specimens prepared with URM-fly ash-LKD mixtures are greater than 11 (pH > 11). This indicates the presences of two different leaching behavior of Mn(II).



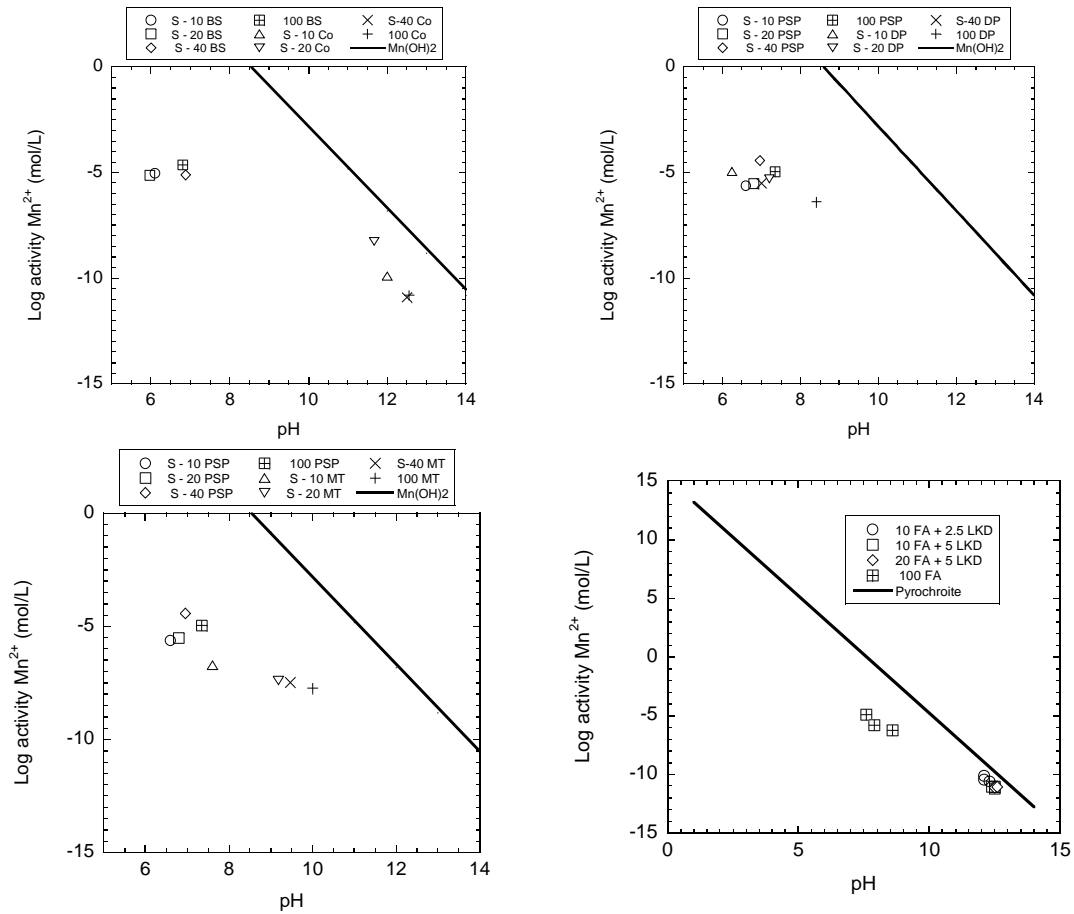


Figure 5.7 Log activity of  $Mn^{2+}$  vs. pH in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, (c) Paul Smith Precipitator and Morgantown fly ashes, and (d) URM-fly ash-LKD mixtures

### 5.2.7 Speciation of Se

Dominant oxidation states of Se metals are Se(IV) as  $\text{HSeO}_3^-$  in the soil-fly ash mixtures used in this study. This finding is consistent with the literature because it is expected that Se forms anionic species at neutral to alkaline pHs (Medina et al. 2010, Su et al. 2011). Figure 5.8 shows that Se(IV) species are significantly under saturated with respect to  $\text{SeO}_2(\text{s})$  indicating that the solubility of selenium like arsenic is not controlled by the dissolution/precipitation of (hydr)oxides. Baur and Johnson (2003) indicated that the solubility of Se(IV) may have been controlled by the  $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$  compound. In addition,  $\text{HSeO}_3^-$  may complex with  $\text{Ca}^{2+}$  and produces  $\text{CaSeO}_3$  solid solutions which controls the solubility of Se(IV) according to the Essington (1988). Moreover, Izquierdo et al. (2011) indicated that solubility of Se(IV) is controlled by gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in the effluent solutions.  $\text{SO}_4^{2-}$  concentrations in the aqueous solutions may have significant impact on the leaching of Se(IV) like it has on leaching of Cr(VI) (Engelsen et al. (2010)). The gypsum effects were not shown herein since neither  $\text{Ca}^{2+}$  nor  $\text{SO}_4^{2-}$  concentrations were measured from the specimens prepared with soil and fly ash. Therefore, such a conclusion cannot be warranted.

The formation of solid solution with ettringite mineral is very common at alkaline conditions, especially for anionic species such as  $\text{CrO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{Sb}(\text{OH})_6^-$  and  $\text{SeO}_3^{2-}$  (Cornelis et al. 2008). Ettringite minerals present in the aqueous solutions may be the solid solutions responsible for the solubility of Se(IV). However, equilibrium was not obtained between Se(IV) and Ettringite in solid forms and minerals are available in the MINTEQA2 database.

Based on the MINTEQA2 results for the Se(IV) obtained from this study to determine the controlling mechanisms of Se metals, it can be concluded that leaching of Se(IV) from fly ashes and soil-fly ash mixtures are not solubility-controlled. It is well known that leaching of Se(IV) is not solubility-controlled under alkaline conditions (Komonweeraket et al. 2010, Su et al. 2011). Moreover, in alkaline conditions the concentrations of oxyanionic species of Se may decrease significantly due to the adsorption and precipitation of oxyanions with minerals. Gibbsite and  $\text{Fe}(\text{OH})_3$  could provide an effective sorption site for Se(IV) species at pHs between approximately 8 and 9 (Langmuir 1997).

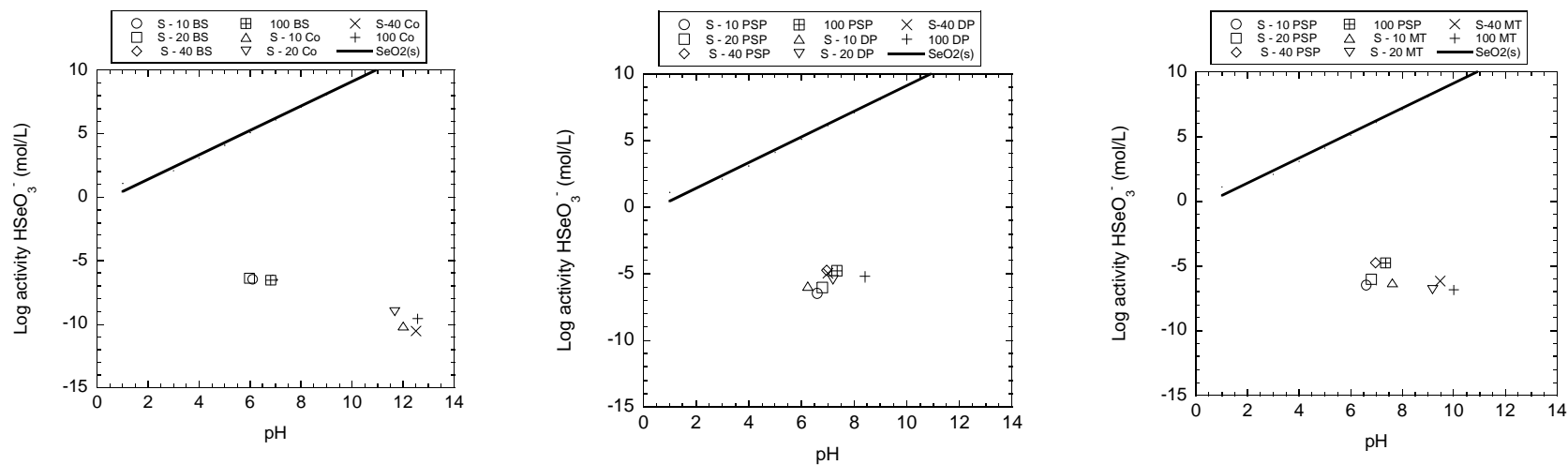


Figure 5.8 Log activity of  $\text{HSeO}_3^-$  vs. pH in leachates from fly ashes and soil-fly ash mixtures: (a) Brandon Shores and Columbia fly ashes, (b) Paul Smith Precipitator and Dickerson Precipitator, and (c) Paul Smith Precipitator and Morgantown fly ashes.

### 5.2.8 Speciation of Cu

The dominant oxidation states of leached Cu metals from URM-fly ash-LKD mixtures were determined to be Cu (II) in the speciation analyses section. Based on Figure 9a, the crystalline phase of CuO mineral Tenorite(c), is controlling the solubility of Cu(II) metal species in the aqueous solutions collected from URM-fly ash-LKD mixtures. Engelsen et al. (2010) also claimed that at  $\text{pH} > 9$ , tenorite or precipitation of  $\text{Cu}(\text{OH})_2(\text{s})$  controls the leaching of Cu(II).  $\text{Cu}(\text{OH})_2(\text{s})$  is also known as a solid phase that controls the leaching of Cu metals especially under alkaline conditions (Apul et al. 2005). Nevertheless, in the current study the leaching of Cu(II) cations are likely to be controlled by CuO(c) rather than  $\text{Cu}(\text{OH})_2(\text{s})$ .

At neutral pHs, the Cu(II) cations tend to coprecipitate with Fe metals and are sorbed/adsorbed by hydrous oxides of Al and Fe minerals (Apul et al. 2005, Engelsen et al. 2010). In the current study the pHs of the URM-fly ash-LKD mixtures were above 11 ( $\text{pH} > 11$ ). At this alkaline conditions it is not expected to observe the sorption of Cu by these minerals since the Fe oxides starts precipitating by themselves while Al oxides starts dissolving to their anion species in the aqueous solutions (Engelsen et al. 2010).

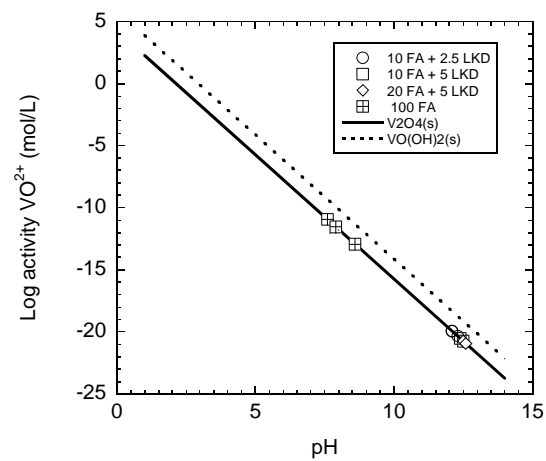
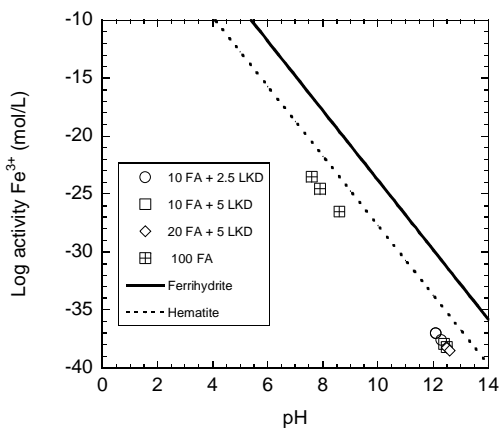
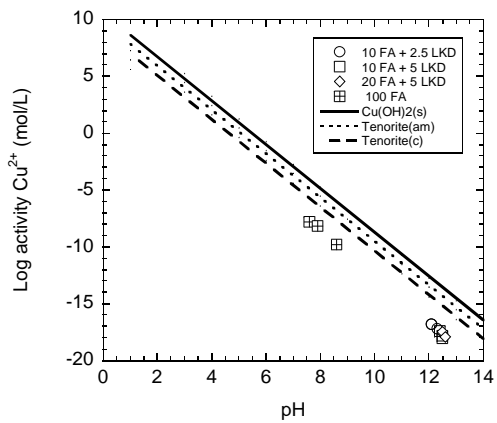


Figure 5.9 Log activity of (a)  $\text{Cu}^{2+}$  vs pH, (b)  $\text{Fe}^{3+}$  vs pH, and (c) V(IV) vs. pH in leachates from fly ashes and soil-fly ash-LKD mixtures.

### 5.2.9 Speciation of Fe

In the speciation analysis it was found that  $\text{Fe}^{3+}$  is the dominant oxidation state of Fe metals in the aqueous solutions of the fly ash-based mixtures. Apul et al. (2005) and Komonweeraket et al. (2010) also claimed that the predominant Fe species in similar waste materials were  $\text{Fe}^{3+}$ . It is well known that Fe solubility, like Al, is controlled by hydroxide minerals (Fruchter et al. 1990, Gitari et al. 2009). Figure 9b indicates that solubility of Fe is more likely controlled by hematite ( $\text{Fe}_2\text{O}_3$ ) minerals rather than  $\text{Fe}(\text{OH})_3$ -amorphous. These results are consistent with Black et al. (1992) which claimed that the solubility of Fe metals was controlled by  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . Fruchter et al. (1990) and Mudd et al. (2004) do not support the findings in this current study about the solubility controlling phase of Fe; however, these previous studies did not include highly conditions, i.e.,  $\text{pH} > 12$  (Figure 9b). At such pHs, it is possible for  $\text{Fe}^{3+}$  to be controlled by hematite instead of ferrihydrite ( $\text{Fe}(\text{OH})_3$ ). In addition, X-ray diffraction analysis indicated that hematite is the primary mineral phase of Fe in the fly ashes used in that study.

### 5.2.10 Speciation of V:

The MINTEQ speciation analyses indicated that the dominant oxidation state of the leached vanadium metals from URM-fly ash LKD mixtures was V(IV) as  $\text{V}(\text{OH})_3^+$  species. Even though previous literature suggested that V metals tend to be present in anionic form at alkaline conditions (Medina et al. 2010, Engelson et al. 2010, Izquierdo et al. 2011), MINTEQA2 speciation analyses conducted in the current study did not agree

with this statement. Figure 9c suggests that the leaching of V is solubility controlled, consistent with the findings of Apul et al. (2005). It is seen that the solubility of V(IV) metal species in this study is controlled by  $V_2O_4(s)$  solid phase at all pH ranges. The V(IV) concentrations remained on the linear solid line that represent  $V_2O_4(s)$  (Figure 9c). It appears that  $VO(OH)_2(s)$  may also have some impact on leaching of V(IV) metals from the URM-fly ash-LKD mixtures used in this study. Izquierdo et al. (2011) claimed that at very high alkaline conditions the complexation of Ca and V metals helps of removing V metals from leachates. This statement is consistent with the findings obtained from the current study because, as shown in Figure 9c, the concentrations of V(IV) decreased with an increase in pH, indicating that V(IV) was removed from the aqueous solutions and Ca-V precipitation could be one of the reasons of this leaching behavior of V(IV). Furthermore, precipitations of V metals with Pb metals are very likely to occur as  $Pb_2V_2O_7$  and  $Pb_3(VO_4)_2$  (Astrup et al. 2006). These  $Pb_2V_2O_7$  and  $Pb_3(VO_4)_2$  solid phases may also have significant effects on controlling the solubility of V metals. Nevertheless, the Pb concentrations leached from URM-fly ash-LKD specimens were below the detection limits and therefore it was not possible to observe a trend between V and Pb concentrations in the aqueous solutions. Figure 9c clearly shows that the dominant controlling mechanism of the leaching of V(IV) metals for the specimens used in this study is the  $V_2O_4(s)$  solid phase.



### 5.2.11 Speciation of Sb

Sb(V) as the  $\text{Sb(OH)}_6^-$  was the dominant oxidation state of Sb metal species in the effluent solutions obtained from URM-fly ash-LKD mixtures. Narukawa et al. (2005) indicated that the dominant Sb species is Sb(III) leached from the fly ashes, but it also indicated that Sb(III) is oxidized to Sb(V) very quickly under aerobic conditions indicating the presence of oxygen in the environment. In this study leachates from the specimens were collected in a beaker exposed to atmosphere and during collection process Sb(III) species may have been oxidized to Sb(V). This could explain Sb(V) as the dominant Sb species for the specimens used in the current study. Similar observations were made by Ettler et al. (2010) during testing of lead residues.

Figure 5.10a shows the variation of  $\text{Sb(OH)}_6^-$  with pH and indicates that the solubility of Sb(V) metal species are not Sb oxides controlled ( $\text{Sb}_2\text{O}_5(\text{s})$ ). Johnson et al. (2005) indicated that calcium antimonate ( $\text{Ca(Sb(OH)}_6)_2(\text{s})$ ) minerals may control the solubility of Sb metals. Figure 5.10b shows the variation of Sb(V) versus Ca(II) concentrations and indicates that the concentrations of Sb(V) metals leached from the URM-fly ash-LKD mixtures are only 2 to 8 magnitudes lower than solid line that represents the  $\text{Ca(Sb(OH)}_6)_2(\text{s})$  solid phase, i.e.,  $-8 < \text{SI} < -2$ . Figure 5.10b also shows that  $\text{Ca(Sb(OH)}_6)_2(\text{s})$  have some ability to control the leaching of Sb(V) metals.

The sorption of Sb metals onto hydrous ferric oxides and aluminum oxides are likely to occur and all these phases can act as possible carriers of Sb through processes of surface complexation and sorption (Ettler et al. 2010). Under very alkaline conditions ( $\text{pH} > 10$ ), the presence of ettringite minerals in the aqueous solutions may also control

the leaching of Sb(V) metals (Cornelis et al. 2008). However, neither sorption nor complexation reactions were included in the geochemical modeling analysis since it was out of the scope of this study. Therefore, it cannot be definitively decided that the leaching of Sb(V) metals from URM-fly ash-LKD minerals are solubility or sorption controlled.

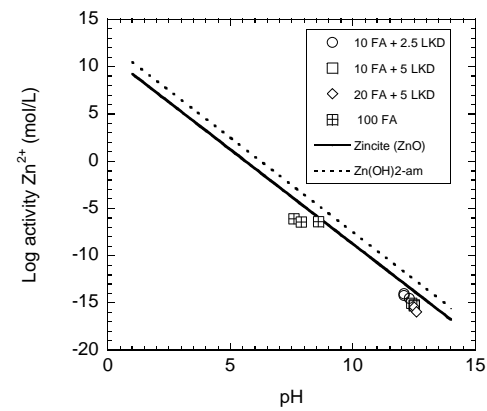
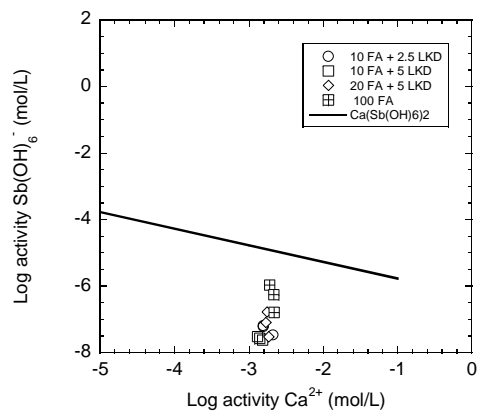
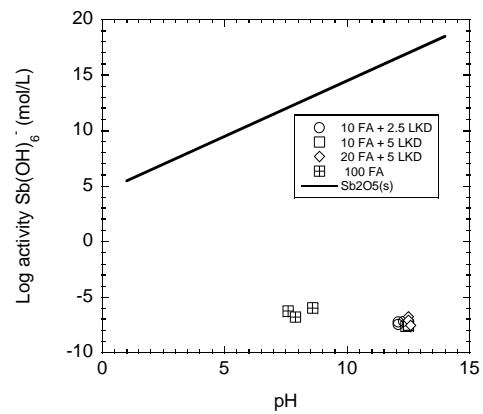


Figure 5.10 Log activity of (a)  $\text{Sb(OH)}_6^-$  vs. pH, (b) vs  $\text{Ca}^{2+}$ , and (c)  $\text{Zn}^{2+}$  vs pH in leachates from fly ashes and soil-fly ash-LKD mixtures.

### 5.2.12 Speciation of Zn

Zn concentrations in the effluent solutions were only measured for specimens prepared with URM-fly ash-LKD materials. Speciation analyses indicated that the dominant oxidation state of the Zn metals leached from these specimens is Zn(II) as  $Zn^{2+}$ . Solubility of Zn metals are mainly controlled by precipitation and dissolution reactions in the soil matrix (Murarka et al. 1992). Figure 5.10c shows that the leaching of Zn(II) metal species is controlled by zincite (ZnO) minerals especially for the specimens providing very high alkaline aqueous solutions ( $pH > 9$ ). The solid line that represents the solubility of ZnO in the Figure 5.10c is covering the all  $Zn^{2+}$  cations leached from the specimens prepared with URM-fly ash-LKD materials. This confirms that ZnO is the main inorganic chemical compound that has a significant effect on the leaching of  $Zn^{2+}$  metals. Moreover, Astrup et al. (2006) and Karamalidis and Voudrias (2009) also found that the solubility of  $Zn^{2+}$  is controlled by the ZnO minerals in the aqueous solutions.  $CaZn_2(OH)_6 \cdot 2H_2O(s)$ , often found in the soil matrix during cementitious reactions, could be another solid phase that may affect the solubility of  $Zn^{2+}$  under very alkaline conditions (Engelsen et al. 2010). The MINTEQA2 analysis, however, did not provide any information about the possibility of the occurrence of such mineral. Therefore, this mineral was not taken into account in the determination of the solid phases that may control the leaching of  $Zn^{2+}$  from the specimens used in this study.

Dijkstra et al. (2002) suggested that including surface precipitation of Zn on the soil particles in the speciation analyses would provide more detailed information about the leaching behavior of Zn. This, however, was not the scope of this study, therefore it

was not included in the MINTEQA2 analysis of the Zn. The adsorption of Zn onto Fe and Al (oxy)hydroxide minerals tends to occur often at neutral pHs (Dijkstra et al. 2004). Since the pH of the effluent solutions of the specimens prepared with URM-fly ash-LKD materials are very high and the ZnO solid line closely matches the  $Zn^{2+}$  concentrations (Figure 5.10.c). The sorption of Zn onto Fe and Al (oxy)hydroxide minerals was not observed in the current study.

Apul et al. (2005) claimed that Zn may form  $Zn(OH)_2(am)$  at  $pH > 8$ . Even though the  $Zn^{2+}$  concentrations are under-saturated with respect to  $Zn(OH)_2(am)$  solid line phase in Figure 5.10c, it may have some controlling capabilities on leaching of  $Zn^{2+}$  cations into the aqueous solutions. This finding is also consistent with those reported by Apul et al. (2005).

Leached metals could be present as carbonates, oxides and hydroxides and Zn could also be adsorbed on metal hydroxides, particularly Fe-oxide minerals. It is very well known that hydrous ferric (HFO) is a very important mineral in the immobilization of heavy metals via sorption and sorption of Zn onto HFO is very likely to occur at  $pH \sim 9.5$  (Engelsen et al. 2010). Karamalidis and Voudrias (2009) indicated that dominant mechanisms controlling the leaching of  $Zn^{2+}$  are the combination of surface complexation and dissolution/precipitation of the minerals that includes Zn. However, Figure 5.10 suggests that the zincite ( $ZnO$ ) minerals were controlling the solubility of the  $Zn^{2+}$  for the specimens used in this study.

### 5.2.13 Speciation of B

B(III) as  $\text{H}_3\text{BO}_3$  was the dominant oxidation state of the boron metal that was leached from soil-fly ash mixtures. Engelsen et al. (2010) also determined that B(III) is generally the dominant boron species in the environment. However, MINTEQA2 was not able to provide any solid phase that may control the solubility of B(III) in the aqueous solutions. Therefore, no log graph was created to determine whether the leaching of B(III) metal species are solubility controlled or sorption controlled. These findings are consistent with the previous studies on leaching controlling mechanisms of boron metal. Fruchter et al. (1990) indicated that borate minerals such as pinnoite, inderite and nobleite do not control the solubility of B and was not able to define any geochemical reactions that could control the leaching of B. Furthermore, Mudd et al. (2004) claimed that borate minerals do not have any impact on controlling the leaching of B and mentioned that the leaching of B could be sorption controlled instead of being solubility controlled.

The pHs of the effluent solutions of the all soil-fly ash mixtures ranged from 6 to 10, the pH conditions that the leaching of B is minimal (Querol et al. 1995) The leaching controlling mechanisms of the B(III) in the aqueous solutions could be the precipitation of B with  $\text{CaCO}_3$  minerals (Hollis et al. 1988). Gitari et al. (2009) and Engelsen et al. (2010) reported that ettringite minerals at high pH ( $\text{pH} > 8$ ) may also have impact on controlling the leaching behavior of B(III). However, neither  $\text{SO}_4^{2-}$  nor  $\text{CO}_3^{2-}$  concentrations were measured in the current study, therefore such a conclusion cannot be warranted.

### 5.3 CONCLUSIONS

MINTEQA2 equilibrium geochemical code and laboratory column leaching tests results were used to determine the dominant oxidation states of the Al, As, B, Cr, Cu, Fe, Mn, Sb, Se, V, Zn metals and define the leaching controlling mechanisms of the leached dominant metal species in the leachates. The geochemical modeling code was conducted on the URM-fly ash-LKD mixtures (URM: Unpaved road material, Fly Ashes: Brandon Shores, Paul Smith, Dickerson Precipitator, LKD: Lime kiln dust) and soil-fly ash mixtures (Soil: Sandy Borrow Material, Brandon Shores, Paul Smith Precipitator, Dickerson Precipitator, Morgantown, Columbia Power Plants). The findings from the current study can be summarized as follows:

- 1) MINTEQA2 speciation analysis indicated that the As, Fe, Cu, Mn, Sb and V were typically present in the oxidized forms As(V), Fe(III), Cu(II), Mn(II), Sb(V) and V(IV) respectively, with some exceptions discussed as follows. For chromium, the dominant oxidation states of the Cr metals leached from soil-fly ash mixtures were in a reduced form as Cr(III) while the dominant oxidation states of Cr metals from URM-fly ash-LKD mixtures were in an oxidized form as Cr(VI). The speciation analysis indicated that, even though the Se(IV) was the dominant oxidation states of the leachates, there were still reasonable amounts of the oxidized form of Se as Se(VI) in the aqueous solutions. For aluminum, even though Al is not redox sensitive metal element, speciation analysis indicated that Al(III) is the dominant oxidations state of the leached Al metals both for soil-fly ash mixtures and URM-fly ash-LKD mixtures.

- 2) Dissolution-precipitation reactions identified by the MINTEQA2 database were used to determine the leaching controlling mechanisms of all metals studied in the current study. Al(III), Cr(III), Mn(II), Cu(II), Fe(III), V(IV) and Zn(II) metals were able to be defined by these dissolution-precipitation reactions, indicating that leaching of these metals are solubility controlled. However, no relationships were observed between the As(V), Sb(V), and Se(IV) metals indicating that leaching of these metals likely are sorption controlled. The confirmation of this is the out of the scope of this study and the subject of future work. Therefore, it was not possible, from the current research, to conclude which sorption reaction may control the leaching of As(V), Sb(V), and Se(IV) metal species.
- 3) Al(OH)<sub>3</sub>(Gibbsite) was the dominant solid phase that controls the leaching of Al(III) in the aqueous solutions. B(III) as H<sub>3</sub>BO<sub>3</sub> was the dominant oxidation state of the boron metal leached from soil-fly ash mixtures. However the MINTEQA2 geochemical modeling program was not able to provide a solid phase that may control the solubility of B(III) in the aqueous solutions. Therefore, no log graph was could be created to further characterize the leaching behavior of B(III) metal species.
- 4) Cr(III) was mainly controlled by Cr(OH)<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>(s) minerals rather than Cr(OH)<sub>3</sub>(am). Cr<sub>2</sub>O<sub>3</sub>, one of the original contents of all fly ashes, varied from 2% to 5%. It is expected to see the solubility of Cr metals controlled by this chromium oxide mineral. In addition, the solubility of Mn(II), Cu(II), Zn(II) and V(IV) were controlled by Mn(OH)<sub>2</sub>, Cu(OH)<sub>2</sub>, ZnO and V<sub>2</sub>O<sub>4</sub>(s) minerals respectively.



- 5) Based on MINTEQA2 results, As(V) was not controlled by As(hydro)oxides. The geochemical analysis indicated that the solubility of As(V) is generally controlled by the  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  compound. It is expected to see that in the presence of adequate As(V) concentrations; it is likely to observe the complexation of  $\text{AsO}_4^{3-}$  with  $\text{Mn}^{2+}$ .
- 6) None of the solid phases provided by MINTEQA2 geochemical analyses had control over the leaching of Se(IV) metal species. Previous studies agree that leaching of Se(IV) is not solubility controlled in alkaline conditions. The concentrations of oxyanions decrease significantly compared to metallate solubility due to the adsorption and solid solution formation of oxyanions with minerals at high pHs. Gibbsite and  $\text{Fe}(\text{OH})_3$  could provide an effective sorption site for Se(IV) species at pHs around 8 and 9. However, a separate study on the sorption mechanisms was not conducted.
- 7) The solubility of Sb(V) metal species were not controlled by Sb-oxide minerals such as  $\text{Sb}_2\text{O}_5(\text{s})$ . Calcium antimonate ( $\text{Ca}(\text{Sb}(\text{OH})_6)_2(\text{s})$ ) minerals may control the solubility of Sb metals. Based on MINTEQA2 analyses, it can be concluded that  $\text{Ca}(\text{Sb}(\text{OH})_6)_2(\text{s})$  have some ability to control the leaching of Sb(V) metals. The sorption of Sb metals onto hydrous ferric oxides and aluminum oxides is highly likely. All phases can act as possible carriers of Sb through processes of surface complexation and sorption. However, neither sorption nor complexation reactions were included in the geochemical modeling analysis.

- 8)  $\text{Fe}^{3+}$  was the dominant oxidation state of Fe metals in the aqueous solutions of fly ash-soil, fly ash-soil-LKD mixtures. The solubility of Fe was probably controlled by the hematite ( $\text{Fe}_2\text{O}_3$ ) minerals rather than  $\text{Fe}(\text{OH})_3(\text{am})$ ,  $\text{Fe}(\text{OH})_3(\text{s})$ . X-ray diffraction analysis indicated that hematite is the primary mineral phase of Fe in the fly ashes used in that study, suggesting that leaching of Fe metals was controlled by  $\text{Fe}_2\text{O}_3$  minerals.
- 9) The leaching of Cr(VI) in the effluent solutions are not controlled by chromium (hydr)oxides. The solubility of Cr(VI) could be controlled by  $\text{BaCrO}_4$  solid phase.  $\text{Ba}(\text{S,Cr})\text{O}_4$  could be one of the main solid phases that may control the leaching of Cr(VI); however, further  $\text{SO}_4^{2-}$  anion measurements are necessary to prove this phenomenon.

## 6 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 CONCLUSIONS

Coal power plants are very important in production of electricity in the United States. Approximately 50% of the electricity in United States is generated by coal combustion processes (Daniels and Das 2006). As a result of this, large amount of coal combustion byproducts especially fly ashes are produced annually. Only 40% of these fly ashes can be reused successfully in applications such as cement, concrete productions and soil stabilization and most of these reused fly ashes are classified as Class C and Class F fly ashes according to ASTM C618. Rest of these waste materials are high carbon fly ashes (HCFAs) and being landfilled each year. HCFAs contain significant amounts of unburned carbon (i.e., high loss on ignition) and cannot be used as a concrete additive (Cetin et al. 2010). The only alternative for this byproduct is to landfill unless no beneficial reuse is offered. Continuous disposal of these HCFAs are causing significant environmental and economical problems.

Highway structures pose great potential for these landfilled HCFAs to be reused in many different applications such as stabilizer in highway base layers or as a soil amended in embankment constructions. Even though mechanical properties of the fly ash-amended highway base layers and embankments are deemed satisfactory, one key issue that precludes highway base layer stabilization with fly ash is the potential for groundwater impacts caused by metals in the fly ash (Jankowski et al. 2006, Wang et al. 2006, Bin-Shafique et al. 2006). The main objective of this research study was to investigate the environmental suitability of high carbon fly ash (HCFA) stabilized highway base layers and HCFA amended embankments. This research study was conducted in 2 phases: First phase was experimental evaluation of environmental

suitability of HCFAs amended soils while the second phase was numerical evaluation of environmental suitability of HCFAs amended soils.

Experimental studies started with physical and chemical characterization of the fly ashes that were mainly collected from Maryland. Then a series of three different laboratory tests which were water leach tests (WLTs), toxicity characteristic leaching procedure tests (TCLPs), and column leach tests (CLTs), were conducted to determine the environmental suitability of utilization of high carbon fly ashes into the geotechnical applications. These three leaching tests were specifically chosen since they were significantly different from each other. WLTs are simulating the short term leaching behavior of metals while CLTs are simulating the long term leaching behavior of metals. In addition, TCLP tests were also conducted since it is always required by EPA if environmental suitability of any type of waste materials is being tested. Laboratory tests were performed on soil alone, fly ash alone, soil-fly ash-lime kiln dust, and soil-fly ash mixtures. This research study was focused on leaching of 12 different metals which were arsenic (As), aluminum (Al), antimony (Sb), barium (Ba), boron (B), copper (Cu), chromium (Cr), iron (Fe), manganese (Mn), selenium (Se), vanadium (V), and zinc (Zn).

In the second phase of this study, the results obtained from first phase were used as an input parameter in the groundwater contamination numerical computer model WiscLEACH. WiscLEACH were used to predict the leached metal concentrations in the field. WiscLEACH simulations were conducted to study the locations of maximum metal concentrations in the soil vadose zone and groundwater (e.g., at the centerline of the pavement structure, at the vicinity of point of compliance) and create contours of trace metals at different years as a function of depth physical and chemical properties of the fly ash amended soils. In addition, geochemical

computer model MINTEQA2, was used to conduct speciation analyses and determine the most dominant species of the leached metals that actually existed in the leachate and it was also used to estimate the leaching controlling mechanisms of the metals. Total peak metal concentrations from column leach tests, leachate pH, electrical conductivity (EC) and leachate Eh, were used as an input in the MINTEQA2 geochemical modeling program. The results of all these experimental and numerical tests were discussed in detail in the previous sections. In this chapter only general conclusions will be summarized as follows:

1. An increase in fly ash content increased the pH of the effluent solutions of the soil-fly ash, URM-fly ash-lime kiln dust mixtures regardless of the fly ash types. Even though most of the fly ashes did not have significant amount of CaO and MgO contents, it had been appeared that the release of these minerals had still impact on effluent pHs.
2. Addition of fly ash content generally caused an increase in the leached metal concentrations with few exceptions. Fly ashes were the main metal source in the soil mixtures. Therefore, it was expected to see an increase in metal concentrations in the aqueous solutions by increasing the fly ash content in the soil mixtures.
3. Lime kiln dust (LKD) addition has significant impact on the pH of the leachates of the URM-fly ash-LKD mixtures. The concentrations of the metals studied in this research are greatly influenced by the pH of the effluent solution significantly which suggest that the addition of LKD is very critical on evaluation of the environmental suitability of using fly ashes as a stabilizing agent in highway base layer constructions.
4. The concentrations of metals were generally below the EPA MCLs, WQLs and Maryland ATLS. Al was only the exception for the specimens prepared with URM and LKD. It

should be noted that Al is on the EPA list of secondary drinking water regulations, and there are no limits for Al specified in Maryland groundwater protection guidelines. On the other hand, the concentrations of the metals exceeded the EPA MCLs beyond the addition of 20% of the specimens prepared with only Mt and Co fly ashes.

5. WiscLEACH simulations for both fly ash stabilized highway base layer and fly ash amended embankments indicated that the metal concentrations decreased over time and distance and that all the metals were sufficiently dispersed in the vadose zone. WiscLEACH results also indicated that the metal concentrations of metals were much lower than the metal concentrations obtained from the laboratory leaching tests suggesting that the results of laboratory tests are likely to provide a conservative estimate of field metal leaching.
6. Geochemical model MINTEQA2 indicated that the speciation of metals is highly dependent on pH and Eh of the effluent solutions. Some of the species of the metals leached from soil-fly ash mixtures URM-fly ash-LKD mixtures existed in their toxic forms. This indicates that extra care should be taken in the use of some these soil mixtures in such geotechnical applications.
7. Based on the results obtained from both experimental and numerical tests in the current research study, it can be concluded that reuse of high carbon fly ashes (HCFAs) as a stabilizing agents and soil amendment in geotechnical applications are environmentally safe. However, design of these geotechnical structures must be done very carefully in terms of adjusting the fly ash content in the soil mixture. Addition of large amount of fly ash in the soil-fly ash, soil-fly ash-LKD mixtures may yield excessive amount of

leached metals into the environment and groundwater which may cause significant health issues to the aquatic life and human health.

## 6.2 RECOMMENDATIONS FOR FUTURE STUDIES

Even though the results obtained from the current study was satisfactory in terms of environmental suitability of the soil-fly ash mixtures tested, more static pH laboratory leaching tests could be conducted on the same mixtures to obtain more reliable information about the leaching behavior of metals that were focused. Leaching of metals are highly dependent on the effluent pHs as well as influent pHs. Therefore, it is very crucial to determine the leached metal concentrations from fly ash mixed soils at different stabilized pHs. This would provide more clear information on defining the leaching pattern of the metals and more input data to put in geochemical computer model MINTEQA2.

The boundary conditions of WiscLEACH computer model which was used in the prediction of leached metal concentrations in the groundwater under field conditions should be modified. Although the results obtained from WiscLEACH is very conservative, some of the assumptions made in WiscLEACH could be substituted for the chemical and biological reactions that may occur in the field. Thus, the leached metal concentrations from fly ash mixed soils could be estimated more accurately. WiscLEACH also ignores the surface runoff that may occur on the soil at the edge of the pavement and pavement surface and assumes that the entirety of precipitated water infiltrates thorough the pavement structure and soil vadose zone. This is very conservative assumption and may overestimate the leached metal concentrations in the groundwater. Therefore, including the effects of the loss of precipitated water may yield more accurate prediction of the leached metal concentrations in the field.

Finally, performing large scale of field study on the soil mixtures prepared in the current study would help to compare field leaching tests results to laboratory test results and try to find a correlation between the outputs of these tests that can be used for future studies. In addition, field study would also help to validate the results obtained from numerical computer models and check their accuracy and efficiency.

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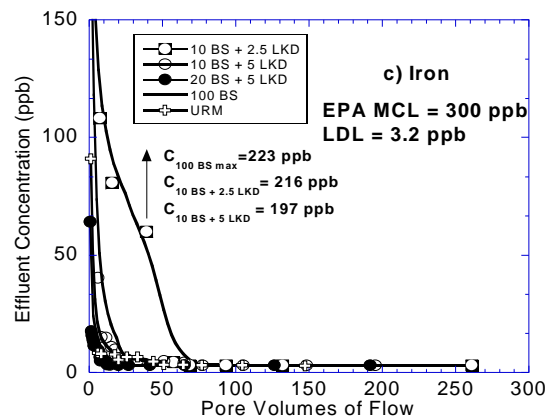
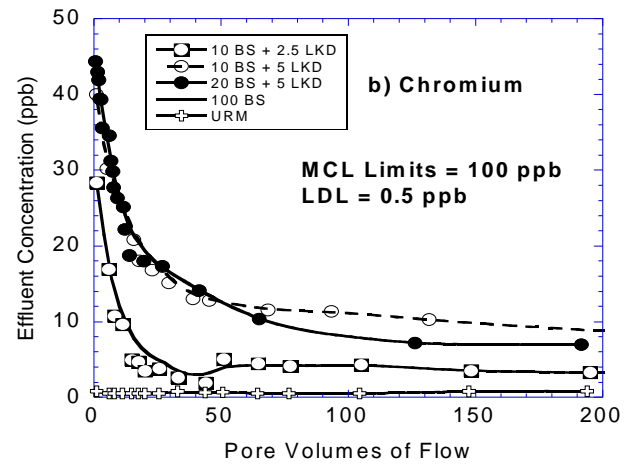
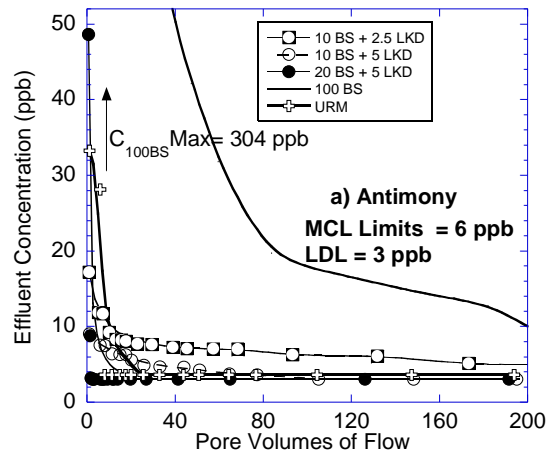
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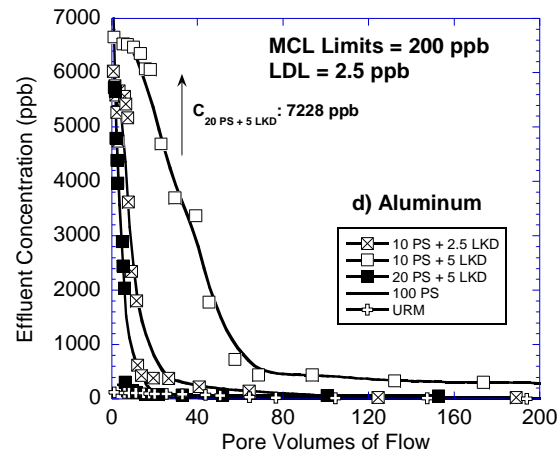
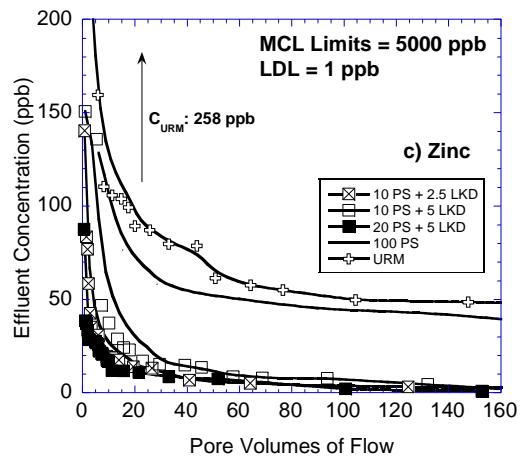
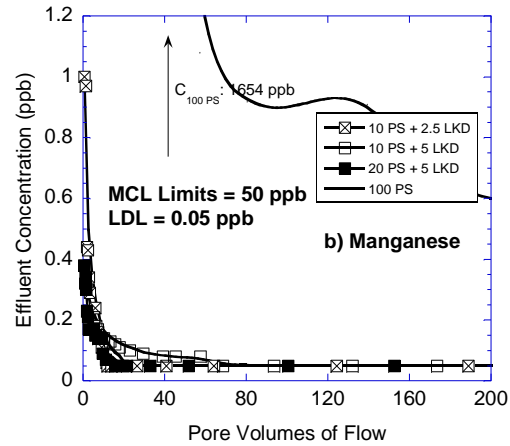
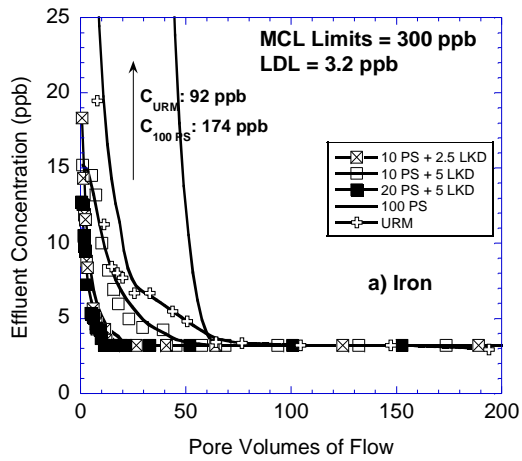


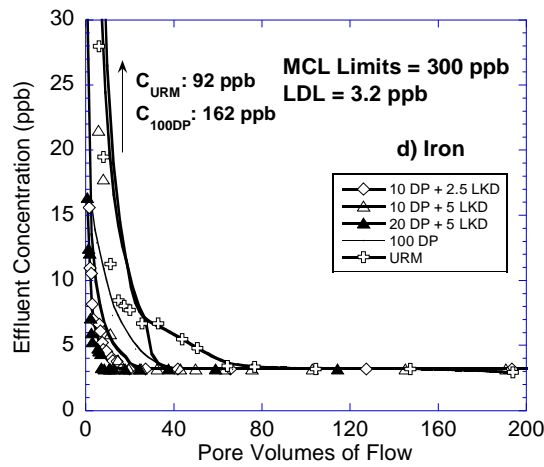
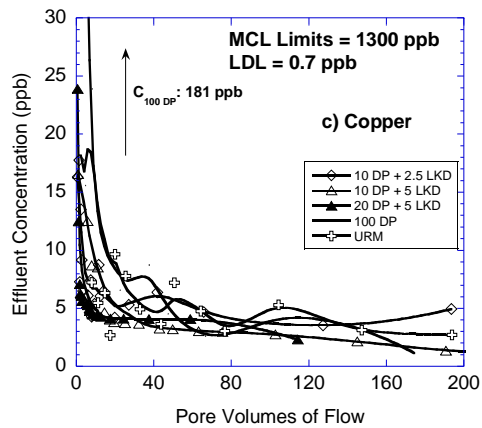
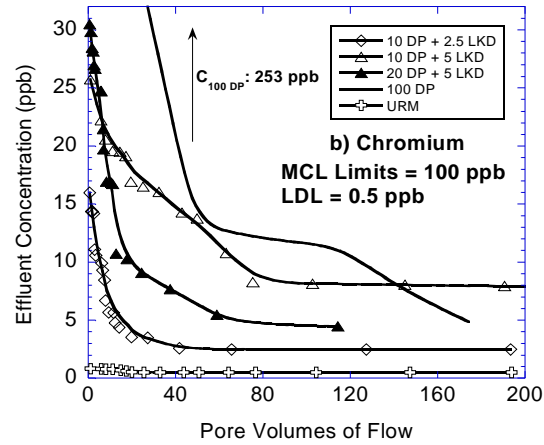
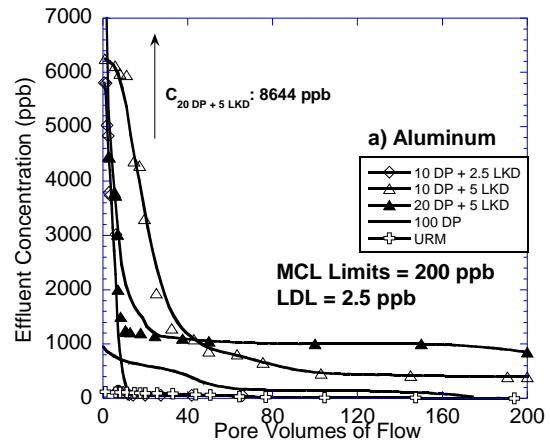
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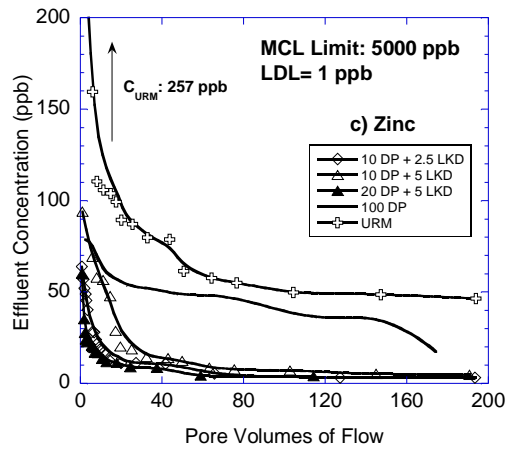
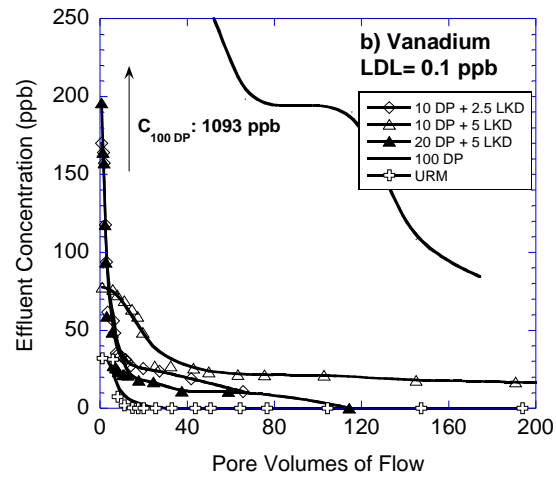
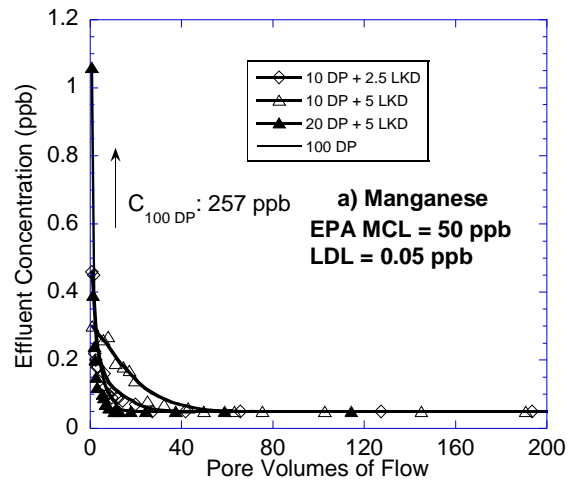
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APPENDIX A: ELUTION CURVES FOR METALS FOR HIGH  
CARBON FLY ASH STABILIZED BASE LAYER

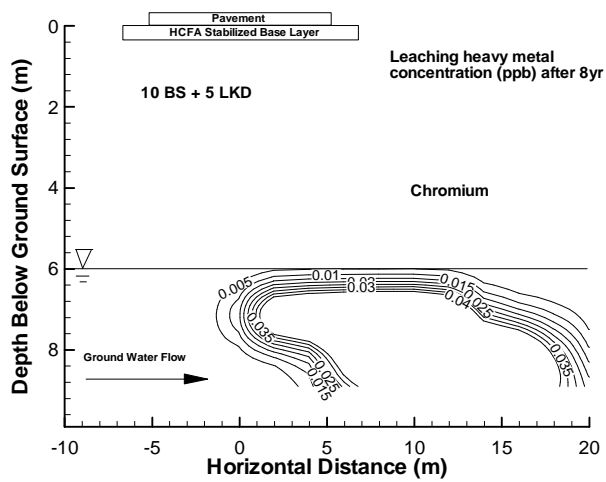
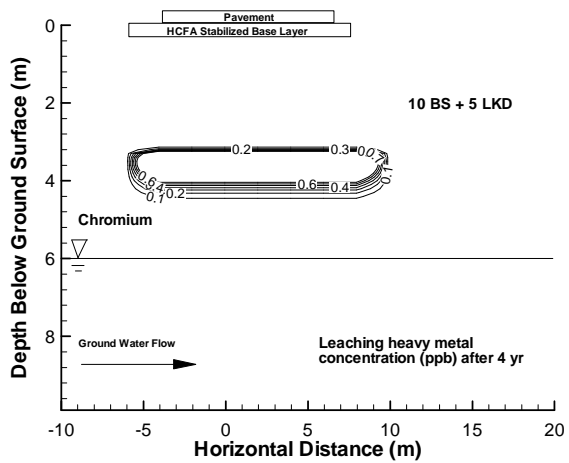
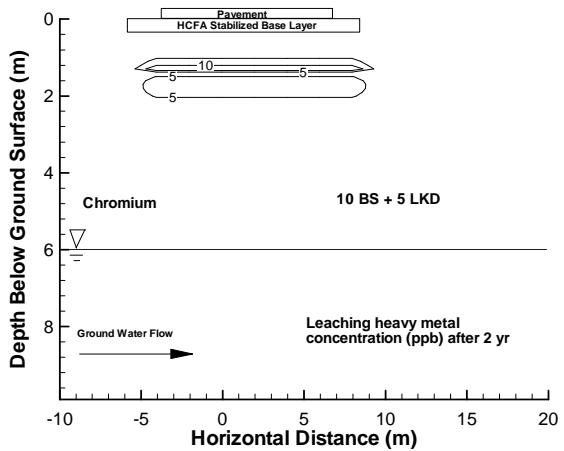
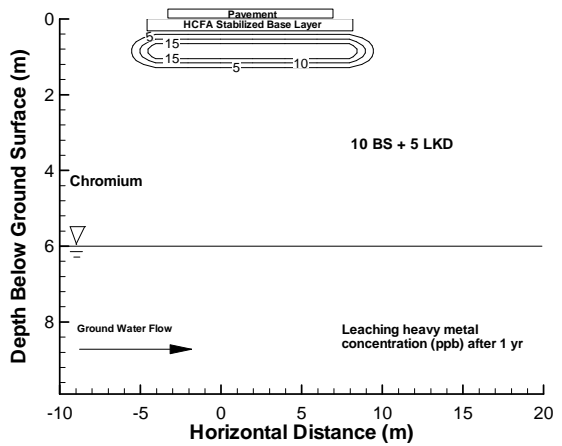




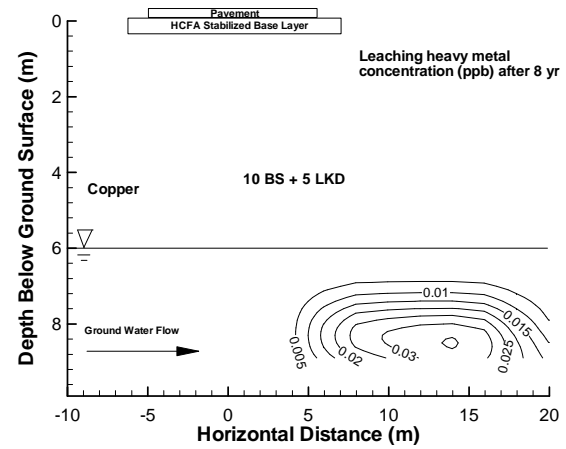
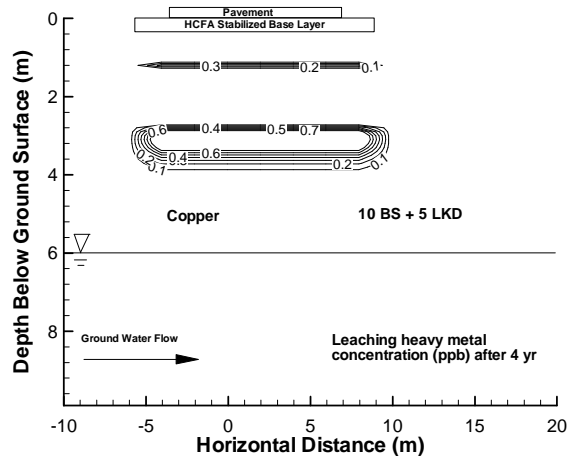
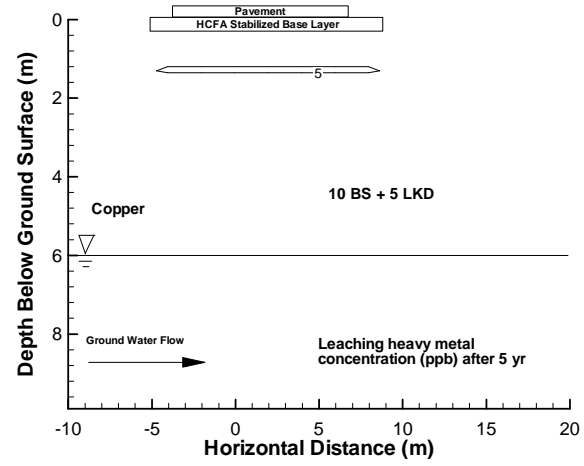
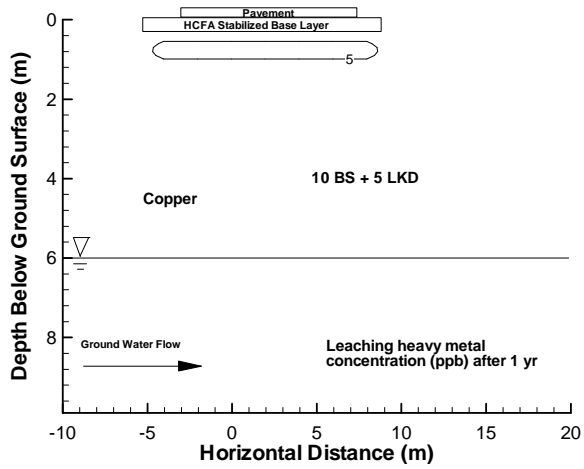


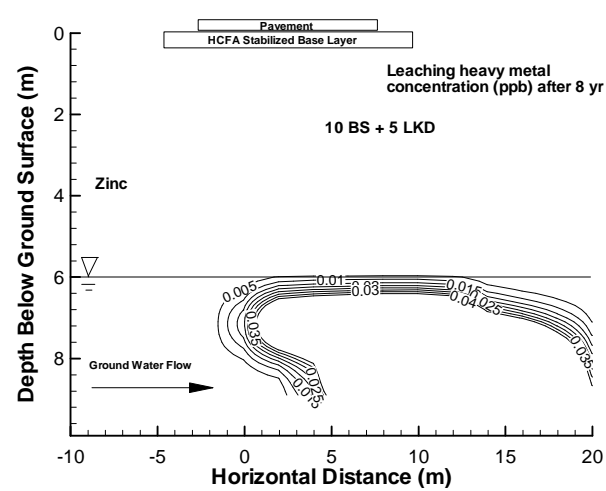
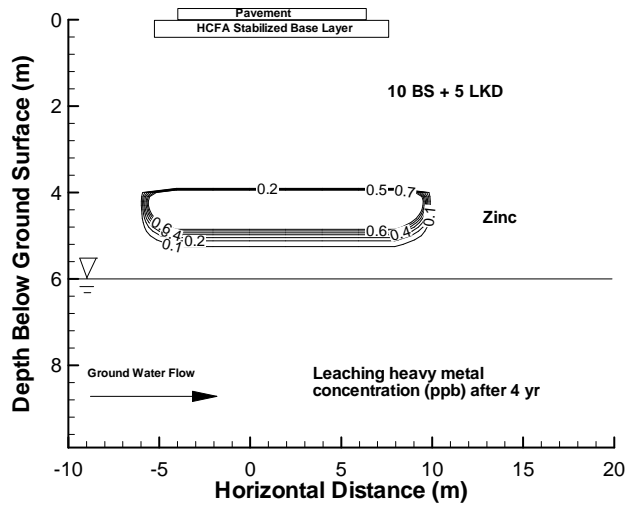
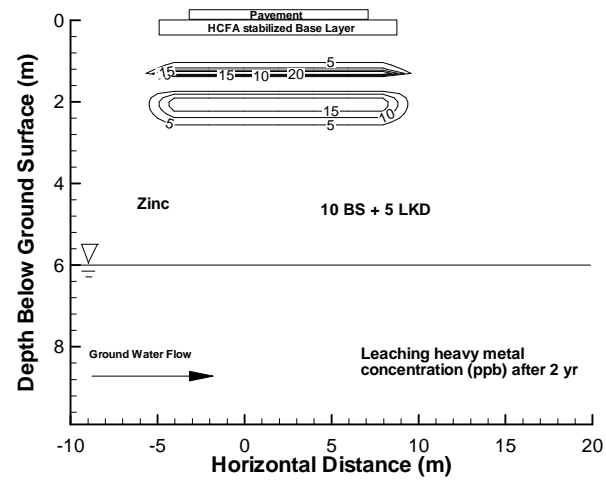
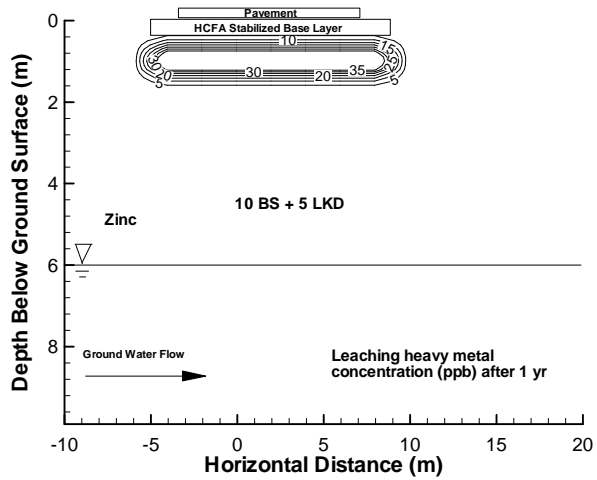


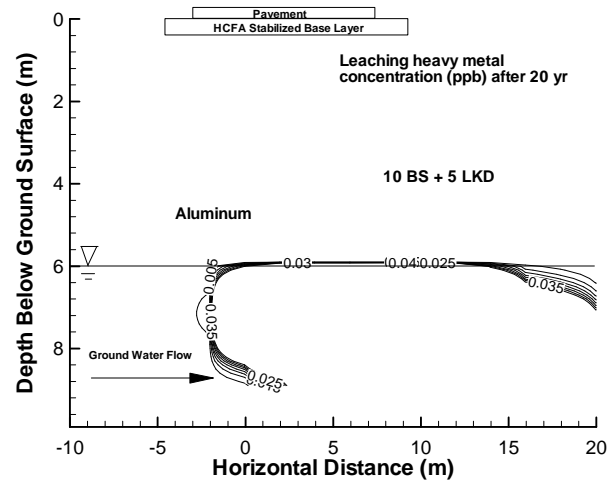
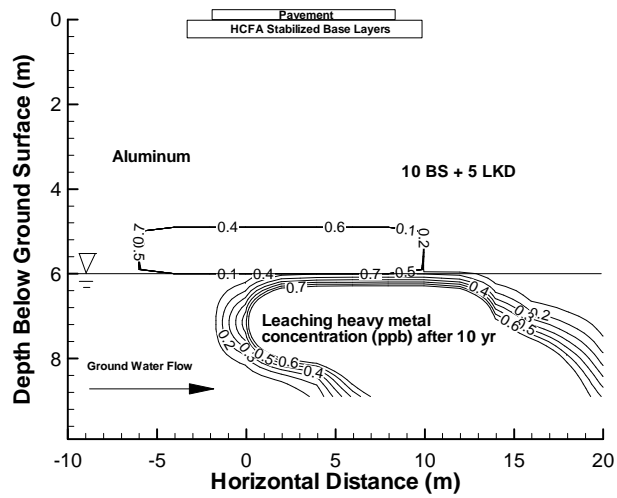
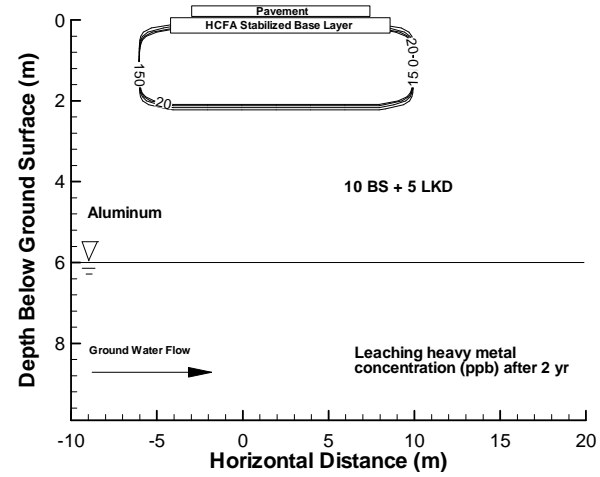
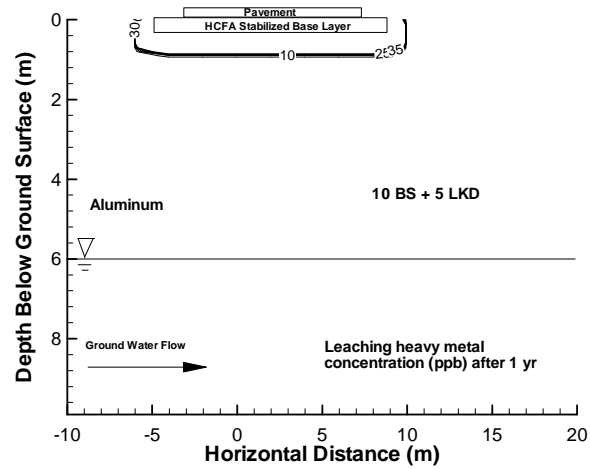
**APPENDIX B: PREDICTED METAL CONCENTRATIONS IN  
VADOSE ZONE AND GROUND WATER FOR HIGH  
CARBON FLY ASH STABILIZED BASE LAYERS**

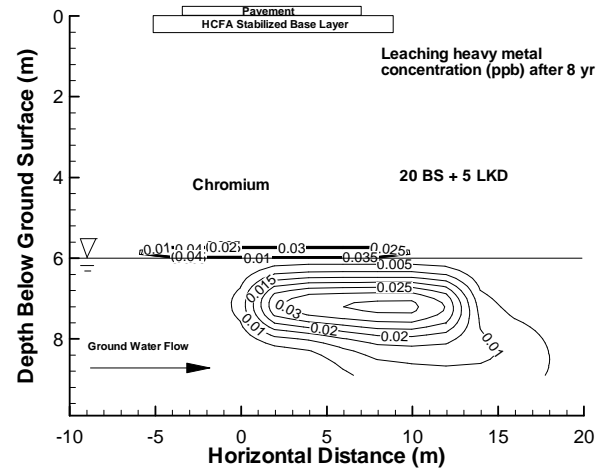
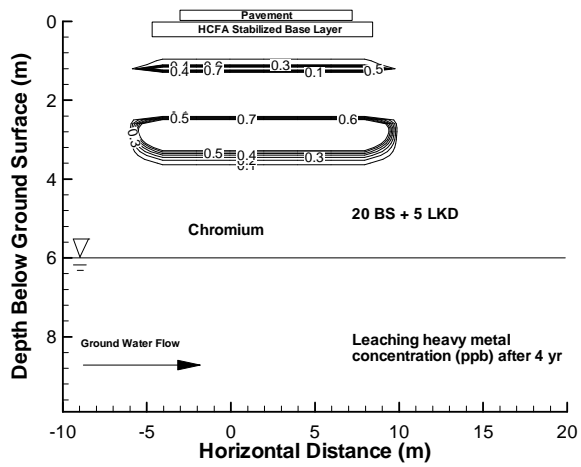
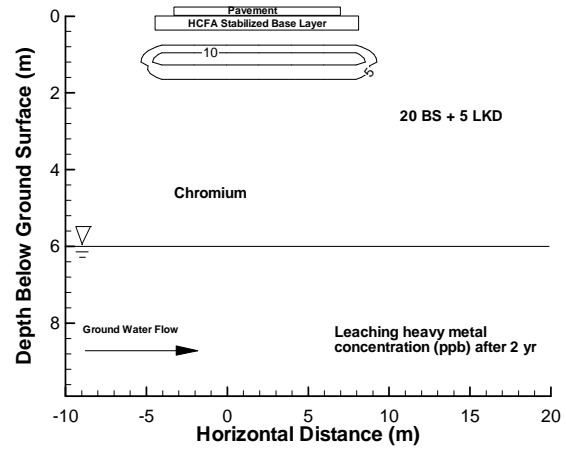
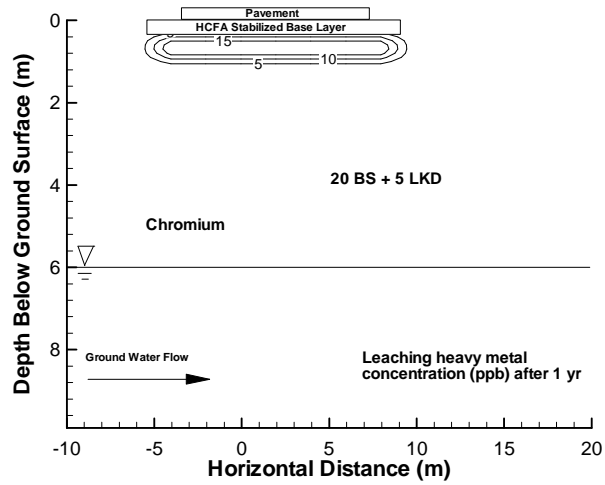


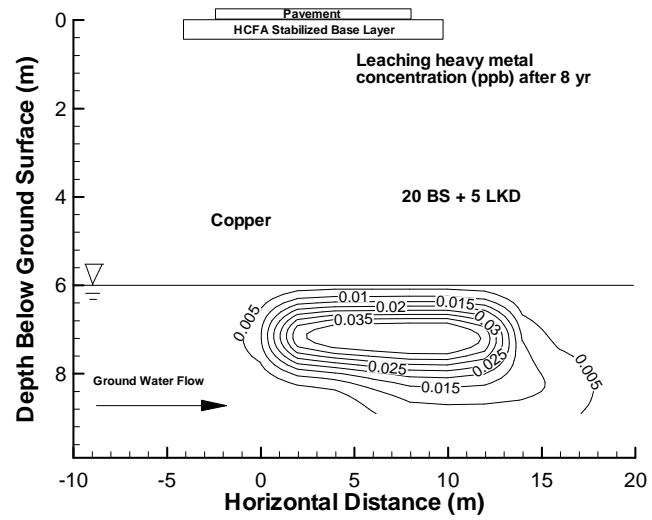
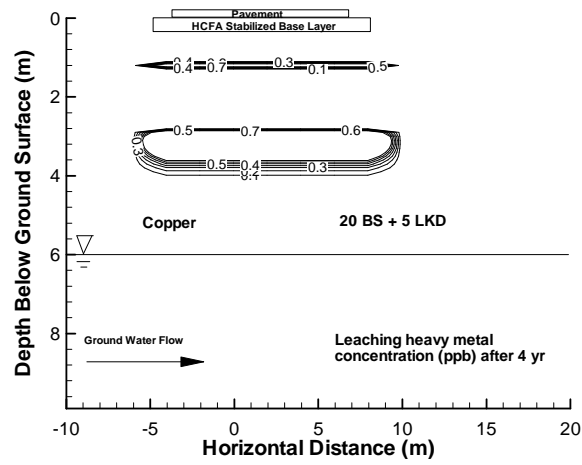
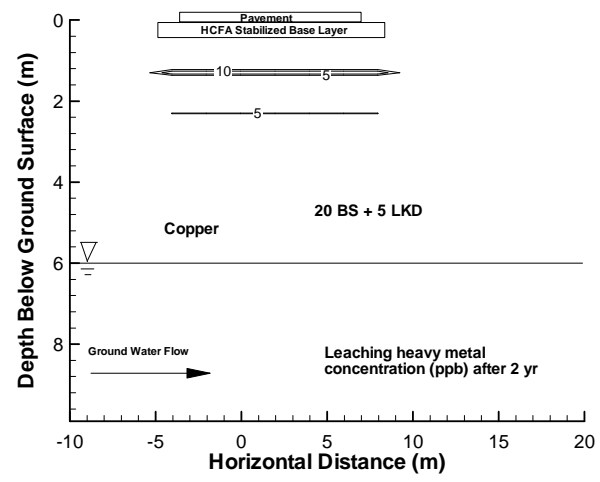
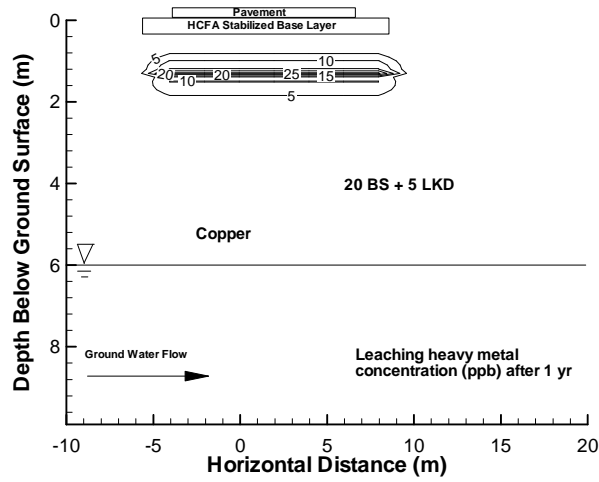


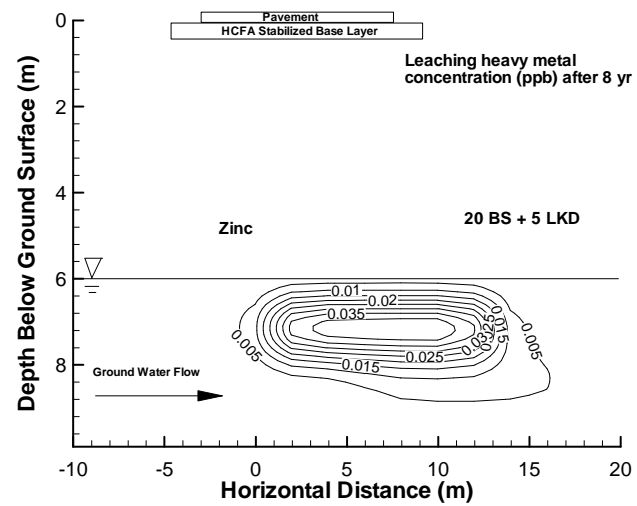
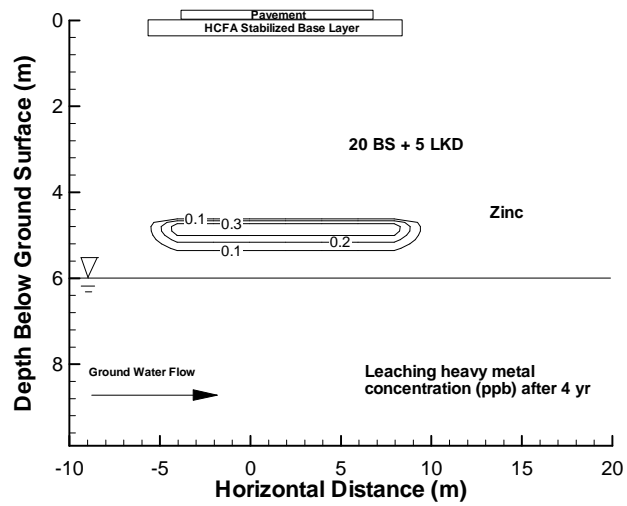
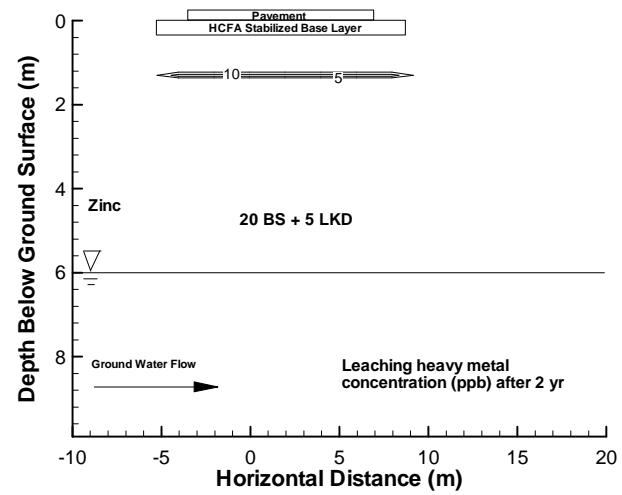
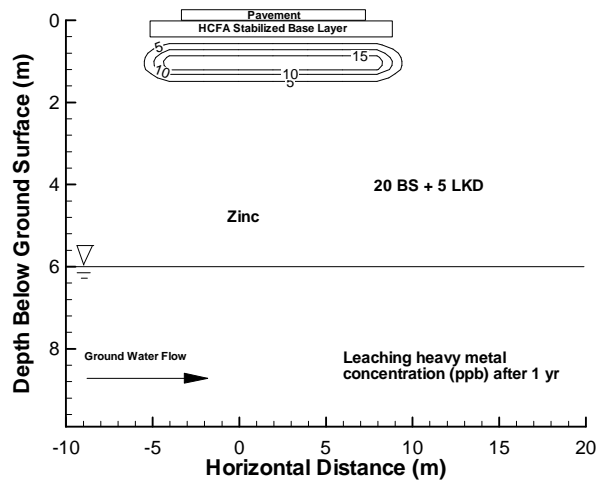


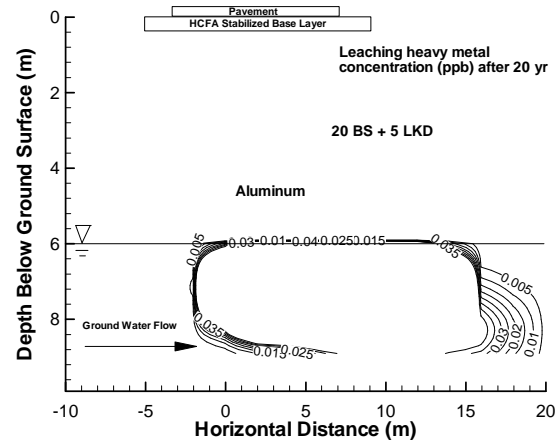
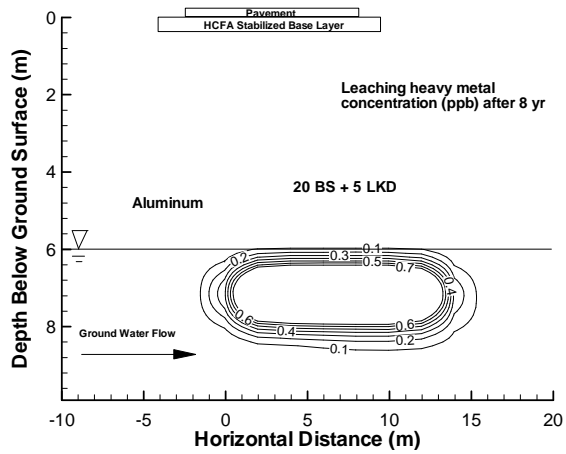
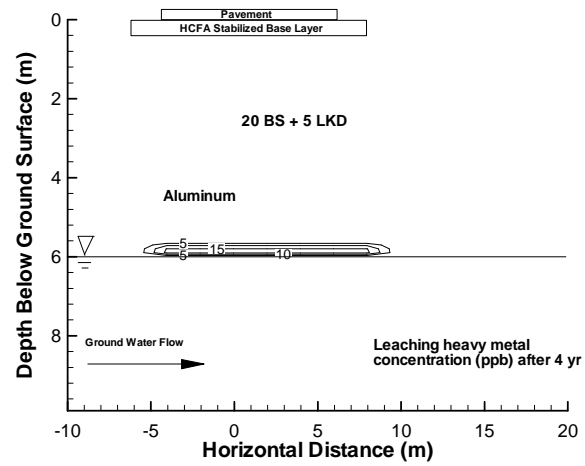
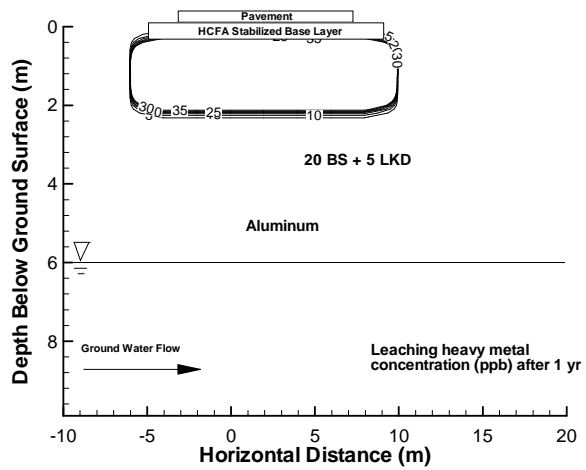


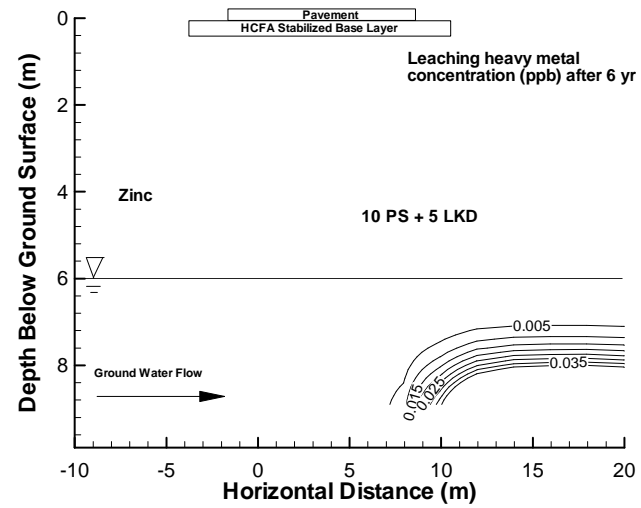
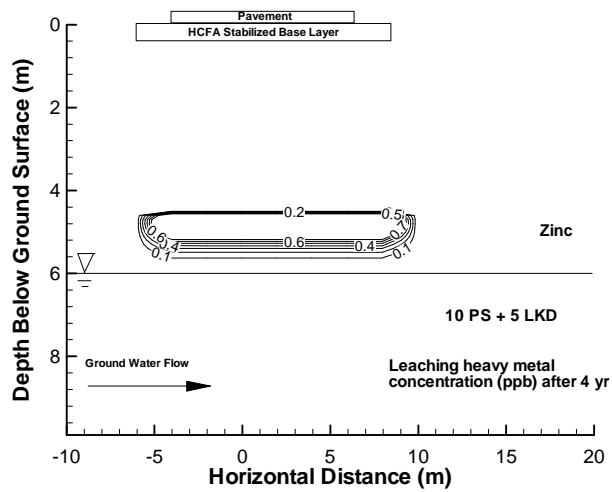
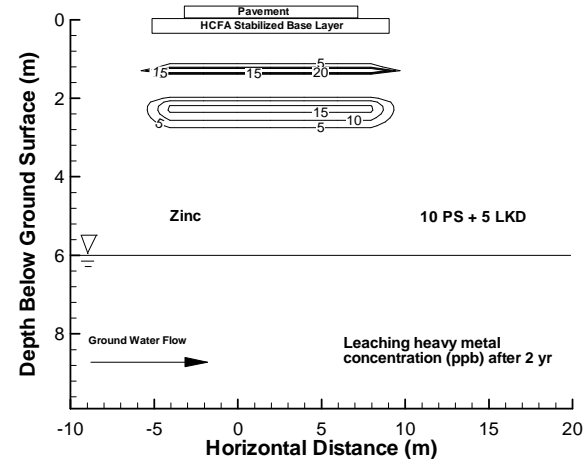
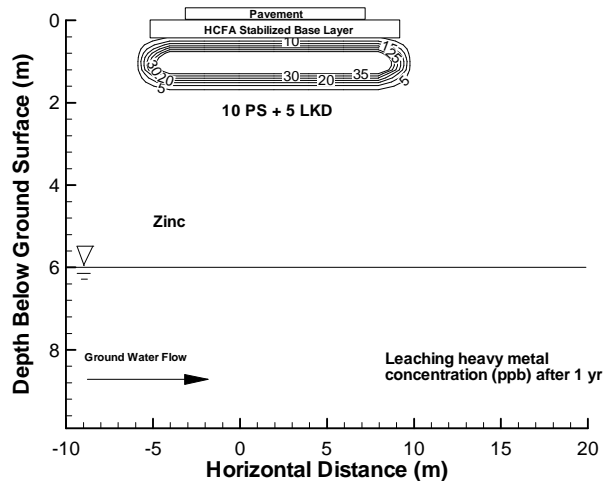




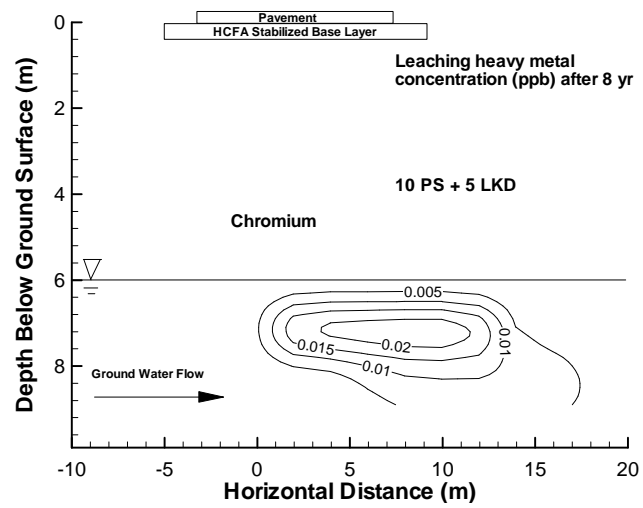
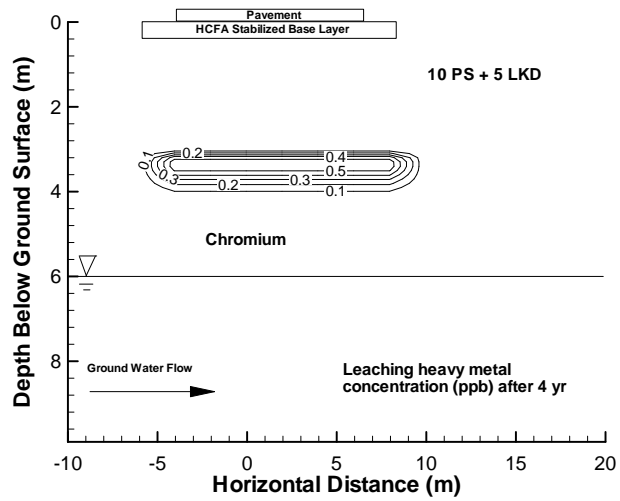
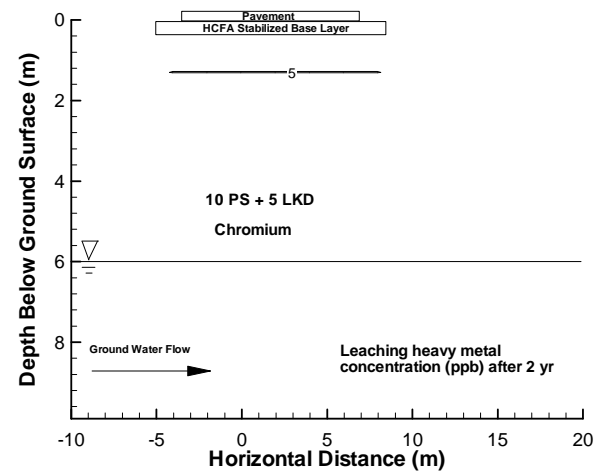
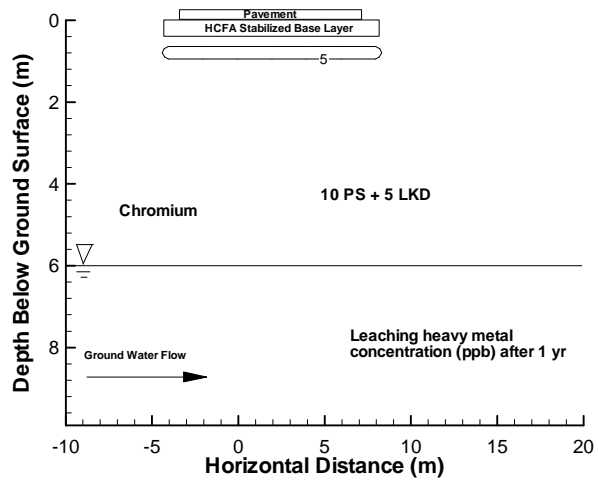


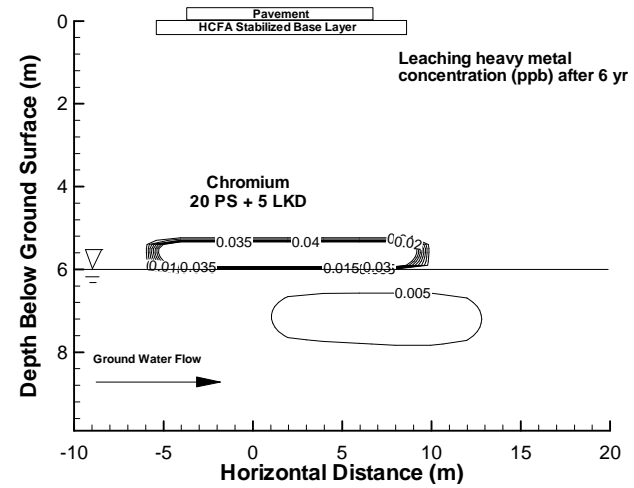
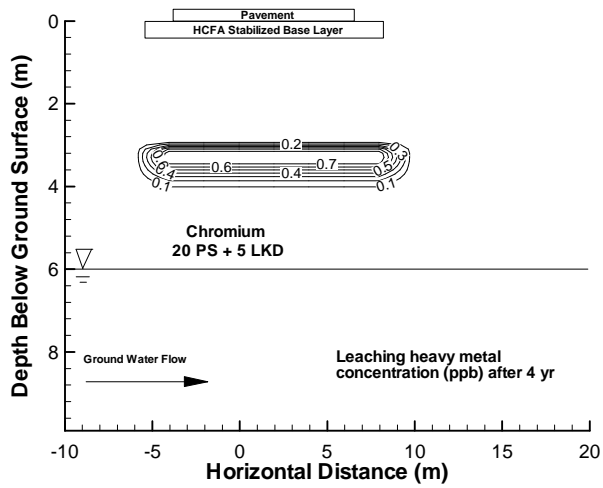
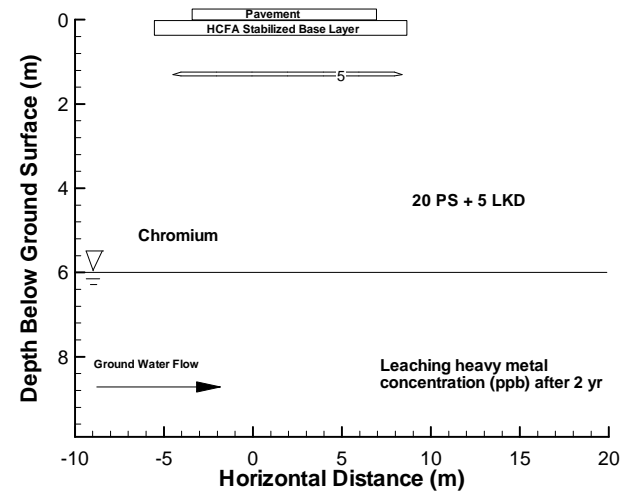
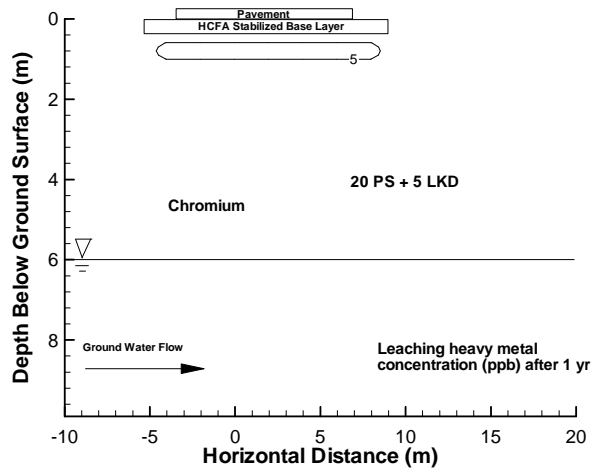


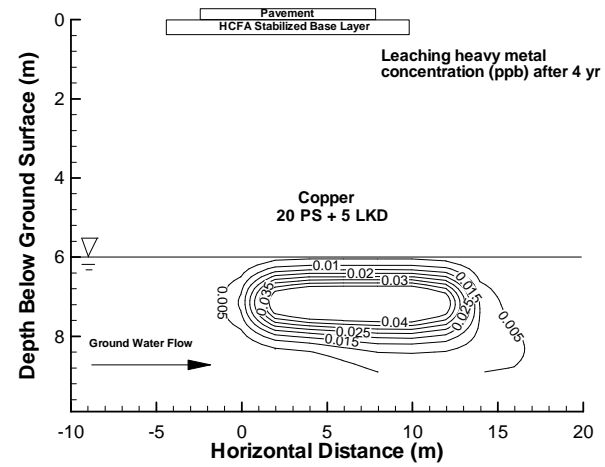
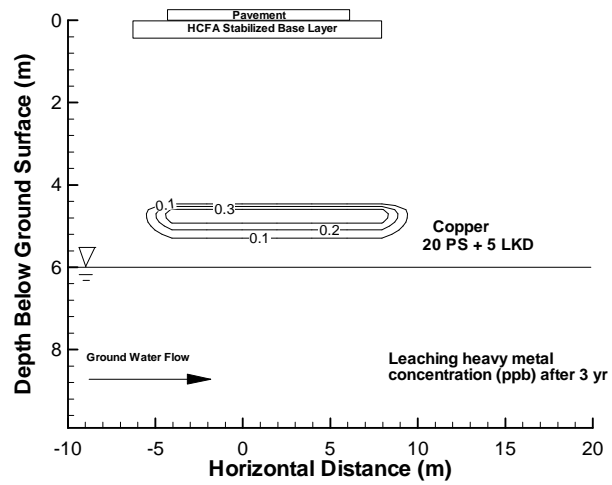
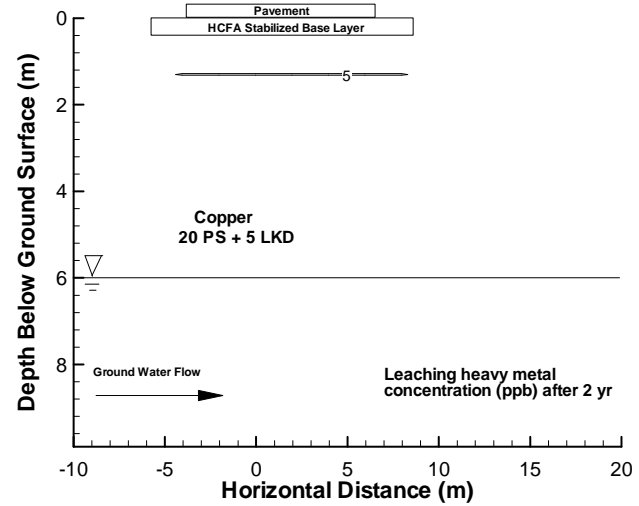
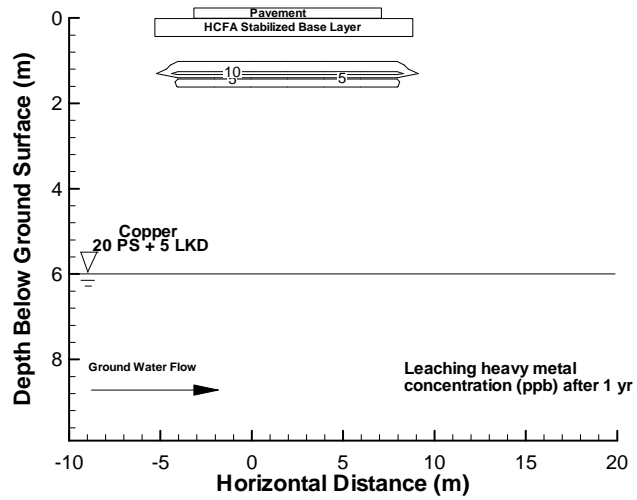


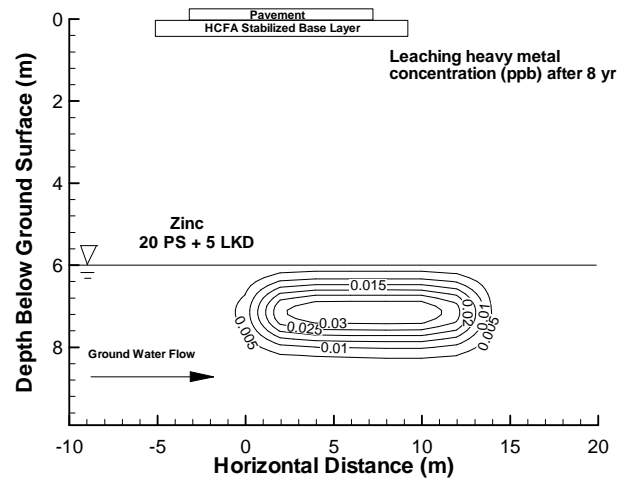
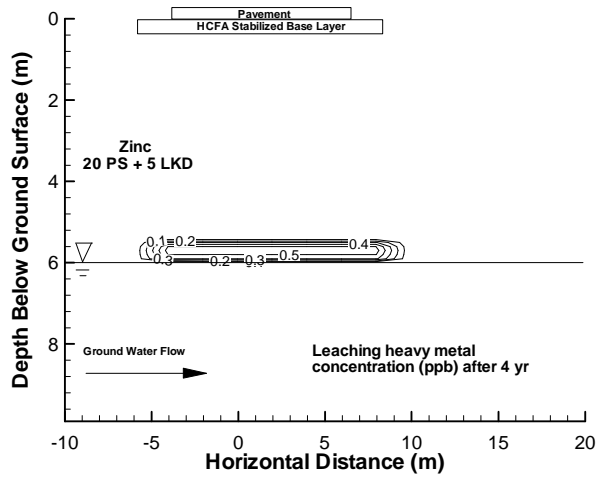
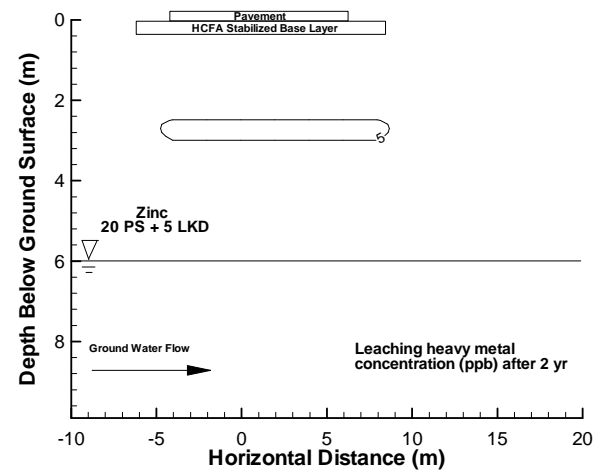
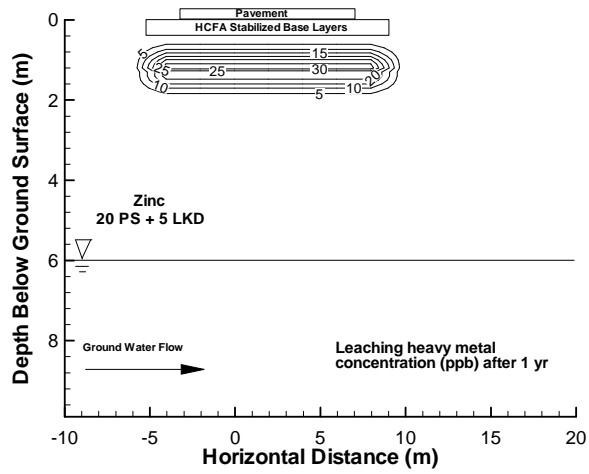


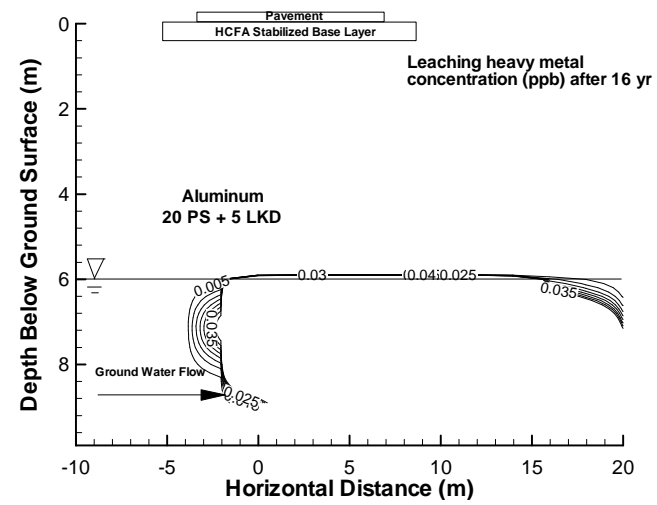
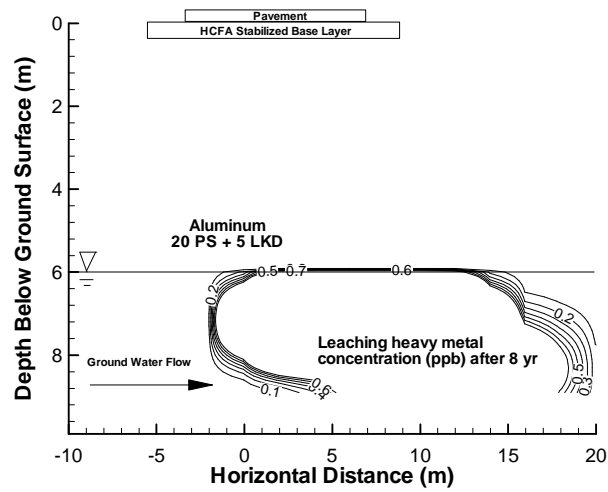
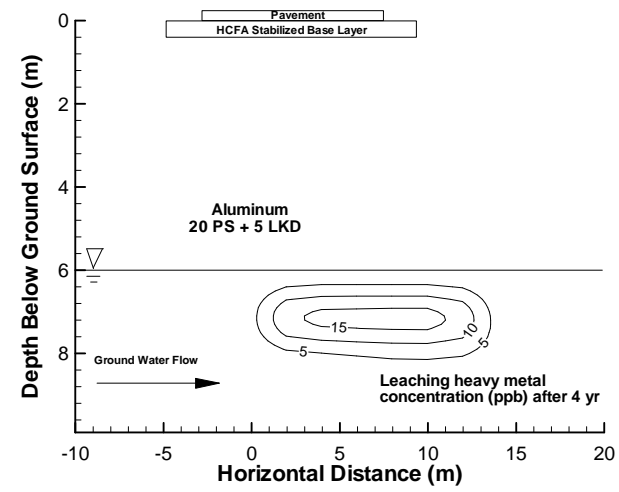
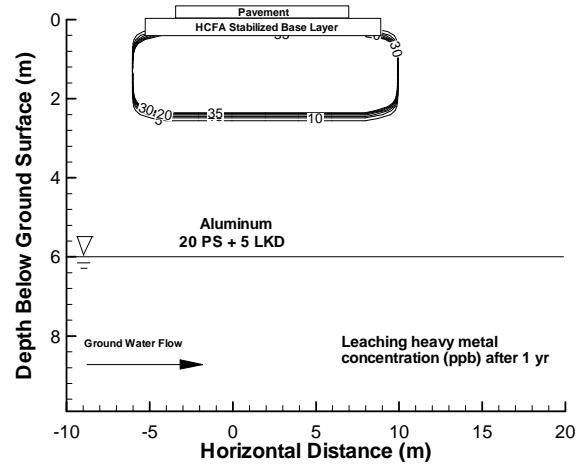


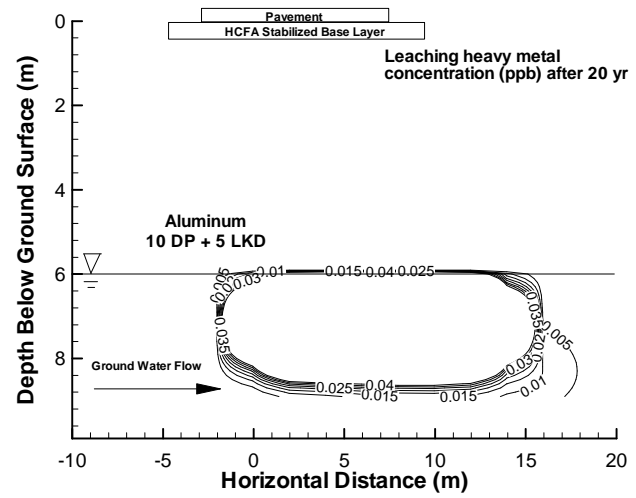
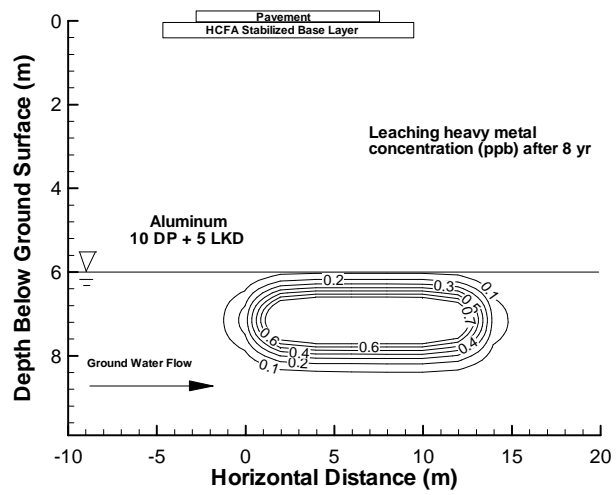
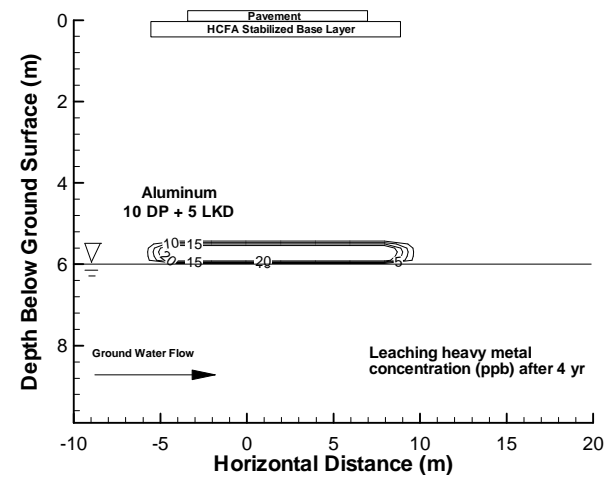
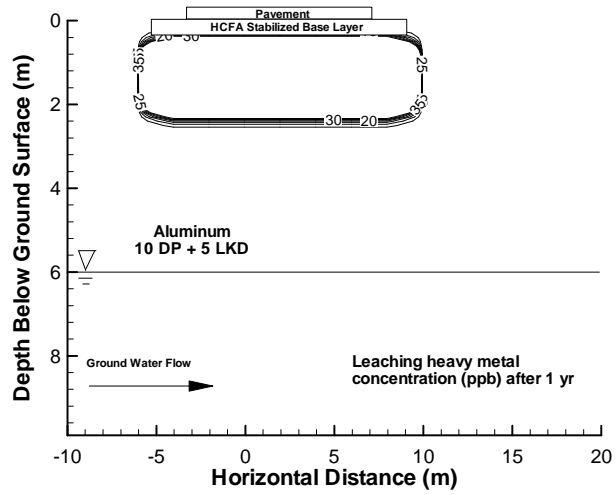


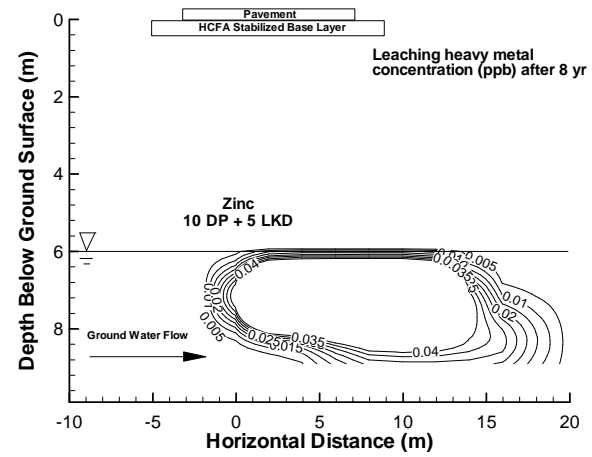
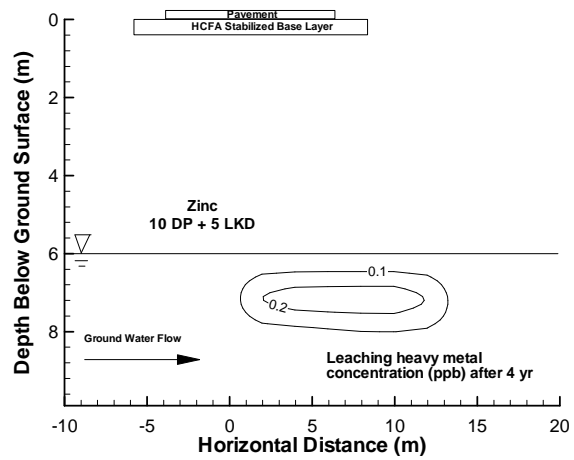
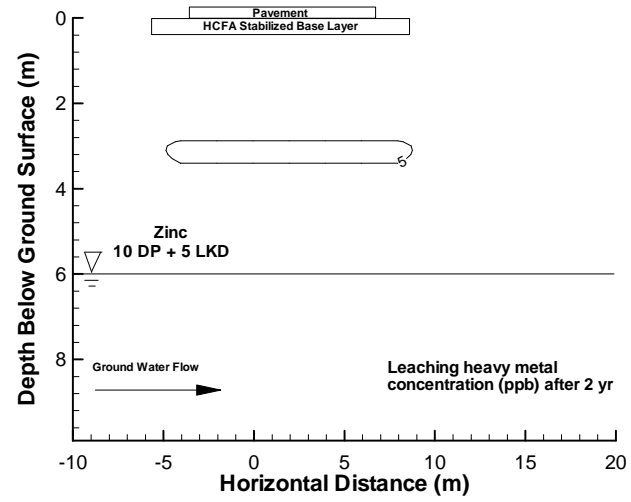
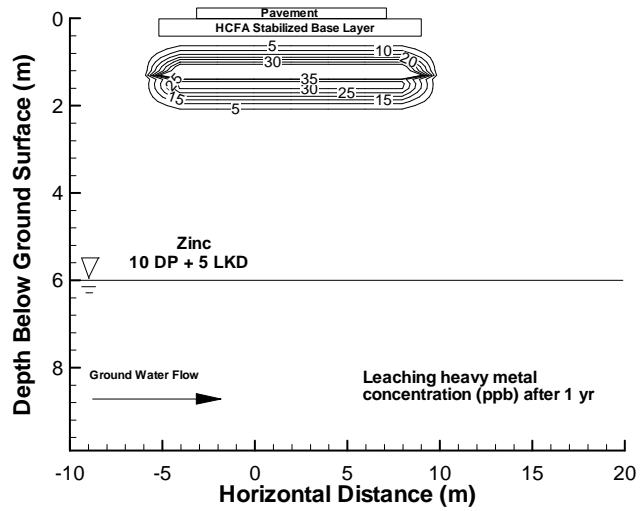


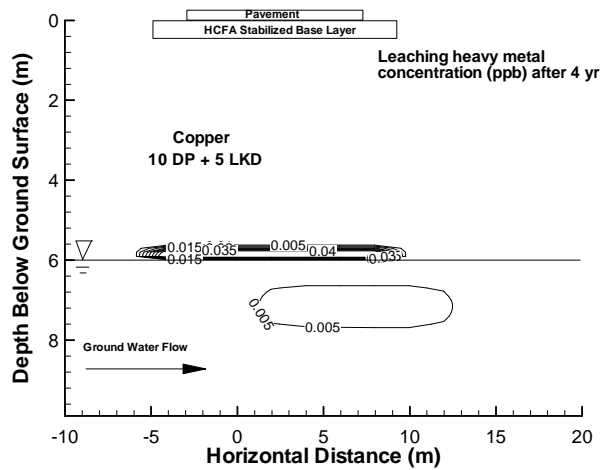
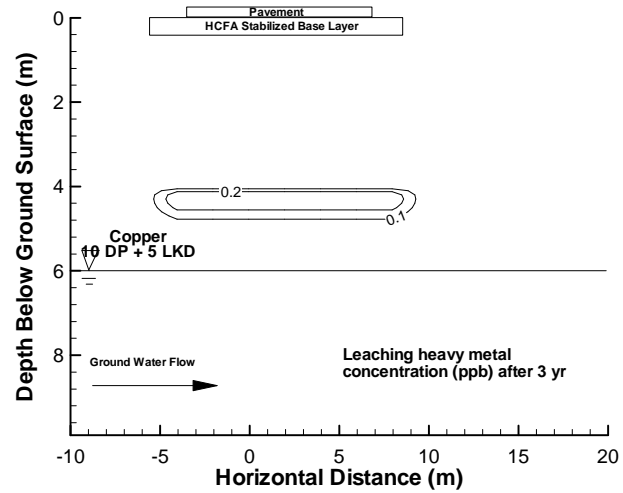
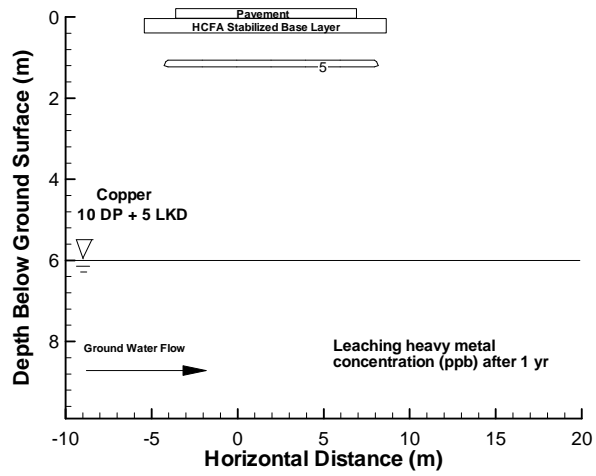




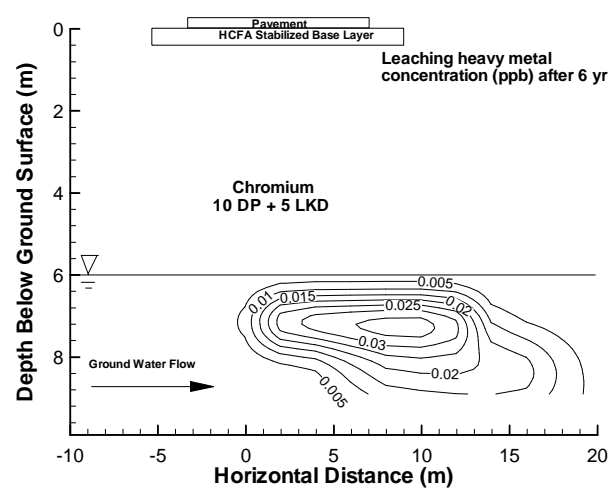
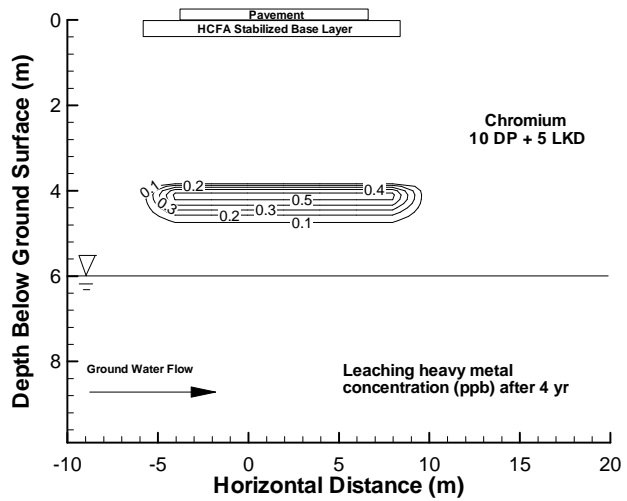
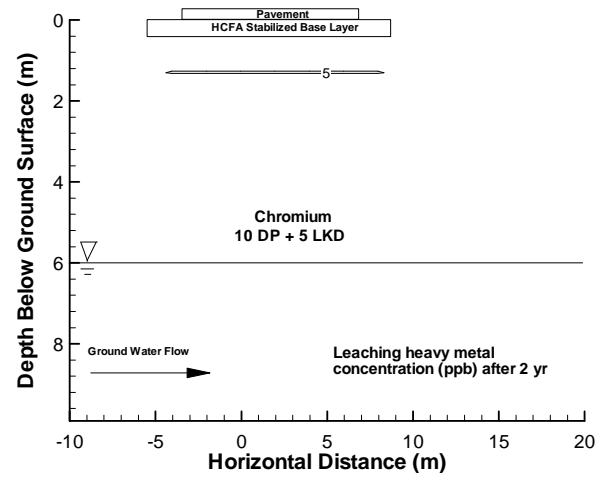
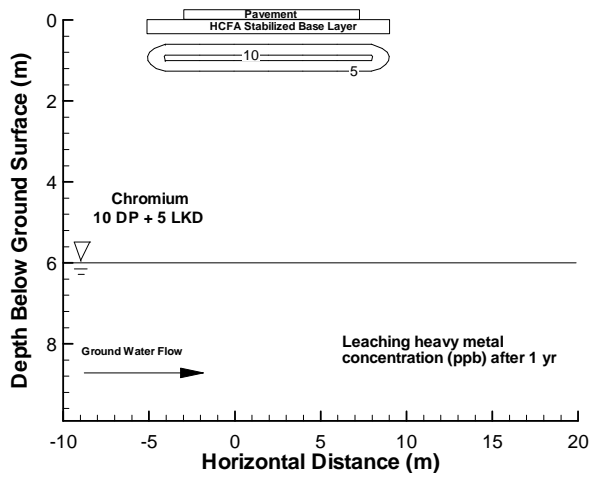


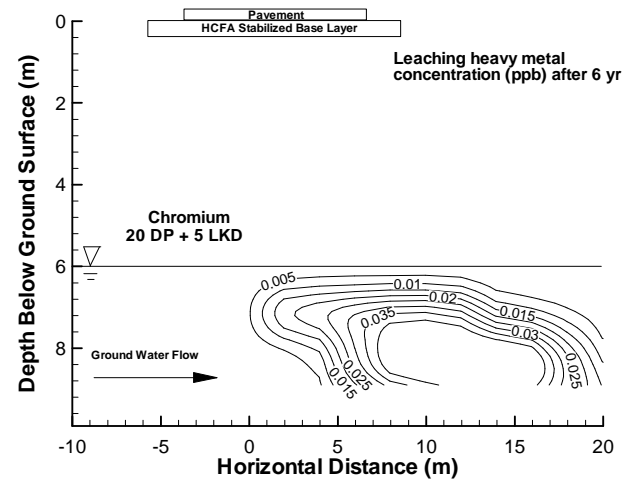
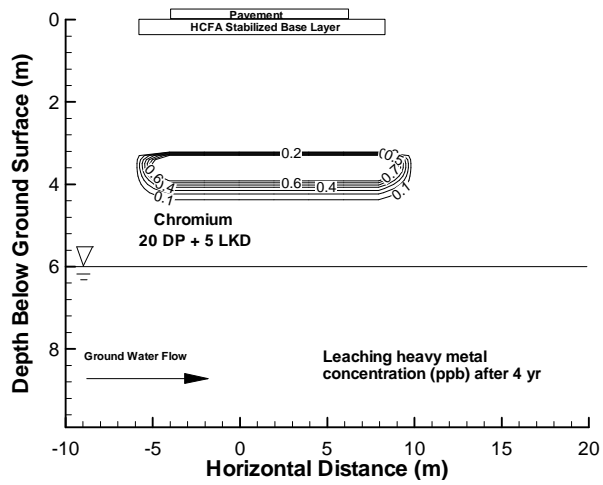
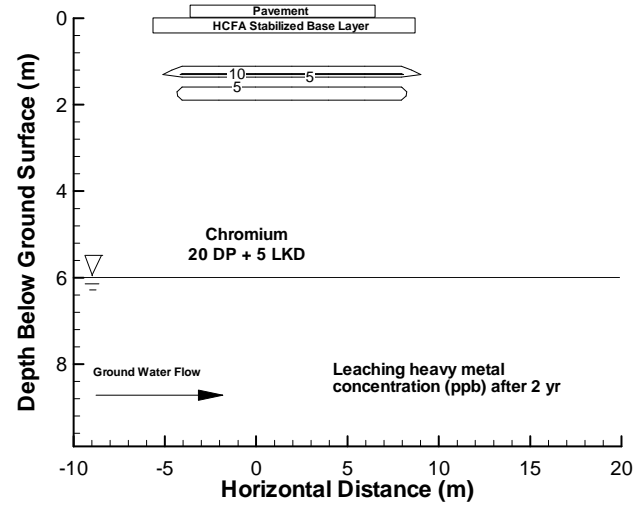
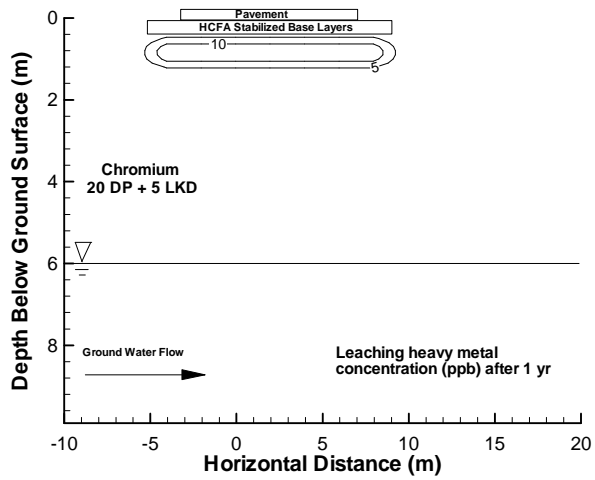


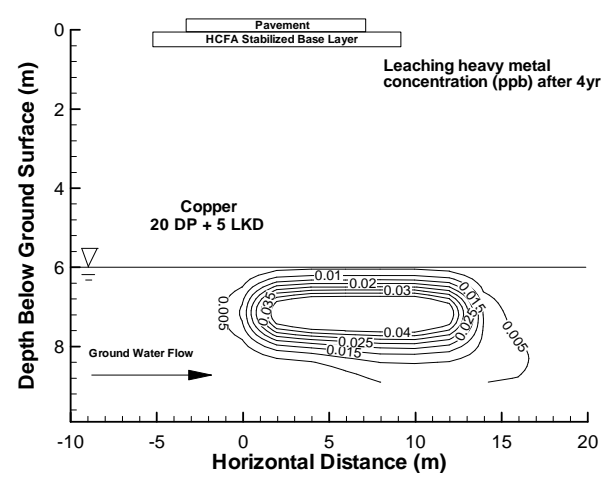
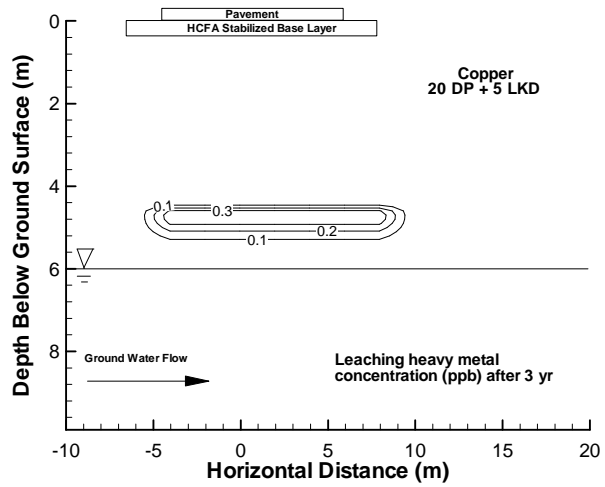
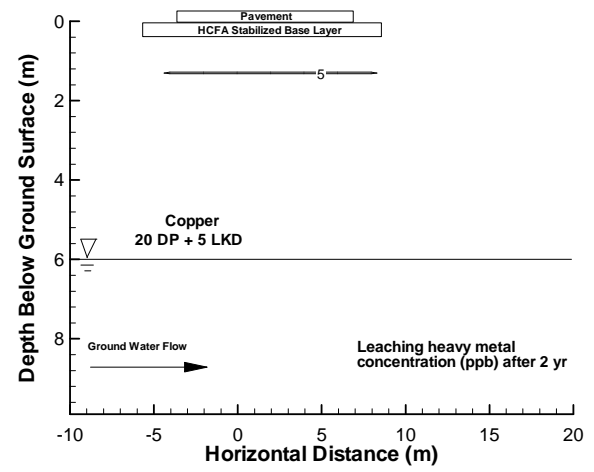
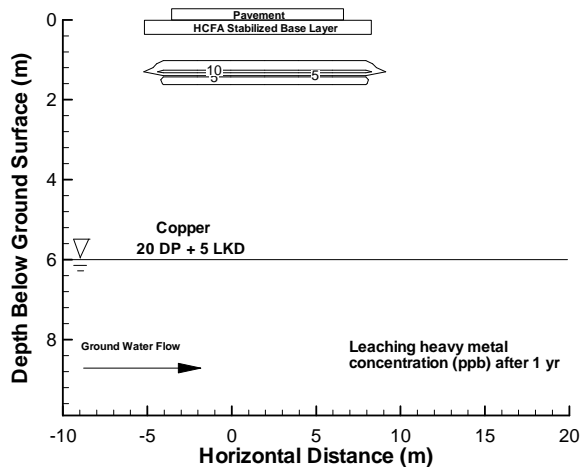


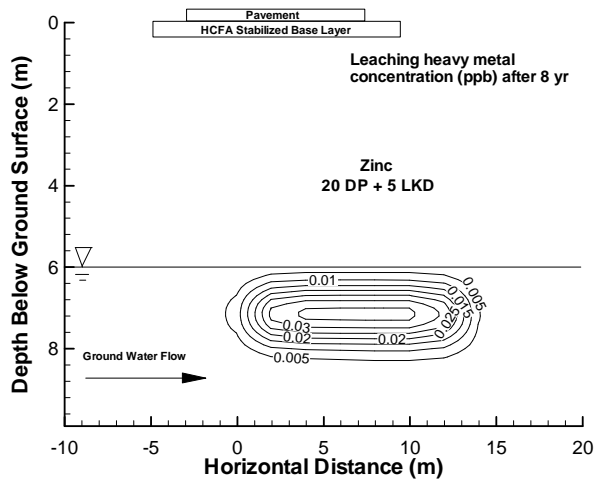
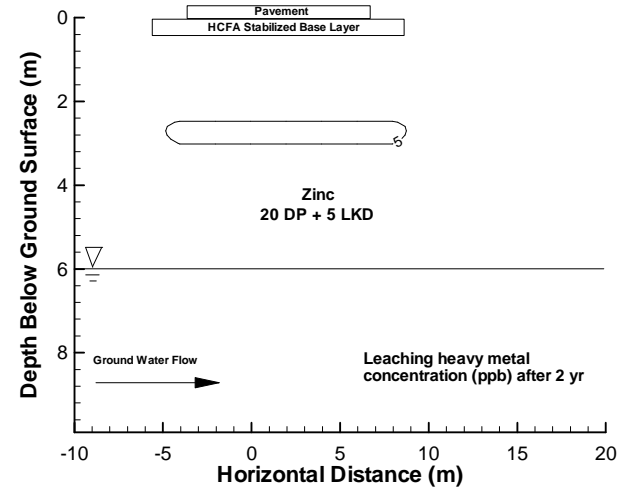
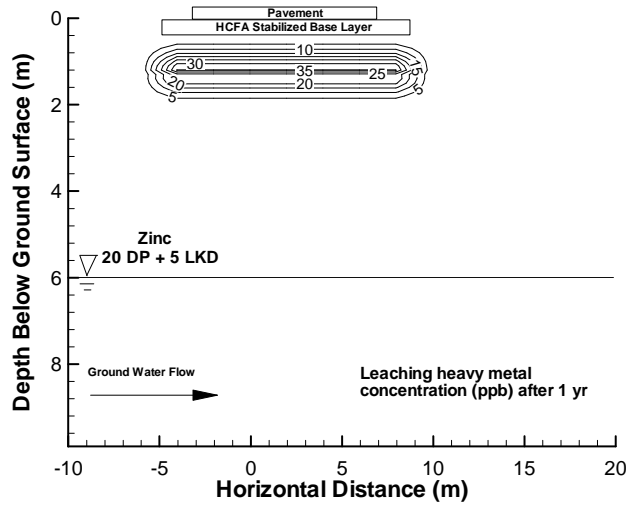


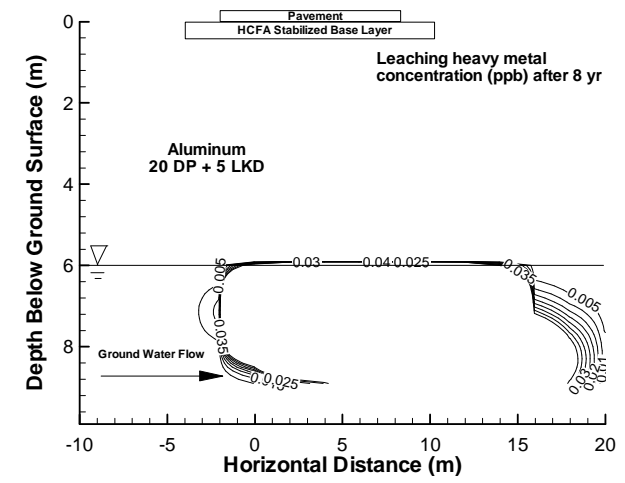
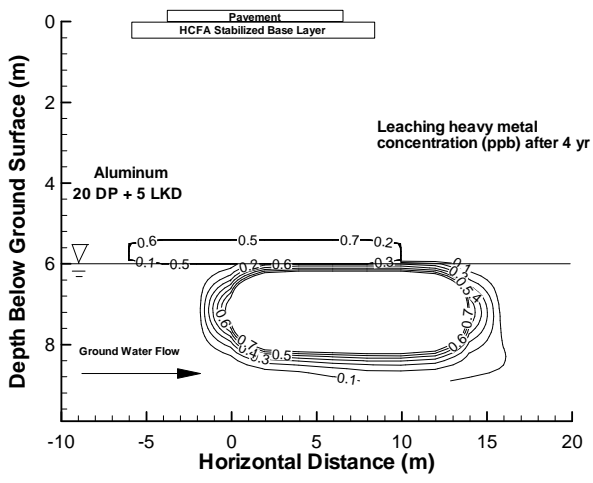
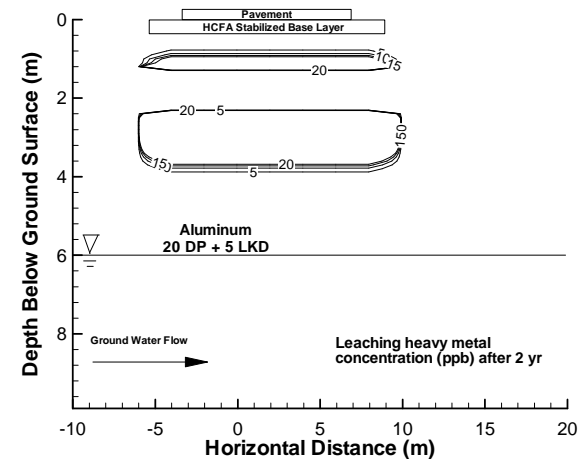
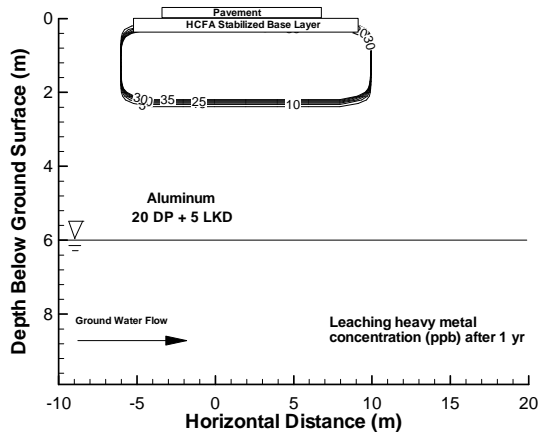












APPENDIX C: MINTEQA2 GEOCHEMICAL ANALYSIS OF  
THE SPECIES OF THE LEACHED METALS

Table 1. Speciation of As, Cr, Mn, and Se calculated using MINTEQA2: Brandon Shores

Species	Concentration (mol/L)			
	S-10 BS	S-20 BS	S-40 BS	100 BS
AsO <sub>4</sub> <sup>-3</sup>	1.01E-13	2.95E-13	2.03E-11	1.89E-10
Cr(OH) <sub>2</sub> <sup>+1</sup>	5.38E-09	4.28E-09	3.38E-08	4.22E-08
Cr(OH) <sub>3</sub> (aq)	2.61E-09	1.49E-09	9.71E-08	9.62E-08
Cr(OH) <sub>4</sub> <sup>-</sup>	1.32E-14	5.77E-15	3.02E-12	2.72E-12
Cr <sup>+3</sup>	7.33E-11	1.36E-10	1.46E-11	4.03E-11
Cr <sub>2</sub> (OH) <sub>2</sub> <sup>+4</sup>	6.40E-14	1.14E-13	8.96E-14	4.37E-13
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	9.82E-34	3.31E-35	2.54E-24	8.86E-25
Cr <sub>3</sub> (OH) <sub>4</sub> <sup>+5</sup>	1.32E-17	2.39E-17	1.34E-16	1.31E-15
CrO <sub>4</sub> <sup>-2</sup>	2.75E-18	3.99E-19	8.74E-13	4.94E-13
CrOH <sup>+2</sup>	1.22E-08	1.43E-08	1.34E-08	2.35E-08
H <sup>+1</sup>	9.16E-07	1.27E-06	1.55E-07	1.93E-07
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	5.36E-22	4.02E-21	7.05E-23	7.83E-22
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	1.26E-07	5.22E-07	6.04E-07	4.86E-06
H <sub>2</sub> CrO <sub>4</sub> (aq)	2.00E-24	4.63E-25	1.62E-20	9.93E-21
H <sub>2</sub> SeO <sub>3</sub> (aq)	1.29E-10	2.24E-10	1.92E-11	2.13E-11
H <sub>3</sub> AsO <sub>3</sub>	5.43E-19	5.32E-18	1.16E-20	1.42E-19
H <sub>3</sub> AsO <sub>4</sub>	1.73E-11	9.30E-11	1.35E-11	1.19E-10
HAsO <sub>3</sub> <sup>-2</sup>	8.21E-30	5.02E-29	6.87E-30	7.74E-29
HAsO <sub>4</sub> <sup>-2</sup>	2.50E-08	8.38E-08	7.58E-07	6.19E-06
HCrO <sub>4</sub> <sup>-</sup>	4.62E-18	8.22E-19	2.31E-13	1.28E-13
HSeO <sub>3</sub> <sup>-1</sup>	4.41E-07	5.88E-07	4.02E-07	4.08E-07
HSeO <sub>4</sub> <sup>-1</sup>	2.73E-15	2.00E-15	9.05E-14	6.64E-14
Mn(OH) <sub>4</sub> <sup>-2</sup>	4.25E-29	1.16E-29	5.09E-26	1.00E-25
Mn <sup>+2</sup>	3.28E-05	2.97E-05	2.98E-05	1.12E-04
Mn <sup>+3</sup>	3.76E-23	3.97E-23	3.74E-23	1.88E-22
Mn <sub>2</sub> (OH) <sub>3</sub> <sup>+</sup>	1.02E-15	2.74E-16	1.63E-13	9.34E-13
Mn <sub>2</sub> OH <sup>+3</sup>	3.96E-14	2.48E-14	2.01E-13	2.54E-12

$\text{MnO}_4^-$	6.85E-49	5.15E-50	1.03E-42	8.87E-43
$\text{MnO}_4^{-2}$	1.97E-46	1.62E-47	3.11E-40	3.21E-40
$\text{MnOH}^+$	6.82E-10	4.17E-10	3.54E-09	9.46E-09
$\text{MnSeO}_4$ (aq)	2.96E-13	1.24E-13	4.91E-11	8.48E-11
$\text{OH}^-$	1.46E-08	1.12E-08	8.96E-08	8.09E-08
$\text{SeO}_3^{-2}$	3.38E-09	3.68E-09	1.96E-08	2.02E-08
$\text{SeO}_4^{-2}$	1.05E-10	6.27E-11	2.21E-08	1.65E-08



Table 2. Speciation of As, Cr, Mn, and Se calculated using MINTEQA2: Paul Smith Precipitator

	Concentration (mol/L)			
	S-10 PSP	S-20 PSP	S-40 PSP	100 PSP
$\text{AsO}_4^{-3}$	8.51E-13	8.70E-12	4.57E-10	3.3E-09
$\text{Cr}(\text{OH})_2^{+1}$	6.2E-09	1.58E-08	2.81E-08	1.3E-08
$\text{Cr}(\text{OH})_3(\text{aq})$	9.33E-09	3.72E-08	9.71E-08	9.5E-08
$\text{Cr}(\text{OH})_4^-$	1.52E-13	9.73E-13	3.62E-12	9.8E-12
$\text{Cr}^{+3}$	9.83E-12	1.07E-11	8.27E-12	1.3E-12
$\text{Cr}_2(\text{OH})_2^{+4}$	1.11E-14	3.27E-14	4.15E-14	5.3E-15
$\text{Cr}_2\text{O}_7^{-2}$	1.36E-28	8.94E-26	1.1E-23	2.1E-20
$\text{Cr}_3(\text{OH})_4^{+5}$	3.08E-18	2.48E-17	5.08E-17	6.3E-18
$\text{CrO}_4^{-2}$	3.36E-15	1.39E-13	2.18E-12	2.9E-10
$\text{CrOH}^{+2}$	4.71E-09	7.77E-09	9.22E-09	2.2E-09
$\text{H}^{+1}$	2.95E-07	1.88E-07	1.28E-07	5.8E-08
$\text{H}_2\text{AsO}_3^-$	3.86E-23	5.80E-23	7.73E-22	7.1E-23
$\text{H}_2\text{AsO}_4^-$	9.12E-08	3.44E-07	9.57E-06	5.3E-06
$\text{H}_2\text{CrO}_4(\text{aq})$	2.26E-22	3.58E-21	2.82E-20	4.1E-19
$\text{H}_2\text{SeO}_3(\text{aq})$	4.02E-11	7.01E-11	9.11E-10	1.4E-10
$\text{H}_3\text{AsO}_3$	1.21E-20	1.14E-20	1.06E-19	3.5E-21
$\text{H}_3\text{AsO}_4$	3.86E-12	9.10E-12	1.78E-10	3.6E-11
$\text{HAsO}_3^{-2}$	1.98E-30	4.86E-30	9E-29	2.7E-29
$\text{HAsO}_4^{-2}$	6.02E-08	3.71E-07	1.43E-05	2.6E-05
$\text{HCrO}_4^-$	1.68E-15	4.28E-14	4.81E-13	1.9E-11
$\text{HSeO}_3^{-1}$	4.44E-07	1.24E-06	2.3E-05	1E-05
$\text{HSeO}_4^{-1}$	2.75E-14	1.93E-13	7.46E-12	2E-11
$\text{Mn}(\text{OH})_4^{-2}$	1.19E-27	9.87E-27	5.03E-25	7.9E-24
$\text{Mn}^{+2}$	9.21E-06	1.21E-05	0.000141	6.1E-05
$\text{Mn}^{+3}$	1.16E-23	1.60E-23	1.75E-22	1.2E-22
$\text{Mn}_2(\text{OH})_3^+$	2.23E-15	1.43E-14	6.43E-12	9.1E-12

$\text{Mn}_2\text{OH}^{+3}$	1E-14	2.76E-14	5.39E-12	2.7E-12
$\text{MnO}_4^-$	1.82E-45	9.22E-44	2.13E-41	9.1E-39
$\text{MnO}_4^{-2}$	5.52E-43	2.88E-41	6.42E-39	3.7E-36
$\text{MnOH}^+$	5.72E-10	1.16E-09	2.03E-08	1.6E-08
$\text{MnSeO}_4$ (aq)	2.4E-12	3.34E-11	2.33E-08	3.9E-08
$\text{OH}^-$	4.71E-08	7.54E-08	1.08E-07	2.9E-07
$\text{SeO}_3^{-2}$	1.14E-08	5.20E-08	1.34E-06	1.9E-06
$\text{SeO}_4^{-2}$	3.54E-09	4.05E-08	2.18E-06	1.9E-05

Table 3. Speciation of As, Cr, Mn, and Se calculated using MINTEQA2: Dickerson Precipitator

	Concentration (mol/L)			
	S-10 DP	S-20 DP	S-40 DP	100 DP
$\text{AsO}_4^{-3}$	2.4E-13	2.51E-10	2.2E-10	1.2E-08
$\text{Cr}(\text{OH})_2^{+1}$	1.2E-08	1.67E-08	2.7E-08	1.4E-11
$\text{Cr}(\text{OH})_3(\text{aq})$	7.5E-09	9.67E-08	9.6E-08	1.3E-09
$\text{Cr}(\text{OH})_4^-$	5.4E-14	6.51E-12	4.2E-12	1.4E-12
$\text{Cr}^{+3}$	1.1E-10	2.14E-12	9.5E-12	6.9E-18
$\text{Cr}_2(\text{OH})_2^{+4}$	2.6E-13	7.83E-15	6E-14	2.1E-23
$\text{Cr}_2\text{O}_7^{-2}$	1.2E-31	1.05E-21	2.8E-23	9.2E-16
$\text{Cr}_3(\text{OH})_4^{+5}$	1.5E-16	7.48E-18	1E-16	1.7E-29
$\text{CrO}_4^{-2}$	4.6E-17	3.95E-11	4.2E-12	6E-07
$\text{CrOH}^{+2}$	2.1E-08	3.49E-09	9.2E-09	1.8E-13
$\text{H}^{+1}$	6.9E-07	7.64E-08	1.2E-07	4.7E-09
$\text{H}_2\text{AsO}_3^-$	2.6E-22	3.54E-23	1.8E-22	2.4E-26
$\text{H}_2\text{AsO}_4^-$	1.2E-07	1.33E-06	2.6E-06	2.4E-07
$\text{H}_2\text{CrO}_4(\text{aq})$	1.5E-23	1.48E-19	3.7E-20	8.5E-18
$\text{H}_2\text{SeO}_3(\text{aq})$	3.3E-10	7.23E-11	4.7E-10	1.5E-14
$\text{H}_3\text{AsO}_3$	1.8E-19	2.70E-21	2.1E-20	1.1E-25
$\text{H}_3\text{AsO}_4$	1.1E-11	1.36E-11	4.2E-11	1.5E-13
$\text{HAsO}_3^{-2}$	6.1E-30	7.93E-30	2.6E-29	8.8E-32
$\text{HAsO}_4^{-2}$	3.5E-08	3.82E-06	4.9E-06	1.1E-05
$\text{HCrO}_4^-$	5E-17	4.54E-12	7.3E-13	4.2E-09
$\text{HSeO}_3^{-1}$	1.6E-06	3.29E-06	1.4E-05	1.1E-08
$\text{HSeO}_4^{-1}$	1.9E-14	3.23E-12	5.3E-12	2.8E-12
$\text{Mn}(\text{OH})_4^{-2}$	2.2E-28	7.10E-25	7.3E-26	2.4E-22
$\text{Mn}^{+2}$	4.7E-05	2.18E-05	1.4E-05	1.1E-07
$\text{Mn}^{+3}$	6.4E-23	3.20E-23	2.2E-23	1.6E-25
$\text{Mn}_2(\text{OH})_3^+$	4.2E-15	6.37E-13	6.2E-14	6.6E-14

$\text{Mn}_2\text{OH}^{+3}$	1.1E-13	2.32E-13	6.3E-14	9.3E-17
$\text{MnO}_4^-$	1.2E-47	2.48E-40	3.9E-42	5.8E-33
$\text{MnO}_4^{-2}$	3.7E-45	8.26E-38	1.3E-39	2E-30
$\text{MnOH}^+$	1.2E-09	4.92E-09	1.9E-09	3.9E-10
$\text{MnSeO}_4$ (aq)	3.4E-12	2.27E-09	1.4E-09	1.6E-10
$\text{OH}^-$	2.1E-08	1.93E-07	1.2E-07	3.1E-06
$\text{SeO}_3^{-2}$	1.9E-08	3.69E-07	1E-06	2E-08
$\text{SeO}_4^{-2}$	1.1E-09	1.82E-06	2E-06	2.6E-05

Table 4. Speciation of As, Cr, Mn, and Se calculated using MINTEQA2: Morgantown

	Concentration (mol/L)			
	S-10 MT	S-20 MT	S-40 MT	100 MT
AsO <sub>4</sub> <sup>-3</sup>	2.3E-11	8.88E-09	7.8E-08	3.1E-07
Cr(OH) <sub>2</sub> <sup>+1</sup>	6.5E-09	1.56E-14	6.2E-16	3.5E-19
Cr(OH) <sub>3</sub> (aq)	9.7E-08	8.13E-12	6.3E-13	1.1E-15
Cr(OH) <sub>4</sub> <sup>-</sup>	1.7E-11	5.53E-14	8.4E-15	5.4E-17
Cr <sup>+3</sup>	1.3E-13	3.17E-22	3.3E-24	2.1E-28
Cr <sub>2</sub> (OH) <sub>2</sub> <sup>+4</sup>	1.9E-16	1.43E-30	6E-34	2.5E-41
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	2E-18	6.30E-14	8E-14	5.3E-15
Cr <sub>3</sub> (OH) <sub>4</sub> <sup>+5</sup>	7.2E-20	1.84E-39	3.1E-44	9.3E-55
CrO <sub>4</sub> <sup>-2</sup>	4.5E-09	3.21E-05	7E-05	6.5E-05
CrOH <sup>+2</sup>	5.4E-10	3.92E-17	8E-19	1.5E-22
H <sup>+1</sup>	3E-08	8.39E-10	4.3E-10	1.3E-10
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	7.2E-26	1.04E-29	6.3E-30	1.5E-31
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	1.8E-08	3.55E-09	8.2E-09	2.2E-09
H <sub>2</sub> CrO <sub>4</sub> (aq)	2.5E-18	1.08E-17	6.2E-18	4.4E-19
H <sub>2</sub> SeO <sub>3</sub> (aq)	7.4E-13	1.18E-18	7E-19	1.6E-20
H <sub>3</sub> AsO <sub>3</sub>	2.1E-24	7.84E-30	2.5E-30	1.6E-32
H <sub>3</sub> AsO <sub>4</sub>	7.1E-14	3.61E-16	4.3E-16	3.3E-17
HAsO <sub>3</sub> <sup>-2</sup>	4.2E-32	2.56E-34	3E-34	2.7E-35
HAsO <sub>4</sub> <sup>-2</sup>	1.3E-07	1.12E-06	5.1E-06	5.1E-06
HCrO <sub>4</sub> <sup>-</sup>	2E-10	3.36E-08	3.8E-08	9.4E-09
HSeO <sub>3</sub> <sup>-1</sup>	8.7E-08	5.41E-12	6.3E-12	4.9E-13
HSeO <sub>4</sub> <sup>-1</sup>	5.6E-13	4.84E-14	2.1E-13	1.9E-13
Mn(OH) <sub>4</sub> <sup>-2</sup>	1.2E-24	1.71E-21	3.3E-21	1.3E-20
Mn <sup>+2</sup>	8.4E-07	6.34E-10	8.5E-11	2.5E-12
Mn <sup>+3</sup>	1.2E-24	1.17E-27	1.6E-28	5.4E-30
Mn <sub>2</sub> (OH) <sub>3</sub> <sup>+</sup>	1.6E-14	3.38E-16	4.6E-17	1.2E-18
Mn <sub>2</sub> OH <sup>+3</sup>	8.8E-16	1.95E-20	6.9E-22	2.1E-24

$\text{MnO}_4^-$	1.8E-38	4.33E-29	1.2E-27	5.6E-25
$\text{MnO}_4^{2-}$	6E-36	1.66E-26	4.7E-25	2.4E-22
$\text{MnOH}^+$	4.8E-10	1.19E-11	3.1E-12	2.8E-13
$\text{MnSeO}_4$ (aq)	3.8E-11	7.42E-14	8.6E-14	6.5E-15
$\text{OH}^-$	5E-07	1.93E-05	3.8E-05	0.00013
$\text{SeO}_3^{2-}$	2.5E-08	6.67E-11	1.5E-10	4.4E-11
$\text{SeO}_4^{2-}$	8.2E-07	2.99E-06	2.6E-05	8.6E-05

Table 5. Speciation of As, Cr, Mn, and Se calculated using MINTEQA2: Columbia

	Concentration (mol/L)			
	S-10 Co	S-20 Co	S-40 Co	100 Co
AsO <sub>4</sub> <sup>-3</sup>	3.7E-07	7.52E-07	1.1E-06	7.3E-07
Cr(OH) <sub>2</sub> <sup>+1</sup>	2.2E-32	4.06E-30	1.4E-35	5.2E-35
Cr(OH) <sub>3</sub> (aq)	8E-27	6.55E-25	1.5E-29	6.1E-29
Cr(OH) <sub>4</sub> <sup>-</sup>	3.5E-26	1.38E-24	2.1E-28	1.1E-27
Cr <sup>+3</sup>	7.8E-46	8.64E-43	7E-50	2.5E-49
Cr <sub>2</sub> (OH) <sub>2</sub> <sup>+4</sup>	4.1E-72	1.01E-66	2.9E-79	4.8E-78
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	1.9E-21	3.40E-20	7.9E-23	4.7E-21
Cr <sub>3</sub> (OH) <sub>4</sub> <sup>+5</sup>	6E-99	3.41E-91	4E-109	3E-107
CrO <sub>4</sub> <sup>-2</sup>	3.4E-06	7.29E-06	2.4E-06	2.3E-05
CrOH <sup>+2</sup>	7.6E-38	3.30E-35	1.7E-41	6.1E-41
H <sup>+1</sup>	1.2E-12	2.71E-12	4.1E-13	3.6E-13
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	3E-39	9.66E-38	6.5E-41	1.9E-41
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	4.5E-13	3.15E-12	9.6E-14	3.6E-14
H <sub>2</sub> CrO <sub>4</sub> (aq)	3.1E-24	2.57E-23	1.8E-25	1.1E-24
H <sub>2</sub> SeO <sub>3</sub> (aq)	1.8E-30	2.30E-28	2.3E-32	1.4E-31
H <sub>3</sub> AsO <sub>3</sub>	3.6E-42	2.36E-40	2.3E-44	5.5E-45
H <sub>3</sub> AsO <sub>4</sub>	7.2E-23	1.04E-21	4.6E-24	1.5E-24
HAsO <sub>3</sub> <sup>-2</sup>	4.4E-41	7.34E-40	3.4E-42	1.2E-42
HAsO <sub>4</sub> <sup>-2</sup>	8.5E-08	3.08E-07	6.6E-08	3.1E-08
HCrO <sub>4</sub> <sup>-</sup>	6.1E-12	2.47E-11	1.2E-12	8.8E-12
HSeO <sub>3</sub> <sup>-1</sup>	5.2E-21	3.27E-19	2.3E-22	1.6E-21
HSeO <sub>4</sub> <sup>-1</sup>	2E-17	2.79E-16	8.9E-18	8.3E-17
Mn(OH) <sub>4</sub> <sup>-2</sup>	5.2E-20	6.03E-20	2.1E-21	2.4E-21
Mn <sup>+2</sup>	1E-19	2.45E-18	4.1E-23	2.7E-23
Mn <sup>+3</sup>	1.6E-37	4.53E-36	8E-41	6E-41
Mn <sub>2</sub> (OH) <sub>3</sub> <sup>+</sup>	3.2E-27	1.48E-25	1.2E-32	6.2E-33
Mn <sub>2</sub> OH <sup>+3</sup>	3.2E-37	8.98E-35	1.7E-43	8.6E-44

$\text{MnO}_4^-$	2.8E-16	1.39E-17	9.8E-16	1.8E-15
$\text{MnO}_4^{2-}$	9.6E-14	5.32E-15	3.9E-13	7.6E-13
$\text{MnOH}^+$	1.4E-18	1.42E-17	1.6E-21	1.1E-21
$\text{MnSeO}_4$ (aq)	3.9E-24	5.11E-22	1.7E-27	1E-26
$\text{OH}^-$	0.01233	5.98E-03	0.04085	0.04833
$\text{SeO}_3^{2-}$	3.8E-17	1.24E-15	6.1E-18	5.4E-17
$\text{SeO}_4^{2-}$	7.4E-07	5.33E-06	1.2E-06	1.4E-05



Table 6. Speciation of Cu, Cr, Fe, Mn, Sb and V calculated using MINTEQA2: BS+LKD

	Concentration (mol/L)			
	10 BS + 2.5 LKD	10 BS + 5 LKD	20 BS + 5 LKD	100 BS
$\text{Cr}(\text{OH})_2^{+1}$	1.40E-29	1.35E-32	1.14E-24	4.93E-15
$\text{Cr}(\text{OH})_3$ (aq)	6.17E-24	1.40E-26	1.22E-18	6.93E-13
$\text{Cr}(\text{OH})_4^-$	3.43E-23	2.09E-25	1.77E-17	1.21E-15
$\text{Cr}^{+3}$	3.70E-43	8.23E-47	5.93E-39	1.25E-21
$\text{Cr}_2(\text{OH})_2^{+4}$	1.39E-66	3.93E-73	2.12E-57	1.61E-30
$\text{Cr}_2\text{O}_7^{-2}$	2.99E-23	8.01E-24	1.05E-23	7.13E-16
$\text{Cr}_3(\text{OH})_4^{+5}$	1.45E-90	5.75E-100	2.24E-76	5.68E-40
$\text{CrO}_4^{-2}$	5.67E-07	8.10E-07	8.91E-07	8.67E-07
$\text{CrOH}^{+2}$	4.07E-35	1.79E-38	1.43E-30	4.47E-17
$\text{Cu}(\text{OH})_2$ (aq)	4.58E-10	1.45E-09	4.73E-12	2.38E-11
$\text{Cu}(\text{OH})_3^-$	2.86E-08	2.42E-07	7.67E-10	4.67E-13
$\text{Cu}(\text{OH})_4^{-2}$	5.76E-09	1.41E-07	4.20E-10	2.92E-17
$\text{Cu}^{+1}$	6.16E-21	1.91E-21	2.52E-21	1.94E-17
$\text{Cu}^{+2}$	1.23E-17	7.57E-18	2.25E-20	6.25E-12
$\text{Cu}_2(\text{OH})_2^{+2}$	3.13E-21	6.19E-21	5.94E-26	8.23E-17
$\text{Cu}_2\text{OH}^{+3}$	4.66E-29	4.64E-29	4.03E-34	3.78E-21
$\text{Cu}_3(\text{OH})_4^{+2}$	1.26E-24	8.01E-24	2.48E-31	1.72E-21
$\text{CuOH}^+$	2.51E-13	3.37E-13	1.07E-15	4.09E-11
$\text{Fe}(\text{OH})_2$ (aq)	1.06E-26	2.41E-27	1.01E-24	2.05E-25
$\text{Fe}(\text{OH})_2^+$	3.46E-19	1.44E-19	1.41E-19	1.09E-15
$\text{Fe}(\text{OH})_3^-$	5.41E-25	3.29E-25	1.34E-22	3.28E-27
$\text{Fe}(\text{OH})_3$ (aq)	1.92E-16	1.89E-16	1.91E-16	1.92E-16
$\text{Fe}(\text{OH})_4^-$	6.15E-12	1.62E-11	1.59E-11	1.94E-15
$\text{Fe}^{+2}$	5.22E-30	2.30E-31	8.86E-29	9.87E-22
$\text{Fe}^{+3}$	7.45E-37	7.17E-38	5.96E-38	2.25E-26
$\text{Fe}_2(\text{OH})_2^{+4}$	7.15E-52	3.80E-53	2.74E-53	6.59E-38
$\text{Fe}_3(\text{OH})_4^{+5}$	3.41E-67	1.10E-68	6.61E-69	9.49E-50
$\text{FeCrO}_4^+$	1.26E-36	9.88E-38	1.16E-37	6.19E-26
$\text{FeOH}^+$	1.34E-27	1.29E-28	5.27E-26	8.14E-23

$\text{FeOH}^{+2}$	2.90E-27	5.55E-28	5.11E-28	2.84E-20
$\text{H}^{+1}$	9.95E-13	4.15E-13	4.07E-13	3.13E-09
$\text{H}_2\text{CrO}_4$ (aq)	2.91E-25	5.38E-26	6.48E-26	4.55E-18
$\text{H}_2\text{V}_2\text{O}_4^{+2}$	1.09E-22	2.08E-23	1.92E-23	1.07E-15
$\text{HCrO}_4^-$	7.41E-13	3.66E-13	4.28E-13	3.64E-09
$\text{Mn}(\text{OH})_4^{-2}$	3.42E-17	1.49E-17	2.31E-14	6.48E-23
$\text{Mn}^{+2}$	2.65E-17	2.88E-19	4.49E-16	5.00E-09
$\text{Mn}^{+3}$	1.82E-36	4.31E-38	1.45E-37	5.48E-26
$\text{Mn}_2(\text{OH})_3^+$	3.71E-22	5.03E-25	1.40E-18	4.34E-16
$\text{Mn}_2\text{OH}^{+3}$	2.79E-32	8.74E-36	2.07E-29	3.14E-19
$\text{MnO}_4^-$	4.15E-20	9.51E-18	1.25E-27	9.42E-29
$\text{MnO}_4^{-2}$	3.87E-16	5.92E-14	3.04E-21	5.28E-27
$\text{MnOH}^+$	4.28E-16	1.02E-17	1.69E-14	2.60E-11
$\text{OH}^-$	1.59E-02	4.18E-02	4.10E-02	5.00E-06
$\text{Sb}(\text{OH})_2^+$	1.37E-41	6.14E-44	5.82E-38	9.15E-31
$\text{Sb}(\text{OH})_3$	5.66E-31	5.97E-33	5.82E-27	1.20E-23
$\text{Sb}(\text{OH})_4^{-1}$	1.37E-30	3.88E-32	3.67E-26	9.15E-27
$\text{Sb}(\text{OH})_5$ (aq)	7.18E-17	1.42E-17	7.96E-17	4.09E-12
$\text{Sb}(\text{OH})_6^{-1}$	1.74E-07	9.23E-08	5.03E-07	3.12E-06
$\text{V}(\text{OH})_2^+$	1.52E-27	1.47E-28	6.00E-26	9.26E-23
$\text{V}(\text{OH})_3^+$	3.72E-14	1.55E-14	1.52E-14	1.17E-10
$\text{V}^{+3}$	5.63E-44	1.25E-45	4.34E-43	3.28E-32
$\text{V}_2(\text{OH})_2^{+4}$	5.14E-67	1.46E-69	1.83E-64	1.76E-50
$\text{VO}^{+2}$	2.89E-20	5.53E-21	5.10E-21	2.84E-13
$\text{VOH}^{+2}$	1.16E-34	5.11E-36	1.96E-33	2.19E-26

Table 7. Speciation of Cu, Cr, Fe, Mn, Sb and V calculated using MINTEQA2: PS+LKD

	Concentration (mol/L)			
	10 PS + 2.5 LKD	10 PS + 5 LKD	20 PS + 5 LKD	100 PS
$\text{Cr}(\text{OH})_2^{+1}$	2.62E-27	3.09E-30	6.01E-27	1.27E-13
$\text{Cr}(\text{OH})_3$ (aq)	1.78E-21	3.18E-24	6.18E-21	1.78E-12
$\text{Cr}(\text{OH})_4^-$	1.61E-20	4.78E-23	9.31E-20	3.12E-16
$\text{Cr}^{+3}$	3.25E-41	1.98E-44	3.91E-41	3.29E-18
$\text{Cr}_2(\text{OH})_2^{+4}$	2.57E-62	2.24E-68	8.72E-62	1.10E-25
$\text{Cr}_2\text{O}_7^{-2}$	1.69E-24	7.05E-25	1.09E-24	2.05E-13
$\text{Cr}_3(\text{OH})_4^{+5}$	5.93E-84	7.87E-93	6.06E-83	1.02E-33
$\text{CrO}_4^{-2}$	2.23E-07	2.43E-07	3.04E-07	1.48E-06
$\text{CrOH}^{+2}$	5.11E-33	4.19E-36	8.20E-33	1.16E-14
$\text{Cu}(\text{OH})_2$ (aq)	3.61E-11	2.12E-10	2.48E-09	9.59E-11
$\text{Cu}(\text{OH})_3^-$	3.66E-09	3.57E-08	4.18E-07	1.89E-13
$\text{Cu}(\text{OH})_4^{-2}$	1.24E-09	2.11E-08	2.49E-07	1.19E-18
$\text{Cu}^{+1}$	3.97E-21	2.59E-21	3.52E-19	1.94E-16
$\text{Cu}^{+2}$	4.21E-19	1.14E-18	1.34E-17	2.54E-09
$\text{Cu}_2(\text{OH})_2^{+2}$	8.46E-24	1.36E-22	1.87E-20	1.35E-13
$\text{Cu}_2\text{OH}^{+3}$	8.81E-32	1.05E-30	1.46E-28	6.28E-17
$\text{Cu}_3(\text{OH})_4^{+2}$	2.69E-28	2.57E-26	4.15E-23	1.14E-17
$\text{CuOH}^+$	1.28E-14	4.96E-14	5.82E-13	1.65E-09
$\text{Fe}(\text{OH})_2$ (aq)	1.33E-25	2.21E-26	1.88E-27	5.07E-26
$\text{Fe}(\text{OH})_2^+$	2.23E-19	1.45E-19	1.07E-21	1.09E-14
$\text{Fe}(\text{OH})_3^-$	1.11E-23	3.04E-24	2.60E-25	8.15E-29
$\text{Fe}(\text{OH})_3$ (aq)	1.91E-16	1.89E-16	1.39E-18	1.92E-16
$\text{Fe}(\text{OH})_4^-$	9.95E-12	1.63E-11	1.20E-13	1.94E-16
$\text{Fe}^{+2}$	2.85E-29	2.17E-30	1.87E-31	2.47E-20
$\text{Fe}^{+3}$	2.25E-37	7.55E-38	5.66E-40	2.29E-23
$\text{Fe}_2(\text{OH})_2^{+4}$	1.57E-52	4.18E-53	2.33E-57	6.82E-34
$\text{Fe}_3(\text{OH})_4^{+5}$	5.68E-68	1.27E-68	5.33E-75	1.00E-44
$\text{FeCrO}_4^+$	1.17E-37	2.91E-38	2.66E-40	1.05E-22
$\text{FeOH}^+$	1.09E-26	1.19E-27	1.02E-28	2.02E-22

$\text{FeOH}^{+2}$	1.25E-27	5.68E-28	4.21E-30	2.87E-18
$\text{H}^{+1}$	6.41E-13	4.18E-13	4.18E-13	3.14E-08
$\text{H}_2\text{CrO}_4$ (aq)	4.18E-26	1.57E-26	1.95E-26	7.69E-16
$\text{H}_2\text{V}_2\text{O}_4^{+2}$	4.71E-23	2.13E-23	2.15E-23	1.08E-13
$\text{HCrO}_4^-$	1.73E-13	1.08E-13	1.34E-13	6.16E-08
$\text{Mn}(\text{OH})_4^{-2}$	1.18E-15	5.66E-16	6.63E-15	1.62E-25
$\text{Mn}^{+2}$	1.44E-16	1.10E-17	1.29E-16	1.25E-07
$\text{Mn}^{+3}$	5.48E-37	1.84E-37	1.87E-37	5.59E-23
$\text{Mn}_2(\text{OH})_3^+$	3.81E-20	7.01E-22	9.47E-20	2.67E-16
$\text{Mn}_2\text{OH}^{+3}$	1.35E-30	1.28E-32	1.75E-30	1.97E-17
$\text{MnO}_4^-$	2.63E-24	5.42E-21	2.98E-25	2.50E-27
$\text{MnO}_4^{-2}$	5.23E-19	3.15E-16	2.03E-19	3.50E-27
$\text{MnOH}^+$	3.49E-15	3.82E-16	4.44E-15	6.46E-11
$\text{OH}^-$	2.57E-02	4.21E-02	4.21E-02	5.01E-07
$\text{Sb}(\text{OH})_2^+$	9.76E-40	4.62E-42	1.87E-39	2.88E-30
$\text{Sb}(\text{OH})_3$	6.21E-29	4.44E-31	1.79E-28	3.77E-24
$\text{Sb}(\text{OH})_4^{-1}$	2.45E-28	2.91E-30	1.18E-27	2.88E-28
$\text{Sb}(\text{OH})_5$ (aq)	4.93E-17	1.25E-17	3.74E-17	2.09E-11
$\text{Sb}(\text{OH})_6^{-1}$	1.95E-07	8.21E-08	2.46E-07	1.60E-06
$\text{V}(\text{OH})_2^+$	1.24E-26	1.36E-27	1.58E-26	2.30E-22
$\text{V}(\text{OH})_3^+$	2.40E-14	1.56E-14	1.57E-14	1.17E-09
$\text{V}^{+3}$	2.15E-43	1.21E-44	1.43E-43	8.28E-30
$\text{V}_2(\text{OH})_2^{+4}$	1.80E-65	1.35E-67	1.88E-65	1.12E-47
$\text{VO}^{+2}$	1.25E-20	5.67E-21	5.71E-21	2.86E-11
$\text{VOH}^{+2}$	6.32E-34	4.81E-35	5.63E-34	5.47E-25

Table 8. Speciation of Cu, Cr, Fe, Mn, Sb and V calculated using MINTEQA2: PS+LKD

	Concentration (mol/L)			
	10 DP + 2.5 LKD	10 DP + 5 LKD	20 DP + 5 LKD	100 DP
$\text{Cr}(\text{OH})_2^{+1}$	7.40E-25	1.77E-29	1.74E-26	1.54E-10
$\text{Cr}(\text{OH})_3$ (aq)	3.09E-19	1.49E-23	2.35E-20	4.04E-09
$\text{Cr}(\text{OH})_4^-$	1.82E-18	1.73E-22	4.27E-19	1.50E-12
$\text{Cr}^{+3}$	2.73E-38	1.54E-43	5.71E-41	1.44E-15
$\text{Cr}_2(\text{OH})_2^{+4}$	6.91E-57	8.88E-67	3.12E-61	7.67E-20
$\text{Cr}_2\text{O}_7^{-2}$	8.28E-24	5.67E-24	3.29E-24	4.93E-13
$\text{Cr}_3(\text{OH})_4^{+5}$	5.31E-76	1.53E-90	5.02E-82	1.24E-24
$\text{CrO}_4^{-2}$	3.24E-07	5.26E-07	6.28E-07	5.01E-06
$\text{CrOH}^{+2}$	2.44E-30	2.85E-35	1.73E-32	8.05E-12
$\text{Cu}(\text{OH})_2$ (aq)	9.59E-12	1.98E-10	5.27E-10	6.38E-12
$\text{Cu}(\text{OH})_3^-$	6.32E-10	2.58E-08	1.08E-07	2.66E-14
$\text{Cu}(\text{OH})_4^{-2}$	1.44E-10	1.15E-08	7.42E-08	3.84E-19
$\text{Cu}^{+1}$	6.42E-21	3.19E-21	7.83E-20	1.02E-16
$\text{Cu}^{+2}$	3.08E-19	1.54E-18	1.59E-18	5.18E-11
$\text{Cu}_2(\text{OH})_2^{+2}$	1.66E-24	1.72E-22	4.67E-22	1.86E-16
$\text{Cu}_2\text{OH}^{+3}$	3.03E-32	1.51E-30	2.51E-30	5.45E-20
$\text{Cu}_3(\text{OH})_4^{+2}$	1.41E-29	3.02E-26	2.17E-25	1.06E-21
$\text{CuOH}^+$	5.55E-15	5.69E-14	9.44E-14	5.86E-11
$\text{Fe}(\text{OH})_2$ (aq)	4.93E-25	2.40E-26	9.07E-27	7.40E-25
$\text{Fe}(\text{OH})_2^+$	3.60E-19	1.79E-19	2.87E-21	5.72E-15
$\text{Fe}(\text{OH})_3^-$	2.66E-23	2.55E-24	1.52E-24	2.52E-27
$\text{Fe}(\text{OH})_3$ (aq)	1.90E-16	1.90E-16	4.88E-18	1.89E-16
$\text{Fe}(\text{OH})_4^-$	6.41E-12	1.27E-11	5.11E-13	4.05E-16
$\text{Fe}^{+2}$	2.90E-28	3.43E-30	5.02E-31	1.10E-19
$\text{Fe}^{+3}$	1.08E-36	1.27E-37	7.66E-40	4.37E-24
$\text{Fe}_2(\text{OH})_2^{+4}$	1.38E-51	7.68E-53	7.17E-57	8.98E-35
$\text{Fe}_3(\text{OH})_4^{+5}$	9.52E-67	2.48E-68	3.52E-74	9.98E-46
$\text{FeCrO}_4^+$	6.37E-37	1.33E-37	1.04E-39	3.90E-23
$\text{FeOH}^+$	6.58E-26	1.59E-27	3.76E-28	1.57E-21

$\text{FeOH}^{+2}$	3.42E-27	8.33E-28	8.26E-30	8.66E-19
$\text{H}^{+1}$	1.04E-12	5.16E-13	3.23E-13	1.65E-08
$\text{H}_2\text{CrO}_4$ (aq)	1.39E-25	5.89E-26	2.88E-26	5.37E-16
$\text{H}_2\text{V}_2\text{O}_4^{+2}$	1.29E-22	3.13E-23	1.21E-23	3.25E-14
$\text{HCrO}_4^-$	3.74E-13	3.12E-13	2.39E-13	9.12E-08
$\text{Mn}(\text{OH})_4^{-2}$	1.90E-15	3.56E-16	1.29E-14	1.15E-23
$\text{Mn}^{+2}$	1.47E-15	1.74E-17	9.94E-17	5.59E-07
$\text{Mn}^{+3}$	2.63E-36	3.08E-37	7.30E-38	1.06E-23
$\text{Mn}_2(\text{OH})_3^+$	8.58E-19	1.00E-21	1.37E-19	3.08E-14
$\text{Mn}_2\text{OH}^{+3}$	8.99E-29	2.48E-32	1.28E-30	8.21E-16
$\text{MnO}_4^-$	8.75E-27	3.13E-21	1.04E-25	1.09E-31
$\text{MnO}_4^{-2}$	4.35E-21	1.47E-16	1.12E-19	5.15E-30
$\text{MnOH}^+$	2.10E-14	5.08E-16	4.70E-15	5.02E-10
$\text{OH}^-$	1.65E-02	3.28E-02	5.16E-02	1.05E-06
$\text{Sb}(\text{OH})_2^+$	1.80E-38	7.43E-42	8.02E-40	4.89E-29
$\text{Sb}(\text{OH})_3$	7.01E-28	5.85E-31	1.01E-28	1.20E-22
$\text{Sb}(\text{OH})_4^{-1}$	1.80E-27	2.96E-30	8.02E-28	1.95E-26
$\text{Sb}(\text{OH})_5$ (aq)	4.00E-17	1.42E-17	1.12E-17	3.04E-12
$\text{Sb}(\text{OH})_6^{-1}$	1.03E-07	7.18E-08	8.92E-08	4.92E-07
$\text{V}(\text{OH})_2^+$	7.49E-26	1.81E-27	1.67E-26	1.79E-21
$\text{V}(\text{OH})_3^+$	3.88E-14	1.93E-14	1.21E-14	6.16E-10
$\text{V}^{+3}$	3.84E-42	2.19E-44	7.64E-44	2.34E-29
$\text{V}_2(\text{OH})_2^{+4}$	2.21E-63	2.89E-67	8.99E-66	3.24E-46
$\text{VO}^{+2}$	3.41E-20	8.31E-21	3.22E-21	8.64E-12
$\text{VOH}^{+2}$	6.44E-33	7.60E-35	4.35E-34	2.45E-24

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