**HEAVY METAL SORPTION AND HYDRAULIC
CONDUCTIVITY STUDIES USING THREE TYPES OF
BENTONITE ADMIXES**

by

FRANKY LI

B.A.Sc. (Civil Engineering), University of British Columbia, 1996

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF CIVIL ENGINEERING

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

October, 1999

© Franky Li, 1999

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of CIVIL ENGINEERING

The University of British Columbia
Vancouver, Canada

Date OCTOBER 14, 1999

ABSTRACT

This study investigated the sorption and migration behaviour of heavy metals permeating through clay barriers, the effect of heavy metals on clay barrier hydraulic conductivity, and the use of Forest soil and Spruce bark as potential clay barrier materials.

Bentonite, Forest soil, and Spruce bark were submitted to Batch adsorption testing to determine sorption capacities and investigate competition effects associated with multi-heavy-metal sorption. The heavy metal solutions consisted of single, binary, and ternary combinations of lead (*Pb*), copper (*Cu*), and (*Cd*) ranging from 0 - 1000 mg L⁻¹. According to sorption capacities, the heavy metals ranked as follows: Forest soil > bentonite $\cong$ Spruce bark. An equation based on the Freundlich equation was developed for describing multi-heavy-metal sorption, and expressed the following ranking in terms of sorption competitiveness: $Pb > Cu > Cd$.

A bentonite admix (100:8 ratio of sand:bentonite), Forest soil admix (100:7:1 ratio of sand:bentonite:Forest soil), and Spruce bark admix (100:7:1 ratio of sand:bentonite:Spruce bark) were submitted to Leaching cell testing to investigate the heavy metal compatibility of clay barriers. The admixes were compacted into rigid-walled cells and permeated with 500 mg L⁻¹ solutions of *Pb*, *Cu*, and *Cd*. The hydraulic conductivities of heavy metal leachates were $\approx$ 2 orders of magnitude greater than the blank (0.01 M calcium nitrate) leachate. The Forest soil admix ranked the best in terms of heavy metal retention capacity, and breakthrough points.

After each Leaching cell test, the admix samples were extruded and submitted to Selective Sequential Extractions (SSEs). The SSE determined the distribution of heavy metals amongst five soil components: cation exchangeable, carbonates, *Fe* and *Mn* oxides and hydroxides, organic matter, and the residual. The addition of Forest soil, and Spruce bark in clay barrier mixes promoted stronger heavy metal fixation. In

addition, the SSE results showed a linear relation between the sorption characteristics and sorption concentrations of the admixes.

The Leaching cell and SSE results showed that heavy metals followed unpredictable pathways, and caused significant short-circuiting. In terms of relative mobility, *Cd* was ≈ 1.5 times more mobile than *Cu*, and ≈ 4 times more mobile than *Pb*, respectively.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS	iv
LIST OF FIGURES	viii
LIST OF TABLES	x
ACKNOWLEDGMENTS	xii
CHAPTER 1 INTRODUCTION	1
1.1 STATEMENT OF PROBLEM	1
1.2 SCOPE AND OBJECTIVES	5
1.3 RESEARCH PLAN	7
1.4 RESEARCH CONTRIBUTIONS	9
1.5 ORGANIZATION OF THESIS.....	10
CHAPTER 2 BACKGROUND REVIEW	11
2.1 HEAVY METAL AND SOIL INTERACTIONS	11
2.1.1 Cation exchange	12
2.1.2 Inner-sphere complexation	12
2.1.3 Precipitation	14
2.1.4 The effect of solution pH	14
2.1.5 The effect of heavy metals on clay structure	15
2.2 STUDIES IN HEAVY METAL RETENTION SELECTIVITY	15
2.3 HEAVY METAL RETAINING SOILS AND MINERALS	17
2.4 HEAVY METAL COMPATIBILITY STUDIES	19
2.5 POTENTIAL NEW MATERIALS FOR CLAY BARRIERS	23
2.5.1 Soil organic matter	23
2.5.2 Spruce bark	25

CHAPTER 3	MATERIALS AND METHODS	26
3.1	CLAY BARRIER MATERIALS	26
3.1.1	Origins and Descriptions	26
3.1.2	Admixtures	27
3.1.3	Physical properties	27
3.1.4	Chemical properties	28
3.2	CHEMICAL SOLUTIONS	29
3.3	BATCH ADSORPTION TEST METHOD	30
3.3.1	Batch adsorption test program	30
3.3.2	Batch adsorption test procedure	33
3.4	LEACHING CELL TEST METHOD	36
3.4.1	Leaching cell program	36
3.4.2	Admix preparation for the Leaching cell test	38
3.4.3	Compaction procedure	39
3.4.4	Leaching cell test procedure	40
3.5	SELECTIVE SEQUENTIAL EXTRACTION METHOD	41
3.5.1	Sampling extruded Leaching cell samples	42
3.5.2	SSE procedure	44
CHAPTER 4	RESULTS AND DISCUSSION	48
4.1	SOIL MATERIALS	48
4.2	SORPTION CAPACITIES OF CLAY BARRIER MATERIALS DETERMINED FROM BATCH ADSORPTION TESTS	50
4.2.1	The multi-heavy-metal sorption model	50
4.2.1.1	<i>Isotherm equation selection and general observations</i>	51
4.2.1.2	<i>Modeling binary heavy metal sorption</i>	54
4.2.1.3	<i>Modeling ternary heavy metal sorption</i>	60
4.2.1.4	<i>Summary of sorption equations</i>	63
4.2.2	Heavy metal sorption capacities	64
4.2.2.1	<i>Ranking of materials</i>	66
4.2.2.2	<i>Ranking of heavy metals</i>	67
4.2.3	Heavy metal selectivity and competition	70
4.2.4	Sorption performance of clay barrier materials based on Batch adsorption tests	72
4.2.5	Summary of Batch adsorption test results	73
4.3	THE LEACHING CELL TEST	75
4.3.1	Hydraulic conductivity results	78
4.3.1.1	<i>General observations</i>	78
4.3.1.2	<i>Mechanism of hydraulic conductivity increase</i>	86

4.3.1.3	<i>Effect of heavy metals vs. calcium on hydraulic conductivity</i>	87
4.3.1.4	<i>Importance of initial saturation</i>	89
4.3.1.5	<i>The effect of Pb and Cu on hydraulic conductivity</i>	90
4.3.1.6	<i>Uncertain factors influencing hydraulic conductivity</i>	91
4.3.2	Heavy metal breakthrough results	92
4.3.2.1	<i>General observations</i>	92
4.3.2.2	<i>Migration behavior - non-uniformity and fractured porous media</i>	98
4.3.2.3	<i>Retention capacity versus breakthrough point</i>	100
4.3.2.4	<i>Relative mobility of heavy metals</i>	103
4.3.3	Performance of admixes	104
4.3.3.1	<i>Performance based on hydraulic conductivity</i>	104
4.3.3.2	<i>Performance based on heavy metal breakthrough</i>	106
4.3.4	Summary of Leaching cell results	108
4.4	Selective Sequential Extraction	110
4.4.1	SSE on a set of Batch adsorption tests	111
4.4.1.1	<i>Sorption characteristics of the admixes</i>	113
4.4.1.2	<i>Comparing sorption capacities of mixtures vs. individual materials</i>	114
4.4.1.3	<i>Comparing the sorption capacities of Batch and Leaching cell samples</i>	115
4.4.2	SSE on extruded Leaching cell samples	117
4.4.2.1	<i>Heavy metal migration behavior</i>	117
4.4.2.2	<i>Heavy metal retention mechanisms</i>	129
4.4.3	Summary of SSE results and the performance of the admixes	135
CHAPTER 5	CONCLUSIONS & RECOMMENDATIONS	137
5.1	CONCLUSIONS	137
5.2	RESEARCH CONTRIBUTIONS	141
5.3	RECOMMENDATIONS ON FURTHER RESEARCH	143
REFERENCES		145
APPENDIX A	PHYSICAL PROPERTIES OF CLAY BARRIER MATERIALS	152
APPENDIX B	CHEMICAL PROPERTIES OF CLAY BARRIER MATERIALS	161
APPENDIX C	METHODS SUPPLEMENT	165
APPENDIX D	BATCH ADSORPTION TEST CALCULATIONS AND DATA	173

APPENDIX E	LEACHING TEST CALCULATIONS AND DATA	198
APPENDIX F	SELECTIVE SEQUENTIAL EXTRACTION CALCULATIONS AND DATA	223

LIST OF FIGURES

Figure 1.1.1	Examples of clay barriers.	4
Figure 1.3.1	Flow chart of research plan.	8
Figure 2.1.1	Examples of inner- and outer-sphere complexes.	13
Figure 2.5.1	Fractionation of soil organic matter and humic substances.	23
Figure 3.3.1	Diagram of the Batch adsorption test.	32
Figure 3.4.1	Diagram of Leaching cell test.	37
Figure 3.5.1	Diagram of the SSE.	43
Figure 4.1.1	Grain size distribution of clay barrier materials.	49
Figure 4.2.1	Single heavy metal isotherms.....	52
Figure 4.2.2	Freundlich isotherms of <i>Cu</i> sorption in single & binary heavy metal solutions.	53
Figure 4.2.3	Binary sorption data showing how the presence of <i>Cu</i> and <i>Cd</i> affects <i>Pb</i> sorption.	57
Figure 4.2.4	Binary sorption data showing how the presence of <i>Pb</i> affects <i>Cu</i> & <i>Cd</i> sorption.	58
Figure 4.2.5	Calculated versus actual values for <i>Pb</i> , <i>Cu</i> , and <i>Cd</i> sorption in binary solutions.	59
Figure 4.2.6	Calculated versus actual values for <i>Pb</i> sorption in ternary solutions.	62
Figure 4.2.7	Ternary retention data showing how <i>Cu</i> and <i>Cd</i> change each others' sorption capacities.	62
Figure 4.2.8	Calculated versus actual values for <i>Cu</i> and <i>Cd</i> sorption in ternary solutions.	63
Figure 4.2.9	Heavy metal retention capacities of soil mix materials in single metal solutions.	65
Figure 4.2.10	Final pH graphs showing the influence of <i>Pb</i> , <i>Cu</i> , and <i>Cd</i> , on the final solution pHs of each suspension.	67
Figure 4.2.11	Selectivity of heavy metals in ternary and binary systems.	71
Figure 4.3.1	Hydraulic conductivity results for leachate blanks.	80
Figure 4.3.2	Hydraulic conductivity results for bentonite admix samples.	81
Figure 4.3.3	Hydraulic conductivity results for Forest soil admix samples.	82
Figure 4.3.4	Hydraulic conductivity results for Spruce bark admix samples.	83
Figure 4.3.5	Averaged hydraulic conductivity results grouped by admix type.	84
Figure 4.3.6	Averaged hydraulic conductivity results grouped by leachate type.	85
Figure 4.3.7	Conceptual model for the mechanism of hydraulic conductivity increase in Leaching cells.	88
Figure 4.3.8	Heavy metal breakthrough results for bentonite admix samples.	93
Figure 4.3.9	Heavy metal breakthrough results for Forest soil admix samples.	94

Figure 4.3.10 Heavy metal breakthrough results for Spruce bark admix samples.	95
Figure 4.3.11 Averaged heavy metal breakthrough results grouped by leachate type.	96
Figure 4.3.12 Averaged heavy metal breakthrough curves for bentonite admix permeated with <i>Pb+Cu+Cd</i>	97
Figure 4.3.13 Heavy metal concentration profiles of uniformly migrating plumes.	99
Figure 4.3.14 Conceptual model for the mechanism of non-uniform heavy metal migration.	99
Figure 4.3.15 Discharge pH results grouped by Leachate type.	106
Figure 4.4.1 Distribution of heavy metals in bentonite admix samples leached with <i>Pb</i>	119
Figure 4.4.2 Distribution of heavy metals in bentonite admix samples leached with <i>Cu</i>	120
Figure 4.4.3 Distribution of heavy metals in bentonite admix samples leached with <i>Pb & Cu</i>	121
Figure 4.4.4 Distribution of heavy metals in Forest soil admix samples leached with <i>Pb</i>	122
Figure 4.4.5 Distribution of heavy metals in Spruce bark admix samples leached with <i>Pb</i>	123
Figure 4.4.6 Distribution of heavy metals in Spruce bark admix samples leached with <i>Cu</i>	124
Figure 4.4.7 Distribution of heavy metals in Spruce bark admix samples leached with <i>Pb & Cu</i>	125
Figure 4.4.8 Distribution of heavy metals in bentonite admix samples leached with <i>Pb, Cu, & Cd</i>	126
Figure 4.4.9 Distribution of heavy metals in Forest soil admix samples leached with <i>Cu</i>	127
Figure 4.4.10 Distribution of heavy metals in Forest soil admix samples leached with <i>Pb & Cu</i>	128
Figure 4.4.11 <i>Pb</i> sorption trends over a range of total sorption concentrations.	130
Figure 4.4.12 <i>Cu</i> sorption trends over a range of total sorption concentrations.	131

LIST OF TABLES

Table 1.1.1	Historical changes in global production of metals commonly associated with pollution from mining activities	1
Table 1.1.2	Average levels of heavy metals in typical European household waste.	2
Table 1.1.3	Typical leachate concentrations of heavy metals for municipal waste in the United States.	3
Table 2.2.1	Summary of heavy metal selectivities for clay minerals and soils.	16
Table 2.3.1	Summary of correlation results from several heavy metal adsorption studies.	18
Table 2.3.2	SSE results from several heavy metal adsorption studies.	18
Table 2.4.1	Descriptions of heavy metal compatibility tests.	22
Table 2.5.1	Summary of heavy metal retention studies using bark or bark constituents.	25
Table 3.3.1	Batch adsorption test matrix	30
Table 3.3.2	Heavy metal solution concentrations used in Batch adsorption tests.	31
Table 3.3.3	Heavy metal concentration ranges measured by the atomic absorption spectrophotometer.	34
Table 3.4.1	The Leaching cell test matrix.	36
Table 3.5.1	The SSE program.	41
Table 4.1.1	Physico-chemical properties of soil materials.	48
Table 4.2.1	Summary for Batch adsorption test.	50
Table 4.2.2	Summary of <i>b</i> and <i>n</i> values fitted for single & binary <i>Cu</i> data.	53
Table 4.2.3	Summary of sorption equations for binary heavy metal solutions.	56
Table 4.2.4	Summary of sorption equations for ternary heavy metal solutions.	61
Table 4.2.5	Single <i>Pb</i> , <i>Cu</i> , and <i>Cd</i> sorption equations and their competition functions.	64
Table 4.2.6	Summary of relative heavy metal sorption capacities.	65
Table 4.2.7	Characteristics of <i>Pb</i> , <i>Cu</i> , & <i>Cd</i>	68
Table 4.2.8	Summary of competition amongst <i>Pb</i> , <i>Cu</i> , and <i>Cd</i>	72
Table 4.3.1	Summary for the Leaching cell test.	75
Table 4.3.2	Physical properties of Leaching cell samples.	77
Table 4.3.3	Summary of hydraulic conductivity results from averaged data in Figures 4.3.5 & 4.3.6.	86
Table 4.3.4	Comparison between retention mechanisms of <i>Ca</i> and the heavy metals.	90
Table 4.3.5	Summary of heavy metal breakthrough data from averaged data in	

	Figures 4.3.11 & 4.3.12.	97
Table 4.3.6	Summary of heavy metal breakthrough points & retentions.	102
Table 4.3.7	Heavy metal mobilities of bentonite.	103
Table 4.4.1	Summary for the SSE tests.	110
Table 4.4.2	SSE results for Batch adsorption tests on admixes.	112
Table 4.4.3	Comparison of admixes based on SSE and Batch adsorption samples.	113
Table 4.4.4	Averaged sorption characteristics for admixes based on SSE of Batch adsorption tests	114
Table 4.4.5	Sorption capacities of admixes	115
Table 4.4.6	Comparing max. extractions of Leaching cell and Batch adsorption test samples.	116
Table 4.4.7	SSE data for <i>Cd</i> from the bentonite admix.	132

ACKNOWLEDGMENTS

The author would like to express his sincere gratitude to...

- Dr. Loretta Li, for her guidance, patience, and encouragement throughout the course of this project, and for being a great role model by combining professionalism and graciousness in her life.
- Dr. Les Lavkulich, for providing valuable comments and advice, and for providing a location for collecting Forest soil.
- Prof. Jim Atwater, for providing valuable comments and advice near the end of the project.
- Ms. Susan Harper, and Ms. Paula Parkinson, for their advice, and assistance regarding laboratory equipment and procedures.
- Kurt, for an excellent job in constructing any equipment required for the project.
- William Denham, for his assistance and advice on the project, and for consuming a large quantity of coffee with me during the course of the project.
- All my friends and colleagues in the Geoenvironment group, who have been very supportive in both word and action.
- Forintek Canada Corporation for providing the Spruce bark.

I would also like to thank the many friends that I have met along the way. Your lives have kept my thesis and my life in perspective.

I would like to thank my family and relatives for their incredible support, encouragement, and love.

Finally, I would like to thank God for His grace in my life and work.

"There is a time for everything, and a season for every activity under heaven"

Ecclesiastes 3:1

CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF PROBLEM

Mining, smelting, and industrial activity have caused extensive heavy metal contamination of the environment (Ernst 1995; from Ernst 1974, 1990, and Ernst & Joosse-van Damme 1983, 1989). These activities directly input heavy metals into the surrounding atmosphere, waterways, and soil. The heavy metals may travel long distances due to weathering, wind, water currents, and groundwater flow (Fergusson, 1990). Table 1.1.1 shows the global production of metals commonly associated with pollution from mining activities. Of these, *Cu* and *Pb* are among the top six metals produced (Allan, 1995).

TABLE 1.1.1. Historical changes in global production of metals commonly associated with pollution from mining activities (x 1000 tonnes). (From Nriagu, 1979; Nriagu & Pacyna, 1987.)

Metal	Pre-1850	1850-1900	1900-1940	1950	1960	1970	1980
Copper	45,000	13,000	49,000	2650	4212	6026	7660
Zinc	50,000	15,000	40,000	1970	3286	5469	5220
Lead	55,000	25,000	51,000	1670	2378	3395	3096
Nickel		200	1,500	144	327	639	759
Cadmium				6.0	11	17	15
Silver				6.2	7.5	9.4	11
Mercury				4.9	8.3	9.8	7.1
Gold				1.0	1.4	1.5	1.2

The toxicity of heavy metals lead to reduced crop yields, death of marine life (Crosby, 1998), and serious health problems in humans. Lead (*Pb*) affects the nervous blood systems. Copper (*Cu*) causes tremors, laboured respiration, and hemolysis (Crosby, 1998). Cadmium (*Cd*) affects the renal system, cardiovascular system, and the skeleton. *Cd* also is known to cause cancer in the prostate gland, and lungs (Yasumura, 1980; Fergusson, 1990). Unlike many organic contaminants, heavy metals cannot be degraded; thus, possessing a high potential to bioaccumulate and move up the food chain.

For the case in which heavy metal migration is a high threat to sensitive areas, such as drinking water sources, containment is often the most practical solution. An effective method of containment is the combination of pumping wells and vertical barriers. This method of hydraulic control ensures that contaminated groundwater does not migrate out of the control area. Since heavy metals cannot be degraded, removal is one of the few alternative solutions. The simplest method of removal is excavation of the contaminated soil. Other methods include biological extraction (Ernst, 1995), and soil washing (Ragaini, 1994). Regardless of the removal method, the special waste landfill is often the final disposal facility for heavy metals.

Special waste landfills are constructed for containing heavy metals and other hazardous wastes. However, municipal waste landfills also must account for heavy metal input. Table 1.1.2 shows the average levels of heavy metals found in typical European household waste. Of these, batteries account for 45% of the *Cd*, and scrap iron accounts for 40% of the *Pb* and 30% of the *Cu*. (Rousseaux et al., 1989). Table 1.1.3 shows the typical leachate concentrations of heavy metals from municipal waste in the United States.

TABLE 1.1.2. Average levels of heavy metals in typical European household waste (Rousseaux et al., 1989).

	<i>Hg</i>	<i>Cd</i>	<i>Pb</i>	<i>Zn</i>	<i>Cu</i>	<i>Ni</i>	<i>Cr</i>
Concentration (ppm)	1 - 3	3 - 5	100 - 700	400 - 1000	100 - 300	20 - 50	50 - 100

TABLE 1.1.3 Typical leachate concentrations of heavy metals for municipal waste in the United States (Bagchi, 1990; taken from McGinley & Kmet, 1984, and Lu et al., 1981).

	<i>Hg</i>	<i>Cd</i>	<i>Pb</i>	<i>Zn</i>	<i>Cu</i>	<i>Ni</i>	<i>Cr</i>
Concentration (ppm)	ND - 3.0	ND - 0.4	ND - 14.2	ND - 731	ND - 9.0	ND - 7.5	ND - 5.6

ND - non-detectable

Engineered clay barriers are commonly used as vertical barriers and landfill liners (Figure 1.1.1). Clay barriers are constructed from locally found soils amended with clay. The clay may also be mined locally, or bought commercially. Clay barriers are effective primarily because they possess low hydraulic conductivities. The hydraulic conductivity of a clay barrier is dependent on its composition, and the method used for its construction. Another significant consideration, is the chemical reactivity between the clay barrier, and the contaminant. The current study focuses mainly on the aspect of chemical reactivity. If the contaminant causes the clay barrier to deteriorate, then the clay barrier would be deemed incompatible with that contaminant.

Besides having low hydraulic conductivities, clay barriers also possess the ability to sorb many types of contaminants. Since clay barriers are not impermeable, their contaminant retention ability act as important second lines of defense. **Therefore, the compatibility of a clay barrier to a specific contaminant depends on two factors: the clay barrier's ability to resist any increases in hydraulic conductivity caused by the contaminant, and its ability to retain the contaminants.**

Several studies already have indicated that heavy metals increase the hydraulic conductivity of clay barrier materials (Dunn & Mitchell, 1984; Weber, 1991; Cabral, 1992; Lo et al., 1994). In addition, many studies have explored the heavy metal retention abilities of soils and clay minerals (Soldatini et al., 1976; Rose, 1989; Barry et al., 1995; Arnfalk et al., 1996; Gao et al., 1997). Even though research into the problem of heavy metal compatibility has progressed beyond the initial stage, opportunities abound in understanding the extent and mechanism in which heavy metals affect

hydraulic conductivity, as well as in improving the heavy metal compatibility of clay barriers.

a) Landfill liner.

b) Surface impoundment liner.

c) Vertical barrier wall.

FIGURE 1.1.1. Examples of clay barriers. (a) Landfill liner. (b) Surface impoundment liner. (c) Vertical barrier wall. (Sharma & Lewis, 1994; from USEPA, 1984, 1989)

1.2 SCOPE AND OBJECTIVES

Many of the past studies placed emphasis on comparing various permeameters and testing conditions (see section 2.4) in order to isolate the effect of heavy metals on hydraulic conductivity. However, since many previous compatibility studies, used either distilled water (Weber, 1991; Cabral, 1992), or tap water (Dunn & Mitchell, 1984; Lo, 1994) as blank leachates, the increase in hydraulic conductivities may be due to differences in ionic strength.

Past Leaching cell studies generated much hydraulic conductivity and heavy metal breakthrough data (Dunn & Mitchell, 1984; Peirce et al., 1987; Weber, 1991; Cabral, 1992; Lo et al., 1994); however, few conclusions were made regarding the migration behavior of heavy metals, and the retention mechanisms of clay barriers. Since most of the studies used single heavy metal permeants (Peirce et al., 1987; Weber, 1991; Cabral, 1992; Lo et al., 1994), the effect of competition on heavy metal migration through clay barriers remains uncertain. Within soil science, sorption competition of heavy metals has been the focus of many Batch adsorption studies (Puls & Bohn, 1988; Bladel et al., 1993; Gutierrez & Fuentes, 1993); however, the applicability of the adsorption results to Leaching cell tests remains questionable. More understanding on the sorption and migration behavior of heavy metals would be beneficial in predicting and managing the transport of heavy metals through clay barriers.

Heavy metal compatibility research has focused mainly on clay minerals, such as kaolinite and bentonite (Weber, 1991; Cabral, 1992). Few studies (Lo et al., 1994) focused on finding alternative materials that would improve heavy metal compatibility. These alternative materials would need to be economical, and easily incorporated into clay barriers.

The goals of this thesis aim to improve the heavy metal compatibility of clay barriers, and assist in predicting the migration of heavy metals. The specific objectives are as follows:

1. To find the effects of heavy metals on the hydraulic conductivity of clay barriers.

All synthetic leachate solutions were given a background concentration of 0.01 M calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in order to maintain similar ionic strengths. If heavy metal incompatibility is dependent only on ionic strength, no differences should be observed between the hydraulic conductivities of heavy metal and blank leachates.

2. To investigate the sorption and migration behavior of single and multi-heavy-metal solutions (*Pb*, *Cu*, & *Cd*), through clay barriers.

Specifically, the following issues are investigated:

- a) Which heavy metals are less compatible with clay barriers?
  - b) What is the mechanism of hydraulic conductivity increase due to heavy metals?
  - c) How does competition affect heavy metal sorption and migration?
  - d) What are the preferred retention mechanisms for various heavy metals?
3. To evaluate the applicability of Batch adsorption results to the Leaching cell studies.

Batch adsorption test results often were used as inputs for heavy metal transport models. The current study investigates whether the Batch adsorption results could adequately predict heavy metal migration, heavy metal retention capacities.

4. To explore the use of Forest soil and Spruce bark in clay barriers

Forest soil and Spruce bark were selected as potential materials for clay barrier construction based on their proven heavy metal sorption abilities (Soldatini et al., 1976; Rose, 1989; Barry et al., 1995; Arnfalk et al., 1996; Gao et al., 1997). The current

study uses Leaching cell tests to evaluate the performance of clay barrier admixes that contain Forest soil or Spruce bark. The typical clay barrier admix is represented by 100:8 mix of sand and *Na*-bentonite. Other admixes were created by replacing one part of bentonite with either Forest soil or Spruce bark. Improved compatibility would be evidenced by increased heavy metal retention while maintaining a low hydraulic conductivity.

1.3 THE RESEARCH PLAN

To accomplish the objectives presented in the previous section, a research plan was created containing four main sets of tests. A flow chart outlining the research plan is shown in Figure 1.3.1.

FIGURE 1.4.1. Flow chart of research plan.

1.4 RESEARCH CONTRIBUTIONS

The following list identifies some areas which would benefit from this research:

1. The design of landfill and surface impoundment liners, and vertical barrier walls

Insights gained from investigating the sorption and migration behaviour of heavy metals would increase the reliability of clay barrier designs. In addition, the current study investigates possible improvements to clay barriers by adding Forest soil, and Spruce bark.

2. Modeling the migration of heavy metal through soils

The relationship between sorption competition and heavy metal migration are relevant to transport modeling.

3. Co-disposal of heavy metal contaminated soil

Heavy metal retention characteristics of a clay barrier mix could be altered by the addition of other materials. The results from the current study could be applied to the situation in which heavy metal contaminated soil is mixed with other clean soils or materials.

1.5 ORGANIZATION OF THESIS

The thesis consists of five chapters:

- Chapter 1: Presents the scope, objectives, and research plan.
- Chapter 2: Background information on the interactions between heavy metals and soils are provided. In addition, published literature on heavy metal sorption and permeability testing is summarized.
- Chapter 3: Describes the equipment, materials, and methods used in this study.
- Chapter 4: Presents the results from research program. In addition, discusses the heavy metal compatibility of the three admixes, the sorption and migration behavior of heavy metals, and the relationship between the Batch adsorption results and the Leaching cell test.
- Chapter 5: Presents conclusions, research contributions, and recommendations for future research.

CHAPTER 2

BACKGROUND REVIEW

The heavy metal compatibility of clay barriers are determined by hydraulic conductivity and retention ability. However, the mechanisms and processes that govern these parameters are complex. An understanding of the physical, and chemical interactions that occur between heavy metals and soils will benefit the evaluation of heavy metal compatibility.

Because of the complexity of heavy metal and soil interactions, conclusive formulations are lacking from the results of heavy metal sorption studies. Several studies used Batch adsorption tests and Selective Sequential Extractions (SSEs) to investigate the sorption capacities of different soils and clay minerals. However, heavy metal compatibility studies on clay barriers have been limited to identifying the occurrence and extent of heavy metal incompatibility. Much opportunity exists in researching the effects of heavy metals, and finding improvements for clay barriers.

2.1 HEAVY METAL AND SOIL INTERACTIONS

The three mechanisms for heavy metal retention in soils are cation exchange, the formation of inner-sphere complexes, and precipitation. In addition, an important factor that influences the effectiveness of these mechanisms is solution pH.

2.1.1 Cation Exchange

Cation exchange describes the phenomenon in which cations electrostatically adsorb onto negatively charged soil particles. Because no chemical bonding occurs, the electrostatically held cations are easily displaced by other cations (Evans, 1989). The exchange of cations depend on the type and concentrations of the cations present, and also the chemical environment of the pore water. Cations of higher concentrations displace those of lower concentrations, and high valence cations displace the low valence cations (Tan, 1998). In general, soil organic matter possesses the highest cation exchange capacity (CEC); clay minerals are second; and then follows the rest of the inorganic minerals. Besides having the highest CEC, soil organic matter also have very high specific surface areas. Organic matter accounts for up to 80% of the CEC of soils (Stevenson, 1982).

2.1.2 Inner-Sphere Complexation

When the surface functional group of a soil particle interacts with an ion present in the soil solution to create a stable molecular entity, a surface complex forms (Sparks, 1995). Examples of an outer-sphere and inner-sphere complex are shown in Figure 2.1.1. Outer-sphere complexes are bound ionically. By retaining their water of hydration, ionically bonds are considered nonspecific and is classified under cation exchange. Inner-sphere complexes are bound covalently. These are strong bonds in which electrons are shared amongst the bound ions. Presented below are important surface functional groups associated with minerals and soil organic matter.

For minerals, the hydroxyl groups are important surface functional groups. The divalent transition metals readily form inner-sphere complexes with hydroxyl groups by displacing an H^+ from the hydroxyl group and bonding to the $-O-$. Being divalent, the metal may bond to one or two oxygen atoms (Sparks, 1995).

As for soil organic matter, many surface functional groups are available for complexation. Donor atoms generally are the more electronegative nonmetallic elements, such as O, N, and S. These elements are contained within the basic functional groups, such as amino, carbonyl, alcohol, thioether; and the acidic groups, such as carboxyl, phenolic, enolic, and thiol (Evans, 1989; Sparks, 1995). Livens (1991), states that for soil organic matter, the ease and strength of bonding depends on following:

1. The affinity of the metal ion for that type of site;
2. Stereochemical factors, i.e. the amount of room for the metal ion to fit into the site. This can be affected by the size of any other ligands on the metal;
3. The chemical environment of the site. The nature of the functional groups around the actual complexing group can influence its behaviour.

FIGURE 2.1.1. Examples of inner- and outer-sphere complexes (Adapted from Sparks, 1995; taken from Hayes, 1987).

2.1.3 Precipitation

Precipitation is the formation of an insoluble product from a reaction that occurs in solution (McQuarrie & Rock, 1991). The extent of precipitation and dissolution of a mineral can be described by its solubility product (Tan, 1998). Precipitation will occur when the product of the metal ion and ligand concentrations exceeds their solubility product. Among the most important precipitation reactions, are those that involve the hydroxide (OH^-) ligand. Metals that are expected to precipitate as hydroxides are Fe^{3+} , Al^{3+} , Cu^{2+} , Fe^{2+} , Zn^{2+} , and Cd^{2+} (Evans, 1989). In addition, metal ions also commonly precipitate as carbonates (CO_3^{2-}) and sulphides (S^{2-}). Metals that are expected to precipitate as carbonates are Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} . Although carbonates occur in both oxidizing and reducing conditions, sulphides are stable only in reducing conditions. Metals that occur as sulphides in reducing conditions include Ag^+ , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Fe^{3+} (Evans, 1989).

2.1.4 The effect of solution pH

Heavy metal retention mechanisms are affected by solution pH in several ways. In regards to cation exchange, the high concentration of H^+ ions associated with low pH conditions compete with other cations for exchange sites. Also, the H^+ ions may bond to negatively charged surface functional groups contributing to an overall reduction in the negative charge of the soil particle. As a result, this reduction lowers the cation exchange capacity of the soil particle.

The effect of pH on precipitation is described by the presence of H^+ ions in metal solubility equations. In general, precipitation increases with increasing pH; however, in some cases, metals redissolve at very high pHs (Lindsay, 1979).

2.1.5 The effect of heavy metals on clay structure

Because clays carry a negative charge, cations are attracted to clay surfaces. The negatively charged clay surface, and the surrounding cloud of cations held by electrostatic attraction, form the electric double layer as described by Gouy (1910) and Chapman (1913).

The double layer thickness of clay particles greatly influence their structural arrangement. The double layer thickness of clay particles is inversely proportional to the valence, and square root of the concentration of cations (Tan, 1998). When double layer thicknesses are great, repulsive forces dominate, resulting in a dispersed particle structure. When double layer thicknesses are small, attractive forces dominate, resulting in a flocculated particle structure. Thus, increasing concentrations of heavy metal solutions would cause decreases in the double layer thickness of clay particles, leading to more flocculated structures.

In relation to hydraulic conductivity, flocculation leads to increased pore spaces around the flocculated structures, thereby increasing hydraulic conductivity (Mitchell et al., 1965). Also, dispersed structures results in lower hydraulic conductivity, because "fluid transport through soil pores must overcome the increased energy field established by the repulsive forces" (Yong et al., 1992).

2.2 STUDIES IN HEAVY METAL RETENTION SELECTIVITY

Retention capacity refers to the maximum amount of heavy metals that a soil could retain. The retention capacity for a particular heavy metal is determined by performing sorption tests, in which the soil is placed into solutions containing various concentrations of the heavy metal. Selectivity is based on the relative sorption capacities of many heavy metals contained within the same solution. Often, the order

of selectivity for a group of heavy metals is the same as the order of their individual capacities. Many studies have been conducted to find and explain the selectivity of heavy metals. A survey of these studies shows discrepancies in the orders and explanations for selectivity. Table 2.2.1 contains a selection of studies.

TABLE 2.2.1. Summary of heavy metal selectivities for clay minerals and soils.

Author(s)	Sorbant Material	Order of Selectivity	Reason
Puls & Bohn, 1988	Montmorillonite	$Cd \approx Zn > Ni$	HSAB principle*
	Kaolinite	$Cd \approx Zn > Ni$	HSAB principle*
Bladel et al., 1992	Bentonite, illite, vermiculite	$Zn > Cd$	Ionic potential
Yong & Phadungchewit, 1993	Montmorillonite, kaolinite, illite, natural clay (pH > 4 or 5)	$Pb > Cu > Zn > Cd$	1st hydrolysis product
Morley & Gadd, 1995	Montmorillonite, kaolinite	$Cu \gg Cd > Zn$	Irving-Williams order of stability
Mohamed & Antia, 1998	General soils	$Ca > Mg > Hg > Cd > Zn$ (general order for divalent metals)	Ionic radius
Mohamed & Antia, 1998	General soils	$Cu > Ni > Co > Fe > Mn$ (transitional divalent metals)	Irving-Williams order of stability

* Hard-Soft-Acid-Base principle

Several points can be made to clarify the discrepancies shown in Table 2.2.1. The Irving-Williams order of stability (Irving & Williams, 1953), based on ionic radius and ionization potential, is limited to a subset of the first transitional metal series. In fact, one of the goals of their paper was to stress that no general order exists for transitional metals outside the Irving-Williams list. The selectivity of transitional metals outside the Irving-Williams order would vary depending on the following:

1. The radii and ionization potentials of the metals
2. The type of adsorbents
3. The presence of other ligands in solution, and
4. The chemical environment (pH, redox potential)

Thus, researchers that explained selectivity using only ionic radius or ionic potential were ignoring other important factors. For example, in citing the 1st hydrolysis product, Yong and Phadungchewit (1993), were implying that hydroxide precipitation was the dominant factor in heavy metal retention. This may or may not have been true depending on the factors stated earlier. The Hard-Soft-Acid-Base principle, cited by Puls and Bohn (1988), is not directly linked with fundamental properties, but is a useful classification system. Their efforts to classify the hardness and softness of heavy metals and clay minerals may prove to be useful if a sufficient database can be successfully constructed.

2.3 HEAVY METAL RETAINING SOILS AND MINERALS

Two approaches were used to investigate the retaining abilities of materials. The simpler method involved the Batch adsorption test. The Batch adsorption test was used to determine the amount of heavy metals retained by several different materials. These results were then correlated with certain characteristics, such as clay and organic content, and mineralogy. Table 2.3.1 highlights the correlation results of several studies.

The second method for heavy metal retention studies used the SSE procedure to directly measure the amount of heavy metals retained by four components of a mineral or soil: exchangeable, carbonate, oxide/hydroxide, and organic. Table 2.3.2 shows the SSE results of several studies performed on various soils.

TABLE 2.3.1. Summary of correlation results from several heavy metal adsorption studies.

Author(s)	Soil Description	Retained Heavy Metals	Positive Correlations to Heavy Metal Retention
Soldatini et al., 1976	12 soils side ranging in organic matter, and clay and carbonate content	<i>Pb</i>	Organic and clay content
Rose, S., 1989	Samples from 2 layers of the Hawthorne Formation	<i>Pb, Cu, Zn, Cd</i>	Clay content
Barry et al., 1995	Samples from 6 soil horizons within soil profile	<i>Cd, Ni, Cu</i>	Organic content
Arnfolk et al., 1996	14 different types of minerals and soils	<i>Cd, Cr(III), Cr(VI), Hg, Pb</i>	Organic content
Gao et al., 1997	9 soils	<i>Ni, Cu, Cd, Zn</i>	Organic content

TABLE 2.3.2. SSE results from several heavy metal adsorption studies.

Author(s)	Heavy Metal	Highest Associated Component
Hickey & Kittrick, 1984	<i>Cu</i>	Organic
	<i>Cd</i>	Exchangeable
Yanful et al., 1988	<i>Cu</i>	Organic
	<i>Pb, Zn, Fe</i>	Carbonate
Ramos et al., 1994	<i>Cu</i>	Organic
	<i>Pb, Zn</i>	Oxide
	<i>Cd</i>	Exchangeable & Carbonate

The following observations were made from the Batch adsorption and SSE studies:

1. Heavy metal retention often is associated with the organic and clay fractions of soils.
2. Studies involving clay minerals showed that montmorillonite retained heavy metals better than illite and kaolinite, mainly due to its higher buffering capacity.

2.4 HEAVY METAL COMPATIBILITY STUDIES

Many compatibility studies have been conducted to investigate the compatibility of clay barriers to different types of permeants. Over the last 20 years, much work has been done with organic contaminated permeants (Acar et al., 1985; Fernandez & Quigley, 1985; Foreman & Daniel, 1986; Uppot & Stephenson, 1989; Meegoda & Rajapakse, 1993). In comparison, significantly fewer studies have focused on investigating heavy metal compatibility. Descriptions of five heavy metal compatibility studies are presented in Table 2.4.1. Conclusions from the five studies are summarized below:

1. Dunn and Mitchell (1984), found that a synthetic leachate of *Pb* and *Zn* produced hydraulic conductivities 5 - 100 times greater than tap water. They also found that static compaction produced the best quality of soil samples with the least effort.
2. Peirce et al., (1987), found that hydraulic conductivity values were within one order of magnitude for all scenarios tested using three clay soils. Also, heavy metal breakthrough occurred only for the samples permeated with 300 ppm nickel nitrate ($Ni(NO_3)_2$).
3. Weber (1991) found that for kaolinite clay, hydraulic conductivity values were similar for all conditions tested. For the sand/bentonite mixture, only the 2500 ppm concentration of *Pb* produced hydraulic conductivity values significantly higher than with distilled water. Heavy metal breakthrough occurred in all the kaolinite samples, but in the sand/bentonite samples, only the 2500 ppm *Pb* permeant resulted in breakthrough. All heavy metal breakthroughs coincided with a sudden drop in pH. They also found that the sorption isotherms produced from Batch adsorption tests were

significantly higher than those produced from the ammonium acetate extractions.

4. Cabral (1992) found that hydraulic conductivity values were similar for all conditions tested using kaolinite clay. The consolidation cell produced hydraulic conductivities two orders of magnitude lower than the triaxial cell results when using the sand/bentonite mixtures. These differences were attributed to the incomplete saturation of the consolidation cells. Also, the hydraulic conductivities of the triaxial cells varied significantly depending on the initial gradient applied, saturation and compaction procedures, the heavy metal concentration of permeants, and the type of heavy metal used. *Zn* permeants resulted in higher hydraulic conductivities than *Pb* permeants. In contrast, the hydraulic conductivities of consolidation cell tests were insensitive to the initial gradients applied and the presence of *Pb*. Heavy metal breakthrough occurred for samples permeated with 1750 ppm and 2500 ppm of *Pb*. The retardation factors calculated from the Batch adsorption tests were significantly larger than those calculated from breakthrough curves.
5. Lo et al. (1994), found that for Claymax and composite liners, hydraulic conductivity values were three times greater using the synthetic leachate than tap water. The composite liner was effective in maintaining a low hydraulic conductivity while retaining the *Pb* and 1, 2-dichlorobenzene (DCB).

Of the five studies presented, only Peirce et al. (1987), used a blank solution that contained a standardized ionic concentration. Because his was also the only study that found no heavy metal incompatibilities, one must confirm whether heavy metal incompatibilities were a result of differences in ionic strengths.

In all the presented studies except for Lo et al. (1994), emphasis was placed on experimenting with various permeameters, compaction methods, and experimental procedures, such as hydraulic gradient, and confining pressure. This limited the work done in studying the sorption and migration behavior of heavy metals.

Lo et al. (1994), developed a new composite liner that improved heavy metal compatibility. However, the process in preparing the soils is potentially expensive. Ideally, new materials should be inexpensive and easily incorporated into clay barrier mixes.

TABLE 2.4.1. Descriptions of heavy metal compatibility tests.

	Author	Liner Material	Heavy metal leachate	Blank leachate	Permeameter	Compaction method	Confining pressure	Hydraulic gradient	Adsorption tests
1	Dunn and Mitchell, 1984	2 silty clay soils	200 ppm Zn + 15 ppm Pb (pH 2.5)	tap water	triaxial cell	static, impact, and kneading	150 kPa	20 - 200	none
2	Peirce et al., 1987	3 clay soils	500 ppm FeCl ₃ , 50 ppm Ni(NO ₃) ₂ , and 300 ppm Ni(NO ₃) ₂	0.01 M Ca(SO ₃) ₂	fixed-wall cell, and triaxial cell	dynamic	???	65 - 200	none
3	Weber, 1991	kaolinite, and sand/Na-bentonite mixture	250 - 2500 ppm concentrations of Pb(NO ₃) ₂ (pH 3.6)	distilled water	consolidation cell	static	13.79 - 35.16 kPa	25, 50, and 100	Batch tests, and Pb extraction from extruded Leaching cell samples using ammonium acetate
4	Cabral, 1992	kaolinite, and sand/Na-bentonite mixture	250 - 2500 ppm concentrations of Pb(NO ₃) ₂ , and 2000 ppm ZnSO ₄	distilled water	consolidation cell, triaxial cell	static	60 - 370 kPa (for triaxial) 35 - 49 kPa (for con. cell)	25, 50, and 100	Batch tests, and Pb extraction from extruded Leaching cell samples using ammonium acetate
5	Lo et al., 1994	Claymax, humic acid-aluminum hydroxide coated montmorillonite (HA-AIOH-Clay), and HA-AIOH-Clay & Clay composite liner	62.2 ppm 1, 2 DCB + 69.2 ppm NaCl + 100.6 ppm Pb + pH 7 phosphate buffer	tap water	triaxial cell	???	135.4 kPa	80	Batch tests

Note: Summary of results found earlier in this section.

2.5 POTENTIAL NEW MATERIALS FOR CLAY BARRIERS

This section aims to provide background evidence that Forest soil and Spruce bark would improve heavy metal retention if added to clay barrier mixes.

2.5.1 Soil Organic Matter

Soil organic matter represents all organic compounds in soil excluding undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass (Stevenson, 1982). Figure 2.5.1 shows the fractionation of soil organic matter based on chemical and physical separation techniques.

FIGURE 2.5.1. Fractionation of soil organic matter and humic substances (Sparks, 1995; taken from Hayes & Swift, 1978)

The fact that the heavy metal retention of soils often correlates with their organic contents has been presented in section 2.3. The following are two heavy metal retention studies in which humic substances were mixed with soils and clay minerals.

Hatton and Pickering (1980), mixed 3 mg of humic acid with 7 - 15 mg of three types of clays: *Na*-montmorillonite, kaolinite, and illite. The mixtures were subjected to Batch adsorption tests involving *Pb*, *Cu*, *Zn*, and *Cd*. For pHs set below 6, the humic acids tended to dominate the adsorption process, while for pHs set above 6, heavy metal retention as metal hydroxyl species dominated. Overall, the heavy metal retention of the clay-humic acid mixtures were lower than would be predicted by the addition of individual retention capacities, but higher than the retention capacities of the individual components. This indicated that clays and humic acids interfered with each others' heavy metal retention abilities.

Igloria et al. (1998), conducted leaching tests using two field soils. The artificial leachate solutions had *Cd*, *Cu*, *Pb*, and *Zn* concentrations ($< 1 \text{ mg L}^{-1}$) that simulated average stormwater. Natural organic matter was added to the leachate to produce about a 50 mg L^{-1} total organic carbon (TOC). The natural organic matter was collected by extracting standard garden peat with sodium hydroxide (*NaOH*). Results showed that with the addition of natural organic matter, *Cu* and *Zn* attenuation improved by as much as 40%, while *Pb* and *Cd* attenuation improved by $> 10\%$. Igloria et al (1998) concluded that the results encouraged further studies into the application of peat "covers" onto the bottom of infiltration basins.

The organic matter in the previous studies was extracted from soils using alkali solutions. The current study did not use extracted organic matter, but added soils high in organic matter (Forest soil) directly to the barrier mix. The direct addition of Forest soil would avoid the costly step of first extracting the organic matter.

2.5.2 Spruce Bark

Bark is a common wood waste. Because it is produced in large quantities, efforts have been made to find other uses for it. Bark has been successfully used as industrial fuel, soil amendment, and ground cover (Haygreen and Bowyer, 1996). However, barks from some trees such as Spruce, contain high levels of toxic tannins (Field & Lettinga, 1991). This limits its reusability as well causes disposal problems. Shown in Table 2.5.1, are several studies that have used bark, or bark constituents to retain heavy metals.

TABLE 2.5.1. Summary of heavy metal retention studies using bark or bark constituents

Author(s)	Bark (Constituent)	Heavy Metals Retained
Hatton & Pickering, 1980	Tannic acid (mixed with clay minerals)	<i>Pb, Cu, Cd, Zn</i>
Deshkar et al., 1990	Formaldehyde-modified <i>Hardwickia Binata</i> bark	<i>Hg</i>
Al-Asheh & Duvnjak, 1997	Pine Bark	<i>Pb, Cd, Cu, Ni</i>
Gloaguen & Morvan, 1997	Formaldehyde-modified <i>Picea abies</i> , <i>Pinus sylvestris</i> , <i>Pseudotsuga manziesii</i> , <i>Larix kaempferi</i> , <i>Tectona grandis</i> , and <i>Azalia africana</i> barks	<i>Pb, Zn, Cr, Fe, Cu</i>

The mentioned studies show that bark has the potential to retain heavy metals. Thus, Spruce (*Picea*) bark would be a logical choice for improving the sorption ability of clay barriers. This study evaluates the performance of Spruce bark by adding it in shredded form, to a typical clay barrier mix.

CHAPTER 3

MATERIALS AND METHODS

3.1 CLAY BARRIER MATERIALS

3.1.1 Origins & Descriptions

Bentonite

The Na-bentonite was obtained from Canadian Clay Products in Wilcox, Saskatchewan.

Sand

The sand is a commercial product named Wedron 130.

Forest soil

The Forest soil was sampled at a site near 48th Avenue, East of 152nd Street, in Langley, British Columbia. After removing about 5 cm of forest litter, samples were taken from the top 30 cm of forest soil. The soil samples were placed directly into doubled layered plastic bags, and were kept cool using freezer packs during transport. At the lab the samples were stored under a constant 4 °C, and 100% humidity.

Spruce bark

The Spruce bark provided by Forintek Canada Corporation. Forintek obtained wood waste materials from various sawmills in BC. The Spruce bark material was a mixture of 85% Spruce bark chips, and 15% sawdust.

3.1.2 Admixtures

The clay barrier materials were used to create three admixes (see section 3.4.2 for admix preparation procedure):

Bentonite admix - 100:8 ratio of sand:bentonite.

Forest soil admix - 100:7:1 ratio of sand:bentonite:Forest soil.

Spruce bark admix - 100:7:1 ratio of sand:bentonite:Spruce bark.

The three admixes were designed to have equal parts of reactive material. The bentonite admix represents the typical clay barrier mix to which the other admixes were compared.

3.1.3 Physical properties

Summaries are provided for each test. Full descriptions are found in APPENDIX A.

Particle size distribution

Particle size distributions of the sand, bentonite, Forest soil, and Spruce bark were determined by dry sieving and the hydrometer method according to ASTM D422-63 (ASTM, 1995) (APPENDIX A.1).

Specific gravity

Specific gravities were measured for the admixes using the volume-displacement method described in ASTM D854-92 (ASTM, 1995) (APPENDIX A.2).

Specific surface area

The specific surface of bentonite was determined using an ethylene glycol monoethyl ether (EGME) method adapted from Eltantawy and Arnold (1973). See APPENDIX A.3 for a description of the adapted method.

Atterberg limits

Liquid limits were obtained for the bentonite material, and the three admixes. The plastic limit was obtained only for the bentonite, because the admixes contained too much coarse material. The Atterberg limits were done according to the procedure outlined by ASTM D318-93 (ASTM, 1995).

Maximum dry density and optimum water content

The maximum dry densities and optimum water contents for the admixes were determined using a method adapted from ASTM D1557-91 (ASTM, 1995). See APPENDIX A.4 for a description of the adapted method.

3.1.4 Chemical properties

Summaries are provided for each test. Full descriptions are found in APPENDIX B.

Soil pH

The pHs of the clay barrier materials were measured in distilled water, and in 0.01 M calcium chloride (CaCl_2) with a method adapted from McLean (1982). See APPENDIX B.1 for a description of the adapted method.

Cation Exchange Capacity (CEC)

The cation exchange capacity of bentonite was obtained using a method adapted from Standard method 9081 (APHA, AWWA, & WEF, 1995). See APPENDIX B.2 for a description of the adapted method.

3.2 CHEMICAL SOLUTIONS

All blank and heavy metal solutions contained a background of 0.01 M calcium nitrate ($\text{Ca}(\text{NO}_3)_2$). The heavy metal solutions also contained combinations of lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate ($\text{Cu}(\text{NO}_3)_2$), and cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$). All solutions were prepared by dissolving solid crystals of $\text{Ca}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$, into distilled water. To ensure that all the cations remained dissolved, all solutions were set to a pH of 4.0, using nitric acid (HNO_3). The combinations and concentrations of heavy metals used, are described in later sections that detail the individual tests. All heavy metal solution concentrations were confirmed using a Video 22 Thermo Jarrell Ash aa/ae Spectrophotometer - Model 957.

3.3 BATCH ADSORPTION TEST METHOD

3.3.1 Batch adsorption test program

The Batch adsorption test was used to find the heavy metal sorption isotherms of the clay barrier materials and admixes. Each Batch test was performed in duplicate to ensure accuracy. The sorption isotherms developed for single, binary, and ternary heavy metal solutions, were used to evaluate sorption capacities, selectivities, and competition. The combinations of materials and heavy metal solutions tested are shown in Table 3.3.1, and the concentrations of solutions used for each test are shown in Table 3.3.2. A diagram summarizing the Batch adsorption test is found in Figure 3.3.1. An equipment list is shown in APPENDIX C.1. The admix samples submitted to Batch testing were later submitted to Selective Sequential Extraction (SSE).

Because of time constraints, Forest soil was not tested in a ternary heavy metal system. The ternary data for the bentonite and Spruce bark materials would be sufficient to investigate competition in ternary systems. The set of heavy metal solutions used on the admix materials was the same as that for the Leaching cell samples (Table 3.4.1). This allowed for direct comparisons to be made between the Batch adsorption and Leach cell test results.

TABLE 3.3.1. Batch adsorption test matrix.

Materials tested	Single system			Binary system		Ternary system
	<i>Pb</i>	<i>Cu</i>	<i>Cd</i>	<i>Pb+Cu</i>	<i>Pb+Cd</i>	<i>Pb+Cu+Cd</i>
Bentonite	√	√	√	√	√	√
Forest soil	√	√	√	√	√	
Spruce bark	√	√	√	√	√	√
Bentonite admix	√	√		√		√
Forest soil admix	√	√		√		
Spruce bark admix	√	√		√		

TABLE 3.3.2. Heavy metal solution concentrations used in Batch adsorption tests.

	Single system	Binary system		Ternary system
	<i>Pb, Cu, Cd</i>	<i>Pb+Cu</i>	<i>Pb+Cd</i>	<i>Pb+Cu+Cd</i>
	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹
<u>Materials</u>	0	250+0	250+0	203+203+203
Bentonite	50	250+50	250+50	797+203+203
Forest soil	100	250+100	250+100	203+797+203
Spruce bark	200	250+250	250+250	797+797+203
	500	250+500	250+500	203+203+797
	1000	250+1000	250+1000	797+203+797
		1000+0	1000+0	203+797+797
		1000+50	1000+50	797+797+797
		1000+100	1000+100	0+500+500
		1000+250	1000+250	1000+500+500
		1000+500	1000+500	500+0+500
		1000+1000	1000+1000	500+1000+500
				500+500+0
				500+500+1000
				500+500+500
				203+500+203
				203+203+500
<u>Admixes</u>	500	500+ 500		500+500+500
Bentonite admix				
Forest soil admix				
Spruce bark admix				

1. Batch Samples agitated for 24 hrs.
2. Heavy metal concentrations measured before and after agitation.
3. Admixes stored at 4° C to await Selective Sequential Extraction.
4. Heavy metal concentrations used to graph adsorption isotherms.

FIGURE 3.3.1. Diagram of the Batch adsorption test.

3.3.2 Batch adsorption test procedure

All the materials were tested at their natural water contents (see Table 4.1.1). Prior to the Batch test, the Forest soil, and Spruce bark were mechanically sieved to remove coarse fractions. At its natural state, the Forest soil tended to stick together in clusters. To account for this overestimation in particle size, a larger sieve was used for the Forest soil. Thus, an 840 micron sieve was used for the Forest soil, and a 500 micron sieve was used for the Spruce bark.

Two soil:solution ratios were used in this study. For the admixes, a 1 g : 10 ml, soil:solution ratio was used as recommended by the EPA (1987). For the individual materials, the soil:solution ratio was lowered to 1:50, because more solution was required to create a bentonite suspension.

For the admixes, 4 g (dry weight) of material and 40 ml of heavy metal solution were placed into a 50 ml polypropylene centrifuge test tube. For the individual clay barrier materials, 0.5 g (dry weight) of material and 25 ml of heavy metal solution (bentonite, Forest soil, or Spruce bark) were placed into a 50 ml polypropylene centrifuge test tube. The test tubes were inserted into a mechanical rotator, and rotated for 24 hr. The mechanical rotator was powered by a Dayton Model 4Z134 motor, and set to rotate at approximately 22 rev/minute.

After 24 hr., the test tubes were removed from the rotator, and then placed into a centrifuge. After centrifuging the test tubes for 15 min. at a G force of about 2200 in a Beckman GS-6 centrifuge, the final heavy metal concentration of the supernatant was determined using a Video 22 Thermo Jarrell Ash aa/ae Spectrophotometer - Model 957 (AAS). In addition, the equilibrium pH of the supernatant was measured using an Orion model 1 420A pH meter. The Forest soil and Spruce bark contained fractions that floated even after centrifuging. For such materials, test tube pre-filters were used to remove the floating fractions before the heavy metal concentration and pH determinations.

The concentration ranges measured by the AAS are shown in Table 3.3.3. For heavy metal concentrations outside these ranges, dilution was required. After discarding the supernatant, the Batch samples prepared for SSE were stored in the centrifuge tubes at 4 °C.

TABLE 3.3.3. Heavy metal concentration ranges measured by the atomic absorption spectrophotometer.

Heavy metal	<i>Pb</i>	<i>Cu</i>	<i>Cd</i>
Wavelength	283	327	228
Range (mg L ⁻¹)	0 - 500	0 - 100	0 - 30

Prior to further data analysis, the heavy metal concentrations were converted from mass to moles. The conversion calculations are shown APPENDIX D.1. The conversion of data from mass to moles was necessary, because sorption phenomena is best described in terms the *number* of molecules, as opposed to the *mass* of molecules. The atomic weights of *Pb*, *Cu*, and *Cd*, are 207.2 g mol⁻¹, 63.55 g mol⁻¹, and 112.4 g mol⁻¹, respectively. Thus, for equal masses of *Pb*, *Cu*, and *Cd*, the number of *Cu* moles would be 3.3 times greater than *Pb*, and 1.8 times greater than *Cd*.

The heavy metal sorption concentration for the sorbent was calculated with the following equation:

$$q = \frac{(C_i - C_f) * V}{M}$$

where q is heavy metal sorption concentration (cmol kg⁻¹), C_i is the initial concentration of solution (cmol L⁻¹), C_f is the equilibrium (final) concentration (cmol L⁻¹), V is the volume of the solution (L), and M is the mass of sorbent (kg).

Sorption isotherms were constructed by plotting q (cmol kg^{-1}) vs. the initial heavy metal solution concentration (mmol L^{-1}). Equilibrium pH graphs were constructed by plotting equilibrium pH vs. initial heavy metal solution concentration (mmol L^{-1}).

3.4 LEACHING CELL TEST METHOD

3.4.1 Leaching cell test program

The Leaching cell test was used to find the hydraulic conductivities of the compacted admix samples. In addition, the breakthrough results were used to determine the breakthrough points, retention capacities, and migration behavior of the heavy metals through the compacted admix samples. All tests were done in triplicate to provide contingency, and assess variability. The combinations of admixes and heavy metal solutions tested are shown Table 3.4.1. Only the bentonite admix was used to investigate heavy metal sorption and migration behaviour in ternary systems. Data from the single and binary systems would be sufficient for comparing the performances of the different admixes. Shown in Figure 3.4.1, is a diagram of the Leaching cell test.

TABLE 3.4.1. The Leaching cell test matrix.

Admix	Single		Binary	Ternary
	<i>Pb</i>	<i>Cu</i>	<i>Pb+Cu</i>	<i>Pb+Cu+Cd</i>
	500 mg L ⁻¹	500 mg L ⁻¹	500 mg L ⁻¹ each	500 mg L ⁻¹ each
Bentonite admix	√	√	√	√
Forest soil admix	√	√	√	
Spruce bark admix	√	√	√	

A list of equipment is shown in APPENDIX C.1. Also included are schematics of the compaction hammer, compaction mold, and the Leaching cell. All equipment used were made of materials that are non-reactive with heavy metals.

FIGURE 3.4.1. Diagram of Leaching cell test.

3.4.2 Admix preparation for the Leaching cell test

Bentonite admix

Each set of admix prepared was enough for about four Leaching cells. Three cells were made for the triplicate Leaching cell test, and the fourth was compacted for water content confirmation. Three thousand five hundred grams of sand was weighed into a plastic container. To achieve a 100:8 sand:bentonite ratio, 280 g (dry mass) of bentonite was measured out. The dry mass was calculated using the natural water content of the bentonite (Table 4.1.1).

Because bentonite tends to aggregate when wetted, the sand and bentonite must be thoroughly mixed before adding water. The sand was divided into six parts, and the bentonite was evenly mixed into the six portions. After each portion was individually mixed, they were combined to form three portions. Then the three portions were combined into one large mixture.

In order to ensure an even water content and thorough mixing, the sand/bentonite mixture was again divided into smaller portions. The dry sand/bentonite mixture was divided into six portions, and an equal amount of tap water was added to each portion. The portions then were mixed individually; combined to form three portions; and then combined into one. A total of 550 ml of water was added to give the mixture a water content of 14.5%. This water content - which was 2% greater than the optimum water content - was selected to produce consistently low hydraulic conductivities for the admix.

The admix was left undisturbed in a 100% humidity room to allow the water content to equilibrate throughout the whole mixture. After one day, the water content was checked again. After re-adjusting the water content to 14.5% (if necessary), the admix was stored in the 100% humidity room for 1 - 3 days before compaction.

Forest soil and Spruce bark admixes

The Forest soil and Spruce bark admixes contained a 100:7 sand:bentonite ratio. A dry mass of 245 g of bentonite was measured out for 3500 g of sand. The procedure for mixing and wetting the sand and bentonite, was exactly the same as for the bentonite admix. To prevent the Forest soil from drying, it was added after the sand/bentonite mixture was wetted. Adding Forest soil to a dry sand/bentonite mixture would dry out the Forest soil, and alter its sorption properties. For consistency, the Spruce bark was added the same way as the Forest soil.

Before adding the Forest soil or Spruce bark, the wetted sand/bentonite mixture was divided into six portions. A dry weight of 35 g of Forest soil or Spruce bark was measured out, and mixed evenly into the six portions. The dry weights of the Forest soil and Spruce bark were calculated from their natural water contents (Table 4.1.1). Next, the six portions were combined to form three portions; and then into one. The resulting ratio was 100:7:1 of sand:bentonite:Forest soil or Spruce bark. The water content check, and storage specifics were the same as for the bentonite admix.

3.4.3 Compaction procedure

No standardized method exists for rigid-wall Leaching cells; however, the hydraulic conductivity results in Daniel (1995), showed good agreement between the flexible-wall, and rigid-wall Leaching cells. The admix sample was compacted directly into the Leaching cell. Detailed compaction procedures are shown in APPENDIX C.2. The compaction procedure was modified from the modified Proctor procedure used in ASTM D1557-91 (ASTM, 1995). Weber (1991), and Cabral (1992) used static compaction because it was able to produce more consistent results; however, dynamic compaction, used in the current study, causes higher remolding of the soil (Mitchell et al., 1965). The higher remolding was expected to negate any inconsistencies from uneven mixing.

3.4.4 Leaching cell test procedure

Figure 3.4.1 shows an illustration of the Leaching cell test setup. Prior to starting the Leaching cell test, the reservoir was filled with 5 L of heavy metal solution. This was enough heavy metal solution to permeate nine pore volumes through each of the triplicate samples. Two ports were located at the influent end of the Leaching cell. The center port was where the influent tube was connected. The edge port was used to remove air bubbles from the influent end before the start of permeation. To remove air bubbles, the Leaching cell was turned onto its side, in which the edge port was above the center port. With the edge port open, heavy metal solution was allowed to flow into the Leaching cell. The heavy metal solution filled the influent end of the Leaching cell and flowed out of the edge port. As the solution began to flow out, the edge port was sealed with a cap. This procedure removed most of the air bubbles from the influent end.

To begin the Leaching cell test, the pressure in the reservoir tank was increased to 0.5 psi gauge. Every 2 hours, the pressure was increased about 1 psi, until the desired pressure was reached. For most of the tests, the pressure was increased to about 5.2 psi gauge; however, in order to speed up some tests, pressures up to 7 psi gauge were used. These pressures translated to hydraulic gradients between 65 - 88. As the heavy metal solution permeated through the Leaching cell, the time and volume of discharge was noted, periodically. In addition, the discharge was analyzed for heavy metal concentrations, and pH. From these data, graphs of hydraulic conductivity vs. discharge volume, breakthrough concentration vs. discharge volume, and pH vs. discharge volume, were created. The calculations for hydraulic conductivity are found in APPENDIX E.1. The tests were terminated when heavy metal breakthrough concentrations attained near equilibrium, or when discharge volumes reached about 1500 ml (≈ 8.5 pore volumes).

3.5 SELECTIVE SEQUENTIAL EXTRACTION METHOD

The purpose of the Selective Sequential Extraction (SSE) is to determine the distribution of metals amongst the various constituents of the soil. Specifically, the SSE determines the distribution of metals amongst five components of the soil: exchangeable, carbonates, *Fe* and *Mn* oxides, organic matter, and residual (within the crystal structure of primary and secondary minerals).

For the current study, the SSE was used to determine heavy metal distributions within the Leaching cells, and the sorption characteristics of the admixes. SSEs were performed on Leaching cell, and Batch adsorption samples. For the Leaching cell samples, two sampling methods were used. Table 3.5.1 shows the SSE program. A list of important equipment is shown in APPENDIX C.1.

TABLE 3.5.1. The SSE program.

Admix	Heavy metal solution*	Leaching cell samples (4 layers for each cell)		Batch test samples
		Center & edge sampling	Composite sampling	
Bentonite	<i>Pb</i>	√		√
	<i>Cu</i>	√		√
	<i>Pb+Cu</i>	√		√
	<i>Pb+Cu+Cd</i>		√	√
Forest soil	<i>Pb</i>	√		√
	<i>Cu</i>		√	√
	<i>Pb+Cu</i>		√	√
Spruce bark	<i>Pb</i>	√		√
	<i>Cu</i>	√		√
	<i>Pb+Cu</i>			√

* All heavy metal solutions contained 500 mg L⁻¹ of each heavy metal specified.

3.5.1 Sampling extruded Leaching cell samples

After stopping the Leaching cell test, and before extruding the admix sample, the cell was weighed to get a final weight of the sample. The extruded sample was sliced into four, 14 mm layers using a wire saw. Two sampling methods were used on the extruded samples.

For most of the extruded samples, two 5 g admix samples were taken from the center and edge regions of each layer for duplicate testing (Figure 3.5.1). For three Leaching cell trials, each layer was thoroughly remolded into uniform mixtures; then two 5 g composite samples were taken from each mixture. The composite samples represented average heavy metal concentrations for each layer. All admix samples were placed in air-tight, 50 ml polypropylene centrifuge test tubes, and stored at 4 °C to await SSE. In addition to taking samples for SSE, samples were taken from each layer for water content analysis. The weight of the extruded admix sample, and the water contents, were used to calculate the degree of saturation.

FIGURE 3.5.1. Diagram of the SSE.

3.5.2 SSE procedure

The SSE was modified from the method used by Yong et al. (1993). The procedure includes the following:

1. Initial rinse
2. Exchangeable cations extraction
3. Carbonates digestion
4. *Fe* and *Mn* oxides and hydroxides digestion
5. Organic matter digestion
6. Residual digestion

At the sampling and sample preparation stage, the Batch adsorption (section 3.3.3) and Leaching cell samples were stored in air-tight, 50 ml polypropylene tubes, at 4 °C. The weight of each tube was measured before and after the admix was placed into them. Each sample consisted of 4 - 5 g (equivalent dry weight) of admix, and was submitted to the same SSE procedure. After the SSE, the data was plotted onto sample layer vs. sorbed concentration graphs.

Initial Rinse

To remove the heavy metals dissolved in the pore water, 8 ml of distilled water was added to the admix sample. The distilled water was not adjusted to the initial pH (4.0) of the heavy metal solutions (Yong et al., 1993), because at such a pH, precipitated heavy metals in the sample may re-dissolve. After mixing the sample in the rotator for 15 min., the sample was centrifuged at a G force of about 2200 for 15 min., and the supernatant was discarded. Subsequent use of the centrifuge employed the same conditions. Considering the large sorption capacities associated with bentonite (see

sorption results in section 4.2.2), this rinse procedure would sufficiently trivialize the error associated with the pre-contaminated pore water.

Exchangeable cations extraction

For the same reason mentioned earlier, the pH of the reagent, 1 M potassium nitrate (KNO_3), was left at 6 - 7. Eight milliliters of 1 M KNO_3 was added to the admix sample. After the centrifuge tube was weighed, the mixture was agitated for 1 hour in the rotator, and then centrifuged. The atomic absorption spectrophotometer was used to analyze the heavy metal concentration of the supernatant. After discarding the supernatant, the centrifuge tube was weighed again. Eliminated from this work, was the step of rinsing the admix sample with distilled water after each extraction (Yong et al., 1993). This step was eliminated to prevent additional loss of sample from the decanting process. Weighing the centrifuge tube before and after each extraction kept track of the amount of residual reagent transferred from one extraction to the next step. The amount of heavy metals associated with the residual reagent was subtracted from the next extraction.

Carbonates digestion

Eight milliliters of 1 M sodium acetate ($NaOAc$) adjusted to pH 5.0 using acetic acid ($HOAc$), was added to the sample. After weighing the centrifuge tube, it was agitated for 5 hr in the rotator, and then centrifuged. The atomic absorption spectrophotometer was used to analyzed the supernatant for heavy metals. After discarding the supernatant, the centrifuge tube was weighed again.

Fe and Mn oxides and hydroxides digestion

Twenty milliliters of 0.04 M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 25% (v/v) $HOAc$ was added to the sample. The entire mixture was then transferred to a pre-weighed 125 ml glass flask, so that it could be placed in an oven heated to a

temperature of 96 ± 3 °C. A reflux cap was placed onto the flask to prevent the mixture from drying. The sample was left in the oven for 6 hr, and was agitated occasionally by manually swirling the flask. Next, the flask was allowed to cool at room temperature, and the mixture was transfer back to the original centrifuge tube. The flask, containing some residual sample, was weighed again. After centrifuging the mixture, the supernatant was analyzed for heavy metals, and then decanted. The centrifuge tube was weighed before heavy metal analysis, and after decanting.

Organic matter digestion

Three milliliters of 0.02 M nitric acid (HNO_3), and 5 ml of 30% hydrogen peroxide (H_2O_2) was added to the sample. The 30% H_2O_2 was adjusted to pH 2 with HNO_3 before it was added. The mixture was transferred to the 125 ml flask, and placed in the oven at 85 ± 2 °C. A reflux cap was placed onto the flask to prevent the sample from drying, and the sample was agitated occasionally by manually swirling the flask.

After 2 hr, the sample was taken out of the oven, and an additional 3 ml of 30% H_2O_2 was added to the mixture. The mixture then was placed back into the oven for 3 more hours for further digestion.

The mixture was allowed to cool for 15 min. at room temperature, after it was removed from the oven. Then, 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added to the sample, and the mixture was poured back into the centrifuge tube. Approximately 10 ml of distilled water was used to transfer more of the mixture from the flask into the centrifuge tube. Next, the mixture was diluted to the 30 ml mark, and the centrifuge tube was agitated for 0.5 hr in the rotator. During this time, the flask was weighed. Then the centrifuge tube was centrifuged; the heavy metal concentrations were analyzed; and the supernatant was decanted. The centrifuge tube was weighed before heavy metal analysis, and after decantation.

Residual digestion

The rest of the admix sample was digested with HNO_3 (APHA, AWWA, & WEF, 1995), because the Environmental laboratory in the Department of Civil Engineering at UBC was not equipped to handle hydrofluoric acid (HF) (Yong et al., 1993). The HNO_3 digestion method does not digest silica sand.

Fifteen milliliters of distilled water was used to rinse the admix sample into the flask. Boiling beads, and 5 ml of concentrated HNO_3 , were added to the flasks. The mixture was brought to a slow boil by heating the flask with a hot plate. After the mixture boiled down to about 20 ml, an addition 5 ml of concentrated HNO_3 was added. Reflux caps were placed onto the flasks, and the mixture was boiled for approximately two more hours. Next, with the aid of distilled water, the mixture was transferred back to the centrifuge tubes, and diluted to the 40 ml mark. After centrifuging, the supernatant was analyzed for heavy metals. Instead of determining the volume of the supernatant using mass differential, it simply was estimated at 40 ml. Heavy metal sorptions associated with the residual were low enough to allow for this simplification.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SOIL MATERIALS

The physico-chemical properties are presented in Table 4.1.1. The particle size distribution curves for bentonite, Forest soil, and Spruce bark are shown in Figure 4.1.1.

TABLE 4.1.1. Physico-chemical properties of soil materials.

Physico-Chemical Properties	Na-Bentonite	Forest soil	Spruce bark	Silica Sand	Admix 1	Admix 2	Admix 3
Specific gravity	2.64*	n/a	n/a	n/a	2.67	2.65	2.65
Specific surface (m ² /g)	462	n/a	n/a	n/a	n/a	n/a	n/a
Liquid limit	146 %	n/a	n/a	n/a	17.2 %	18.3 %	15.0 %
Plastic limit	70 %	n/a	n/a	n/a	n/a	n/a	n/a
Natural water content	6.8 %	212 %	6.4 %	n/a	n/a	n/a	n/a
CEC (meq/100 g)	59.7	n/a	n/a	0.0	n/a	n/a	n/a
Initial pH (in distilled water)	8.38	4.21	4.34	7.02	n/a	n/a	n/a
Initial pH (in CaCl ₂)	7.61	3.5	4.01	6.45	n/a	n/a	n/a
Max. dry density (kg/m ³)	n/a	n/a	n/a	n/a	1860	1825	1820
Optimum water content	n/a	n/a	n/a	n/a	12.7 %	12.7 %	12.3 %

* From Denham, 1999

Note: Admix 1 - 100:8 of Sand:Bentonite

Admix 2 - 100:7:1 of Sand:Bentonite:Forest soil

Admix 3 - 100:7:1 of Sand:Bentonite:Spruce bark

n/a - not analyzed

FIGURE 4.1.1. Grain size distribution of clay barrier materials.

4.2 SORPTION CAPACITIES OF CLAY BARRIER MATERIALS DETERMINED FROM BATCH ADSORPTION TESTS

Heavy metal sorption capacities were determined for bentonite, Forest soil, and Spruce bark, using the Batch adsorption test. The sorption capacities were used to evaluate the suitability of these materials for clay barriers. In addition, the results were used to develop a sorption model that predicted multi-heavy-metal sorption.

Table 4.2.1 summarizes the Batch adsorption test.

TABLE 4.2.1. Summary for Batch adsorption test.

Materials	Single	Binary		Ternary
	<i>Pb, Cu, Cd</i>	<i>Pb+Cu</i>	<i>Pb+Cd</i>	<i>Pb+Cu+Cd</i>
Bentonite	√	√	√	√
Forest soil	√	√	√	
Spruce bark	√	√	√	√

Details of the Batch adsorption test results are shown in APPENDIX D.3. The results in the following sections used the averaged values of the duplicate samples.

4.2.1 The multi-heavy-metal sorption model

The development of a multi-heavy-metal sorption model is useful for predicting the sorption behavior of different heavy metal systems. For example, a sorption model provides a basis for interpolating and extrapolating data. In addition, a model facilitates the quantitative evaluation of different sorbents. The sorption model developed in this study was able to quantitatively describe competition for multi-heavy-metal systems.

The multi-heavy-metal sorption model is based on an existing model for single heavy metal retention. The extension of the single heavy metal retention equation into

the multi-heavy-metal equation was done empirically based on the Batch adsorption data. A summary of all the equations developed for the single, binary, and ternary retention of heavy metals onto bentonite, Forest soil, and Spruce bark is provided at the end of this section.

4.2.1.1 Isotherm equation selection and general observations

The adsorption isotherm (Sparks, 1995) is a common and convenient form used to describe Batch adsorption data. The isotherm is constructed by plotting the sorbed amount of heavy metal versus the equilibrium (or final) solution concentration of heavy metal. The sorbed concentration of heavy metal is calculated using the following equation,

$$q = \frac{V(C_i - C_f)}{m} \quad (4.1)$$

where q is the amount sorbed on the sorbant, in cmol kg^{-1} , C_f and C_i are the final and initial solution concentrations, in mmol liter^{-1} , V is the solution volume, in liters, and m is the mass of sorbant, in kilograms.

Two equations widely used to describe sorption on soil surfaces are the Freundlich and Langmuir equations. Both equations were originally used to describe gas phase adsorption onto metal surfaces. The assumptions made for their original use are not applicable for sorption onto soil surfaces; therefore, their application for soils can only be considered as empirical (Hinz et al., 1992). For this study, the Freundlich equation was chosen because it could be represented as a general form of the Langmuir equation (Sheindorf et al., 1981). A modification was made to the Freundlich equation in that the C_i was used in place of C_f . The modified Freundlich equation is as follows,

$$q = bC_i^n \quad (4.2)$$

where q is the amount sorbed on the sorbant, in cmol kg^{-1} , C_i is the initial solution concentration, in mmol liter^{-1} , and b and n are curve fitting constants. According to Eqn. 4.1, the use of C_i or C_f for curve fitting is equally valid; however, as shown in Figure 4.2.1, the use of C_i widens the distribution of data, especially at low solution concentrations. The wider spread reduces the sensitivity of the Freundlich model to experimental error, thus leading to a more accurate fit.

FIGURE 4.2.1. Single heavy metal isotherms plotted in terms of (a) Final Pb solution concentration, and (b) Initial Pb solution concentration.

In the Figure 4.2.2, the modified Freundlich equation is applied to single and binary Cu sorption data. Table 4.2.2 shows the b and n values obtained for each set of data from Figure 4.2.2.

TABLE 4.2.2. Summary of b and n values fitted for single & binary Cu data.

Solution type	Bentonite		Forest soil		Spruce bark	
	b	n	b	n	b	n
Cu	3.9706	0.5028	8.4984	0.4876	4.4391	0.4465
Cu w/ 1.15 mmol/L Pb	2.9467	0.4889	5.4463	0.5627	3.3798	0.4197
Cu w/ 4.75 mmol/L Pb	2.4233	0.5058	4.3969	0.5578	2.3186	0.4242

FIGURE 4.2.2. Freundlich isotherms of Cu sorption in single and binary heavy metal solutions. (a) Bentonite. (b) Forest soil. (c) Spruce bark.

The following observations were made from the Cu sorption data:

1. The modified Freundlich equation provided a good fit for all sets of single and binary Cu sorption data.
2. The decreasing b values with increasing Pb background concentration were evidence of competition for sorption sites between Cu and Pb .
3. The n values were similar within each sorbent. This indicated that the Cu isotherm was proportionately reduced by the presence of Pb .

The above observations provide a good basis for developing a sorption model for binary heavy metal systems.

4.2.1.2 Modeling binary heavy metal sorption

The third observation made in the last section indicated that the presence of *Pb* caused a percentage change in *Cu* sorption, independent of the initial *Cu* concentration. For example, the bentonite results in Table 4.2.2 shows that the addition of 4.75 mmol L⁻¹ of *Pb* into a *Cu*-only solution caused a 39% decrease in *Cu* sorption. The 39% decrease was irrespective of whether the initial *Cu* concentration was 1 mmol L⁻¹ or 10 mmol L⁻¹ (Figure 4.2.2). This is represented mathematically by the following equation:

$$\% \Delta q_{M1} = f(C_{M2}) \quad (4.3)$$

where, $\% \Delta q_{M1}$ is the percentage change of heavy-metal-1 (*M1*) sorption due to the presence of heavy-metal-2 (*M2*), C_{M2} is the initial solution concentration of *M2*, in mmol liter⁻¹, and $f(C_{M2})$ is the competition function which describes the behaviour of $\% \Delta q_{M1}$ in terms of C_{M2} .

To determine the competition function, the single and binary sorption data was first converted to $\% \Delta q_{M1}$ by the following equation,

$$\% \Delta q_{M1} = \frac{q_{M1s} - q_{M1b}}{q_{M1s}} \times 100\% \quad (4.4)$$

where, q_{M1s} and q_{M1b} are the amount of *M1* sorbed in single and binary heavy metal solutions, respectively, in cmol kg⁻¹. Then, these were used to construct plots of $\% \Delta q_{M1}$

versus C_{M2} . For each plot, a relationship was found for $f(C_{M2})$ by using the 'trendline' tool in Microsoft EXCEL. Figures 4.2.3 - 4.2.4 show that the relationships found for $f(C_{M2})$ could be described as power functions,

$$f(C_{M2}) = aC_{M2}^p \quad (4.5)$$

where a and p are constants used to describe the unitless competition function.

Combining Eqns. 4.3 and 4.4 results in,

$$q_{M1b} = q_{M1s}(1 - f(C_{M2})) \quad (4.6)$$

Substituting Eqn. 4.2 and Eqn. 4.5 into Eqn. 4.6 results in,

$$q_{M1b} = bC_{M1}^n(1 - aC_{M2}^p) \quad (4.7)$$

where, C_{M1} is the initial $M1$ concentration, in mmol liter⁻¹, and b and n are the Freundlich constants for $M1$.

Table 4.2.3 shows the binary sorption equations written out in full for $Pb+Cu$, and $Pb+Cd$ binary systems. Shown in Figure 4.2.5, is the level of fit for each equation by plotting actual values versus calculated values. According to Figure 4.2.5, the calculated values closely matched the Batch adsorption data.

TABLE 4.2.3. Summary of sorption equations for binary heavy metal solutions.

Binary System	Sorbed Metal	Equation (q_M in units of cmol kg^{-1} , and C_M in units of mmol L^{-1})
Na-Bentonite in $Pb + Cu$ solution	Pb	$q_{Pb} = 4.546 C_{Pb}^{0.747} (1 - 0.0642 C_{Cu}^{0.574})$
	Cu	$q_{Cu} = 3.971 C_{Cu}^{0.503} (1 - 0.234 C_{Pb}^{0.292})$
Na-Bentonite in $Pb + Cd$ solution	Pb	$q_{Pb} = 4.546 C_{Pb}^{0.747} (1 - 0.0167 C_{Cd})$
	Cd	$q_{Cd} = 2.120 C_{Cd}^{0.760} (1 - 0.300 C_{Pb}^{0.326})$
Forest soil in $Pb + Cu$ solution	Pb	$q_{Pb} = 4.829 C_{Pb}^{0.873} (1 - 0.0429 C_{Cu}^{0.772})$
	Cu	$q_{Cu} = 8.498 C_{Cu}^{0.488} (1 - 0.248 C_{Pb}^{0.305})$
Forest soil in $Pb + Cd$ solution	Pb	$q_{Pb} = 4.829 C_{Pb}^{0.873} (1 - 0.0167 C_{Cd}^{0.693})$
	Cd	$q_{Cd} = 3.238 C_{Cd}^{0.716} (1 - 0.289 C_{Pb}^{0.504})$
Spruce bark in $Pb + Cu$ solution	Pb	$q_{Pb} = 4.971 C_{Pb}^{0.680} (1 - 0.0896 C_{Cu}^{0.688})$
	Cu	$q_{Cu} = 4.439 C_{Cu}^{0.447} (1 - 0.216 C_{Pb}^{0.491})$
Spruce bark in $Pb + Cd$ solution	Pb	$q_{Pb} = 4.971 C_{Pb}^{0.716} (1 - 0.0122 C_{Cd})$
	Cd	$q_{Cd} = 1.970 C_{Cd}^{0.706} (1 - 0.340 C_{Pb}^{0.564})$

FIGURE 4.2.3. Binary sorption data showing how the presence of *Cu* and *Cd* affects *Pb* sorption.
 (a - b) Bentonite. (c - d) Forest soil. (e - f) Spruce bark

FIGURE 4.2.4. Binary sorption data showing how the presence of *Pb* affects *Cu* & *Cd* sorption. (a - b) Bentonite. (c - d) Forest Soil. (e - f) Spruce Bark

FIGURE 4.2.5. Calculated versus actual values for Pb , Cu , and Cd sorption in binary solutions.
 (a - d) Bentonite. (e - h) Forest soil. (i - l) Spruce bark.

4.2.1.3 Modeling ternary heavy metal sorption

In section 4.2.1.2, a model containing a competition function was developed for binary heavy metal sorption. The important next step would be to test the validity of the model for ternary heavy metal sorption. Eqn. 4.3 in section 4.2.1.2 is modified accordingly for application in ternary systems,

$$\% \Delta q_{M1} = f(C_{M2}, C_{M3}) \times 100\% \quad (4.8)$$

where, $\% \Delta q_{M1}$ is the percentage change of heavy-metal-1 (M1) sorption due to the presence of heavy-metal-2 (M2) and heavy-metal-3 (M3), C_{M2} and C_{M3} are the initial solution concentrations of M2 and M3, in mmol liter⁻¹, and $f(C_{M2})$ is a function of C_{M2} which describes the behaviour of $\% \Delta q_{M1}$ in terms of the initial solution concentrations of M2 and M3. If the competition functions developed from the binary systems are assumed to be independent of any other heavy metals in the system, then C_{M2} and C_{M3} within the ternary competition function could be separated; thus, Eqn. 4.4 is modified for ternary systems as,

$$\% \Delta q_{M1} = \frac{q_{M1b}(M1, M2) - q_{M1t}}{q_{M1b}(M1, M2)} \times 100\% = f(C_{M3}) \times 100\% \quad (4.9)$$

where, $q_{M1b}(M1, M2)$ is the amount M1 sorbed in binary heavy metal solutions containing M1 and M2, in cmol kg⁻¹, q_{M1t} is the amount M1 sorbed in ternary heavy metal solutions, in cmol kg⁻¹, and $f(C_{M3})$ is a competition term that reflects the influence of C_{M3} on M1 sorption. After substitution with Eqn. 4.6, and isolating q_{M1t} , Eqn. 4.9 becomes,

$$q_{M1t} = q_{M1s} \times [(1 - f(C_{M3}) - f(C_{M2})(1 - f(C_{M3}))) \quad (4.10)$$

Table 4.2.3, in section 4.2.1.2, contains the competition functions necessary for calculating *Pb* sorption in ternary systems. Comparisons of the calculated *Pb* sorption data versus experimental data for bentonite and Spruce bark are shown in Figure 4.2.6. The plots in Figure 4.2.6 indicate a high correlation between calculated and experimental data.

Because binary data was not available for *Cu*+*Cd* systems, Table 4.2.3 does not contain the necessary competition functions to form ternary equations for *Cu* and *Cd* sorption. However, the ternary Batch adsorption data in conjunction with the available binary data could be used to find the missing competition functions by following Eqn. 4.9. Shown in Figure 4.2.7, are the competition functions solved from the ternary data for Bentonite and Spruce bark. With the competition functions from Figure 4.2.7, another comparison of calculated versus experimental values for *Cu* and *Cd* sorption is shown in Figure 4.2.8. Table 4.2.4 shows the complete set of equations for heavy metal sorption in ternary solutions.

TABLE 4.2.4. Summary of sorption equations for ternary heavy metal solutions.

Material	Sorbed Metal	Equation (q_M in units of cmol kg^{-1} , and C_M in units of mmol L^{-1})
Bentonite	<i>Pb</i>	$q_{Pb} = 4.546 C_{Pb}^{0.747} ((1 - 0.0167 C_{Cd}) - (0.0642 C_{Cu}^{0.574} (1 - 0.0167 C_{Cd})))$
	<i>Cu</i>	$q_{Cu} = 3.971 C_{Cu}^{0.503} ((1 - 0.234 C_{Pb}^{0.292}) - (0.0106 C_{Cd} (1 - 0.234 C_{Pb}^{0.292})))$
	<i>Cd</i>	$q_{Cd} = 2.120 C_{Cd}^{0.760} ((1 - 0.300 C_{Pb}^{0.326}) - (0.0804 C_{Cu}^{0.646} (1 - 0.300 C_{Pb}^{0.326})))$
Forest soil	<i>Pb</i>	$q_{Pb} = 4.829 C_{Pb}^{0.873} ((1 - 0.0167 C_{Cd}^{0.693}) - (0.0429 C_{Cu}^{0.772} (1 - 0.0167 C_{Cd}^{0.693})))$
	<i>Cu</i>	(insufficient data)
	<i>Cd</i>	(insufficient data)
Spruce bark	<i>Pb</i>	$q_{Pb} = 4.971 C_{Pb}^{0.680} ((1 - 0.0122 C_{Cd}) - (0.0896 C_{Cu}^{0.688} (1 - 0.0122 C_{Cd})))$
	<i>Cu</i>	$q_{Cu} = 4.439 C_{Cu}^{0.447} ((1 - 0.216 C_{Pb}^{0.491}) - (0.0106 C_{Cd} (1 - 0.216 C_{Pb}^{0.491})))$
	<i>Cd</i>	$q_{Cd} = 1.970 C_{Cd}^{0.706} ((1 - 0.340 C_{Pb}^{0.564}) - (0.0804 C_{Cu}^{0.646} (1 - 0.340 C_{Pb}^{0.564})))$

a) *Pb* sorption for Bentonite ternary system b) *Pb* sorption for Spruce B. ternary system **FIGURE 4.2.6.** Calculated versus actual values for *Pb* sorption in ternary solutions.

(a) Bentonite. (b) Spruce bark.

a) Effect of *Cd* on *Cu* Sorption for Bentonite b) Effect of *Cu* on *Cd* Sorption for Bentonite c) Effect of *Cd* on *Cu* Sorption for Spruce B. d) Effect of *Cu* on *Cd* Sorption for Spruce B. **FIGURE 4.2.7.** Ternary retention data showing how *Cu* and *Cd* change each others' sorption capacities. (a - b) Bentonite. (c - d) Spruce bark.

a) *Cu* sorption for Bentonite ternary system b) *Cd* sorption for Bentonite ternary system b) *Cu* sorption for Spruce B. ternary system c) *Cd* sorption for Spruce B. ternary system

FIGURE 4.2.8. Calculated versus actual values for *Cu* and *Cd* sorption in ternary solutions. (a - b) Bentonite. (c - d) Spruce bark.

4.2.1.4 Summary of sorption equations

Equation 4.6 describes sorption in binary heavy metal systems:

$$q_{M1b} = q_{M1s}(1 - f_{M1}(C_{M2})) \quad (4.6)$$

Equation 4.10, which describes sorption in ternary heavy metal systems, is rewritten as,

$$q_{M1t} = q_{M1s}(1 - f_{M1}(C_{M2}) - f_{M1}(C_{M3}) + f_{M1}(C_{M2})f_{M1}(C_{M3})) \quad (4.11)$$

where q_{M1s} , q_{M1b} , and q_{M1t} are the amounts of *M1* sorbed in single, binary, and ternary solutions, in units of cmol kg^{-1} , $f_{M1}(C_{M2})$, and $f_{M1}(C_{M2})$, are unitless competition

functions for M_2 and M_3 , on M_1 sorption, and C_{M_2} and C_{M_3} are initial solution concentrations for M_1 and M_2 , in units of mmol L⁻¹. Table 4.2.5 summarizes Pb , Cu , and Cd sorption in single, binary, and ternary solutions for bentonite, Forest soil, and Spruce bark.

TABLE 4.2.5. Single Pb , Cu , and Cd sorption equations and their competition functions.

Material	Sorbed Metal	Sorption equation in single metal solutions (in cmol kg ⁻¹)	Competition function (unitless)		
			Pb	Cu	Cd
Bentonite	Pb	$q_{Pb} = 4.546 C_{Pb}^{0.747}$	n/a	$0.0642 C_{Cu}^{0.574} *$	$0.0167 C_{Cd}^{**}$
	Cu	$q_{Cu} = 3.971 C_{Cu}^{0.503}$	$0.234 C_{Pb}^{0.292} *$	n/a	$0.0106 C_{Cd}^{*}$
	Cd	$q_{Cd} = 2.120 C_{Cd}^{0.760}$	$0.300 C_{Pb}^{0.326} *$	$0.0804 C_{Cu}^{0.646} **$	n/a
Forest soil	Pb	$q_{Pb} = 4.829 C_{Pb}^{0.873}$	n/a	$0.0429 C_{Cu}^{0.772} *$	$0.0167 C_{Cd}^{0.693} *$
	Cu	$q_{Cu} = 8.498 C_{Cu}^{0.488}$	$0.248 C_{Pb}^{0.305} *$	n/a	-
	Cd	$q_{Cd} = 3.238 C_{Cd}^{0.716}$	$0.289 C_{Pb}^{0.504} *$	-	n/a
Spruce bark	Pb	$q_{Pb} = 4.971 C_{Pb}^{0.680}$	n/a	$0.0896 C_{Cu}^{0.688} *$	$0.0122 C_{Cd}^{*}$
	Cu	$q_{Cu} = 4.439 C_{Cu}^{0.447}$	$0.216 C_{Pb}^{0.491} *$	n/a	$0.0106 C_{Cd}^{**}$
	Cd	$q_{Cd} = 1.970 C_{Cd}^{0.706}$	$0.340 C_{Pb}^{0.564} *$	$0.0804 C_{Cu}^{0.646} **$	n/a

n/a - not applicable

* Solved from binary data

** Solved from ternary data

Notes: 1. Sorption equations for binary and ternary solutions shown within this section.
2. C_M in units of mmol liter⁻¹.

4.2.2 Heavy metal sorption capacities

The heavy metal sorption capacities of the clay barrier materials are shown in Figure 4.2.9. In Figure 4.2.9, the isotherms are grouped according to clay barrier material, and heavy metal type. The equations for the isotherms in Figure 4.2.9 are found in Table 4.2.5. Summarized in Table 4.2.6, are the relative sorption capacities of the soil materials, and the sorption orders of the heavy metals.

FIGURE 4.2.9. Heavy metal retention capacities of soil mix materials in single metal solutions. (a - c) Grouped according to heavy metal. (d - f) Grouped according to soil mix material.

TABLE 4.2.6. Summary of relative heavy metal sorption capacities.

	Ranking
<i>Pb</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cu</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cd</i> sorption capacity	Forest soil > Bentonite > Spruce bark
Sorption onto Bentonite	<i>Pb</i> > <i>Cu</i> > <i>Cd</i>
Sorption onto Forest soil	<i>Cu</i> > <i>Pb</i> > <i>Cd</i> (up to initial [metal] of 4 mmol/L, then <i>Pb</i> > <i>Cu</i>)
Sorption onto Spruce bark	<i>Pb</i> > <i>Cu</i> > <i>Cd</i>

4.2.2.1 Ranking of materials

The data shows that for all three heavy metals, Forest soil possesses the highest sorption capacity, while bentonite and Spruce bark are approximately equal. These results could be explained by the retention characteristics of each material. Forest soil, composed almost entirely of soil organic matter, relies on its surface functional groups to retain heavy metals by way of cation exchange and complexation. These retention mechanisms are enhanced by a high specific surface area ranging of up to 800-900 m² g⁻¹ (Sparks, 1995). Although bentonite also possesses high CEC due to isomorphous substitution, its CEC is significantly lower than that of soil organic matter (Sparks, 1995). In addition to cation exchange, precipitation is also associated to bentonite, provided that the equilibrium pH is greater than 5 (Phadungchewit, 1989). Figure 4.2.10 shows that the equilibrium solution pHs for bentonite ranged between 5 - 7.5, signifying the likely occurrence of precipitation.

The main reason why bentonite sorbed less than Forest soil, is because bentonite's specific surface area (462 m² g⁻¹; from Table 4.1.1) is smaller than typical specific surface areas of Forest soil (800-900 m² g⁻¹; from Sparks, 1995). Even assuming that bentonite's combination of precipitation plus CEC could match the Forest soil's combination of complexation plus CEC, Forest soil simply has more area available for sorption. As for Spruce bark, its sorptive ability is attributed to the surface functional groups associated with tannin compounds (Vazquez et al., 1994, Gloaguen & Morvan, 1997). The main sorptive functional groups in tannins are carboxyl and phenolic. As mentioned earlier, Forest soil also relies on surface functional groups; however, these functional groups are associated with humic substances (Sparks, 1995). In addition to carboxyl and phenolic, humic substances possess many other functional groups useful for heavy metal retention. As an indication of sorption site availability, Spruce bark is composed of 5 - 37 % weight tannins (Field et al., 1988), while soil organic matter is composed of 33 - 75% weight humic substances (Sparks, 1995). According to this rough

indication, per unit weight, Forest soil contains more surface functional groups than Spruce bark.

FIGURE 4.2.10. Final pH graphs showing the influence of Pb, Cu, and Cd on the final solution pHs of each suspension. (a) Bentonite. (b) Forest soil. (c) Spruce bark.

4.2.2.2 Ranking of heavy metals

The order of sorption capacity for bentonite and Spruce bark is $Pb > Cu > Cd$, while for Forest soil, the order is $Cu > Pb > Cd$. These orders are only for the range of concentrations tested. The isotherms shown in Figure 4.2.9.d - f, show that within the tested range, are crossover points between Pb and Cu . For bentonite and Spruce bark, the isotherms cross over at very low initial metal concentrations, while for Forest soil, the isotherms cross over at a high concentration (4 mmol L^{-1}). In addition, if the isotherms are extrapolated beyond the tested range, the Cu and Cd isotherms also are expected to cross over. Therefore, even though overall orders of sorption capacity are presented, the crossing over of isotherms indicates that the sorption capacity orders are dependent on the concentration range of the heavy metal solutions tested.

The results are explained by comparing the reaction characteristics of each heavy metal and how they relate to the three main heavy retention mechanisms: cation exchange, surface complexation, and precipitation. Table 4.2.7 shows the ionic radii, the 1st and 2nd hydrolysis products, and the OH^- solubility constants for *Pb*, *Cu*, and *Cd*.

TABLE 4.2.7. Characteristics of *Pb*, *Cu*, & *Cd*.

	<i>Pb</i>	<i>Cu</i>	<i>Cd</i>	<i>Ca</i>
Ionic radii	120 pm*	70 pm**	97 pm*	99 pm*
1st hydrolysis constant***	7.7	7.7	10.1	12.7
2nd hydrolysis constant***	17.75	13.78	20.3	27.99
OH^- solubility constant***	8.16	8.68	13.65	22.8

* Fyfe, 1964

** McQuarrie & Rock, 1991

*** Lindsay, 1979

Cation exchange, is described as the nonspecific adsorption of positively charged hydrated ions (Evans, 1989). According to Coulombs' law, the energy attraction of two ions is proportional to the product of their charges and inversely proportional to the distance between the two centers. Since *Pb*, *Cu*, and *Cd* possess the same charge (+2), the adsorption capacity of these cations can be explained by differences in their hydrated radii. Cations with smaller hydrated radii would be able to pack closer, and take advantage of the stronger attraction energy of being closer to the sorbent. Since the hydrated radii of cations are inversely related to their ionic radii, the order of sorption capacity would be $Pb > Cd > Cu$.

To estimate the importance of complexation, one could examine hydrolysis reactions. The general tendency for a metal to complex can be seen by its degree of hydrolysis. The use of hydrolysis products also are useful because surface complexation on minerals and organic matter often involves the OH^- group. Thus according to the 1st and 2nd hydrolysis products, the order of sorption would be $Cu > Pb > Cd$.

Finally, to estimate the importance of precipitation, one could examine hydroxide (OH^-) solubility products. According to hydroxide (OH^-) solubility products, the order of precipitation would be $Pb > Cu > Cd$.

The dominant sorption mechanisms for each material was presented in section 4.2.2.1. For bentonite, cation exchange and precipitation were expected to dominate. According to hydrated radii, hydrolysis products, and OH^- solubility products (Table 4.2.7), Pb sorption was predicted to be the greatest. In regards to Cu and Cd , cation exchange and precipitation provided opposite predictions. The Batch test results show that the actual ranking is $Pb > Cu > Cd$. This suggests that for bentonite, precipitation dominates over cation exchange. Since for bentonite, sensitivity to declining pH is much higher for precipitation than cation exchange, the pH results in Figure 4.10.a, supports the presented hypothesis.

For Forest soil, cation exchange and surface complexation were expected to dominate. The Batch adsorption results show that below initial heavy metal concentrations of 4 mmol L^{-1} , the ranking is $Cu > Pb > Cd$, and above concentrations of 4 mmol L^{-1} , the ranking becomes $Pb > Cu > Cd$. To harmonize the predictions in Table 4.2.7, with the tested results, surface complexation must be considered dominant at low metal concentrations. As the solution metal concentrations rise, and complexing sites start to fill up, cation exchange becomes more dominant. The cross-over point between the Pb and Cu isotherms in Figure 4.2.9.e, indicates the point at which cation exchange dominates over complexation.

Since Spruce bark also relies on cation exchange and surface complexation for heavy metal sorption, one would expect its order of sorption capacity to be the same as the Forest soil's; however, the results in Table 4.2.6 appear to show that the ranking is $Pb > Cu > Cd$, throughout the entire range. This discrepancy is resolved by pointing out that Forest soil probably has many more complexing sites than Spruce bark. This suggests that cation exchange would begin to dominate at much lower concentrations.

The Spruce bark isotherm in Figure 4.2.9.f, show that the *Pb* and *Cu* isotherms crossed at a very low initial concentration ($\approx 1 \text{ mmol L}^{-1}$).

Within this section, several reasonable, but speculative explanations were provided to harmonize the predictions in Table 4.2.7 with actual results in Table 4.2.6. In section 4.4.3.1, more insights on retention mechanisms will be presented. These insights will support the explanations presented in this section.

4.2.3 Heavy metal selectivity and competition

Heavy metal selectivity is determined by placing the sorbent into a solution containing equal concentrations of each heavy metal. The order of selectivity would be based on the amounts of each heavy metal sorbed. Using this approach, the heavy metal selectivities are shown in Figure 4.2.11. The graphs in Figure 4.2.11 were plotted using the equations in section 4.2.1.4. The concern regarding selectivity graphs is that they are misleading in showing heavy metal sorption competition. For example, Figure 4.2.11.a seems to clearly show that *Pb* out-competes *Cd* for sorption sites. However, the individual sorption isotherms in Figure 4.2.9.d show that even in separate non-competitive environments, *Pb* sorption is higher than *Cd* sorption. In order to identify competition, the selectivity isotherms would need to be compared to the individual sorption isotherms. If the selectivity graphs in Figure 4.2.11 were proportional to the sorption capacity graphs in Figure 4.2.9, then one could conclude that competition amongst the three heavy metals was equal. However, the graphs in Figure 4.2.11 and 4.2.9, show that some heavy metals were more competitive than others.

FIGURE 4.2.11. Selectivity of heavy metals in ternary and binary systems.
(a) Bentonite. (b) Spruce bark. (c - d) Forest soil (binary systems).

The previous discussion demonstrated that selectivity graphs, alone, were insufficient in identifying competition. Competition is shown more effectively by examining the competition functions associated with each sorbent. The competition functions in Table 4.2.5 were rearranged in Table 4.2.8 to show the order of heavy metal competition for each barrier material. Within the tested range, the order of heavy metal competition for all materials is $Pb > Cu > Cd$.

TABLE 4.2.8. Summary of competition amongst *Pb*, *Cu*, and *Cd*.

Material	Type of sorption	Competition functions (unitless)	
		more competitive	less competitive
Bentonite	<i>Pb sorption</i>	$0.0642 C_{Cu}^{0.574}$	$> 0.0167 C_{Cd}$
	<i>Cu sorption</i>	$0.234 C_{Pb}^{0.292}$	$> 0.0106 C_{Cd}$
	<i>Cd sorption</i>	$0.300 C_{Pb}^{0.326}$	$> 0.0804 C_{Cu}^{0.646}$
Forest soil	<i>Pb sorption</i>	$0.0429 C_{Cu}^{0.772}$	$> 0.0167 C_{Cd}^{0.693}$
	<i>Cu sorption</i>	$0.248 C_{Pb}^{0.305}$	?
	<i>Cd sorption</i>	$0.289 C_{Pb}^{0.504}$	?
Spruce bark	<i>Pb sorption</i>	$0.0896 C_{Cu}^{0.688}$	$> 0.0122 C_{Cd}$
	<i>Cu sorption</i>	$0.216 C_{Pb}^{0.491}$	$> 0.0106 C_{Cd}$
	<i>Cd sorption</i>	$0.340 C_{Pb}^{0.564}$	$> 0.0804 C_{Cu}^{0.646}$

4.2.4 Sorption performance of clay barrier materials based on Batch adsorption tests

Based solely on heavy metal retention capacity, Forest soil and Spruce bark, both compare favorably to bentonite under most of the experimented conditions. The single heavy metal sorption isotherms in Figure 4.2.9.a-c, show that Forest soil has the highest sorption capacity for all three heavy metals. In fact, Forest soil's sorption capacity for *Cu* is twice as large as bentonite's and Spruce bark's capacity. As for Spruce bark, its sorption capacity for *Pb* and *Cu* is almost identical to that of bentonite. At higher *Cd* concentrations (> 4 mmol/L), the sorption capacity of Spruce bark is approximately 20 % less than bentonite. In binary and ternary heavy metal solutions (Figure 4.2.11), the three barrier materials rank similar to that in single heavy metal solutions. The only exception was with *Cd*. Because *Cd* sorption by Forest soil and Spruce bark was greatly inhibited by the presence of *Pb* and *Cu*, bentonite moved up to the top ranking when *Pb* and *Cu* were present in significant concentrations. *Cd* sorption was inhibited so greatly for Spruce bark, that its isotherm developed a negative slope at higher concentrations.

Forest soil and Spruce bark have a distinct advantage over bentonite in terms of retention strength. Although all three clay barrier materials rely on cation exchange,

Forest soil and Spruce bark also rely significantly on surface complexation. Heavy metals bound by complexation are not displaced as easily as heavy metals bound by cation exchange. In addition, because the migration of heavy metals is usually within an acidic medium, the bentonite's reliance on precipitation is of concern. Once the neutralizing ability of the bentonite is spent, the precipitated heavy metals would re-solubilize. On the hand, complexation onto Forest soil and Spruce bark is still effective at low pHs (Figure 4.2.10).

A potential disadvantage for Forest soil and Spruce bark is in how they would effect the mobility of heavy metals that remain in solution. Fractions of soil organic matter (Sparks, 1995) and tannins (Haygreen & Bowyer, 1996) dissolve in water. These fractions may strengthen the solubility of the dissolved heavy metals by forming soluble complexes (Evans, 1989; Livens, 1991). Further studies are required to quantify the extent of this phenomenon.

4.2.5 Summary of Batch adsorption test results

1. An empirical model based on the Freundlich equation was developed for the sorption of *Pb*, *Cu*, and *Cd*, onto bentonite, Forest soil, and Spruce bark. This model was capable of predicting single, binary, and ternary heavy metal systems. See Table 4.2.5 for the full set of equations.

2. The sorption capacity rankings of heavy metals and barrier materials are as follows:

	Ranking
<i>Pb</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cu</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cd</i> sorption capacity	Forest soil > Bentonite > Spruce bark
Sorption onto Bentonite	$Pb > Cu > Cd$
Sorption onto Forest soil	$Cu > Pb > Cd$ (up to initial [metal] of 4 mmol/L, then $Pb > Cu$)
Sorption onto Spruce bark	$Pb > Cu > Cd$

3. The order of selectivity for *Pb*, *Cu*, and *Cd* is similar to the order of sorption capacities. Thus, competition amongst heavy metals cannot be directly observed from the order of selectivity.
4. Competition amongst heavy metals was described by the competition functions incorporated in the sorption model. According to the competition functions, the order of competition related all materials tested is $Pb > Cu > Cd$.
5. The *Pb*, *Cu*, and *Cd* sorption capacities of Forest soil and Spruce bark compared favorably to bentonite under most experimental conditions. The exception occurred with *Cd* sorption in competitive environments. The *Cd* sorption capacities of Forest soil and Spruce bark were low in comparison to bentonite when significant concentrations of *Cu* and *Pb* were present. Despite this exception, the sorption performance of Forest soil and Spruce bark was sufficient to incorporate them into Leaching cell testing. The Leaching cell test will determine the sorption and hydraulic conductivity effects of adding Forest soil and Spruce bark into a typical clay barrier mix.

4.3 THE LEACHING CELL TEST

Leaching cell tests were used to investigate the heavy metal compatibility of clay barriers, and the migration behavior of the heavy metals. The Leaching cell tests generated hydraulic conductivity, retention capacity, and heavy metal breakthrough data for evaluating the performance of the three admixes. The bentonite, Forest soil, and Spruce bark admixes were permeated with single and binary solutions of *Pb*, and *Cu*. These results would be sufficient for comparing the different admixes. Only the bentonite admix was permeated with a ternary solution of *Pb*, *Cu*, and *Cd*, to investigate heavy metal migration in a ternary system. Each heavy metal contained in the leachate solutions was present at concentrations of 500 mg L⁻¹. Converted to molar values, the *Pb* concentration was 2.41 mmol L⁻¹; the *Cu* concentration, 7.87 mmol L⁻¹; and the *Cd* concentration, 4.45 mmol L⁻¹. To maintain similar ionic strengths, all leachate solutions including the blanks, also contained 0.01 M Ca(NO₃)₂. The testing matrix is summarized in Table 4.3.1, and detailed Leaching test results are shown in APPENDIX E.3.

TABLE 4.3.1. Testing matrix for the Leaching cell test.

Admix	Leachate (500 mg L ⁻¹ for each metal)			
	<i>Pb</i>	<i>Cu</i>	<i>Pb</i> + <i>Cu</i>	<i>Pb</i> + <i>Cu</i> + <i>Cd</i>
Bentonite (100:8 of Sand:Bentonite)	√	√	√	√
Forest soil (100:7:1 of Sand:Bentonite:Forest soil)	√	√	√	
Spruce bark (100:7:1 of Sand:Bentonite:Spruce bark)	√	√	√	

All the Leaching cell tests were done in triplicate to increase the reliability and gauge the variability of the results. The data analysis, and averaging of the Leaching test triplicate results are shown in APPENDIX E.1. A Leaching cell test was terminated when discharge heavy metal concentrations reached near equilibrium after breakthrough. All of the heavy metal breakthrough concentrations in the current study

attained this state before discharge volumes reached 1500 ml.

Table 4.3.2 shows some physical properties of the Leaching cell samples, as well as the number of test failures. A failed test was identified by high hydraulic conductivities at the start of permeation. This signified side-wall leakage. The high number of test failures is attributed to improper sample handling. Over-handling of the Leaching cell after the compaction procedure may have disturbed the admix sample while it was in the Leaching cell. Movement of the admix sample within the Leaching cell would increase the possibility of side-wall leakage.

All of the hydraulic conductivity data up to a discharge volume of 1500 ml (section 4.3.2) were shown in Figures 4.3.1 - 4.3.4. The averaged hydraulic conductivity data is grouped according to admix type in Figure 4.3.5, and grouped according to leachate type in Figure 4.3.6 (section 4.3.1). Figures 4.3.8 - 4.3.10, present all the breakthrough data up to 1500 ml of discharge, and Figures 4.3.11 - 4.3.12, presents the averaged heavy metal breakthrough curves (section 4.3.2). Shown in Figure 4.3.15 is the discharge pH data (section 4.3.3).

TABLE 4.3.2. Physical properties of Leaching cell samples.

	Permeant	Triplicate #	Initial water content	Initial dry density (kg/m ³)	Initial saturation	Final saturation
Bentonite admix	<i>Blank</i>	1	14.5%	1800.1	80%	
	<i>Blank</i>	2	14.5%	1800.1	80%	
	<i>Blank</i>	3	14.5%	1812.8	82%	
	<i>Pb</i>	1	14.9%	1793.5	81%	
	<i>Pb</i>	2	14.9%	1826.9	86%	
	<i>Pb</i>	x				
	<i>Cd</i>	1	14.6%	1828.5	85%	
	<i>Cd</i>	x				
	<i>Cd</i>	x				
	<i>Pb+Cu</i>	1	14.9%	1797.9	82%	
	<i>Pb+Cu</i>	x				
	<i>Pb+Cu</i>	x				
	<i>Pb+Cu+Cd</i>	1	14.6%	1804.1	81%	
	<i>Pb+Cu+Cd</i>	2	14.6%	1806.2	81%	89%
	<i>Pb+Cu+Cd</i>	x				
Forest soil admix	<i>Blank</i>	1	14.8%	1814.9	85%	
	<i>Blank</i>	x				
	<i>Blank</i>	x				
	<i>Pb</i>	1	15.3%	1784.4	84%	
	<i>Pb</i>	2	15.3%	1783.5	83%	
	<i>Pb</i>	3	15.3%	1786.9	84%	
	<i>Cu</i>	1	14.3%	1799.3	80%	88%
	<i>Cu</i>	2	14.3%	1810.6	82%	96%
	<i>Cu</i>	x				
	<i>Pb+Cu</i>	1	14.5%	1803.0	82%	88%
	<i>Pb+Cu</i>	2	14.5%	1800.5	81%	90%
	<i>Pb+Cu</i>	3	14.5%	1789.1	80%	88%
Spruce bark admix	<i>Blank</i>	1	14.0%	1779.8	76%	
	<i>Blank</i>	2	14.0%	1765.7	74%	
	<i>Blank</i>	x				
	<i>Pb</i>	1	15.0%	1767.1	80%	
	<i>Pb</i>	2	15.0%	1777.3	81%	
	<i>Pb</i>	x				
	<i>Cu</i>	1	14.8%	1757.5	77%	
	<i>Cu</i>	2	14.8%	1789.2	82%	
	<i>Cu</i>	3	14.8%	1791.1	82%	
	<i>Pb+Cu</i>	1	15.5%	1750.7	80%	
	<i>Pb+Cu</i>	2	15.5%	1741.3	79%	
	<i>Pb+Cu</i>	3	15.5%	1745.7	79%	

x - failed tests

4.3.1 Hydraulic conductivity results

The main interests of this section are in determining whether *Pb*, *Cu*, and *Cd*, negatively affect the hydraulic conductivity of clay barriers, and the nature and extent of the negative effects.

4.3.1.1 General observations

The hydraulic conductivity curves in Figures 4.3.2 - 4.3.5, show that all heavy metal permeated samples behaved similarly. Most samples made from bentonite and Spruce bark admixes started at low hydraulic conductivity values, but after discharge volumes of about 100 - 200 ml (≈ 1 pore volume), the hydraulic conductivities increased rapidly. After the short period of rapid increase, the hydraulic conductivity values quickly approached almost constant values. Relative to the other admixes, samples made from the Forest soil admix started at higher hydraulic conductivities, but after a general decline for about 200 ml of discharge, the Forest soil samples experienced the same increase and leveling off as the other admix samples. All samples that were permeated with blank solutions of 0.01 M $\text{Ca}(\text{NO}_3)_2$, maintained very low hydraulic conductivities for the duration of the tests. To facilitate the comparison of results, the triplicate hydraulic conductivity data seen in Figures 4.3.2 - 4.3.5, were averaged and grouped together in Figures 4.3.6 and 4.3.7. Specific hydraulic conductivity values were taken from these and summarized in Table 4.3.3.

Cabral's (1992) results did not show the same, large hydraulic conductivity increases as in the current study. The reason for the discrepancy is likely because Cabral (1992) applied large confining pressures (60 - 370 kPa) to his samples. The confining pressures may have partially collapsed the widened pore channels caused by flocculation. The confining pressures used by Cabral (1992) would be representative of landfills that have already received several lifts of waste. In actual conditions, exposure

to contaminated leachate may occur earlier, at much lower confining pressures. For example, one 3 m lift of waste with a unit weight 5.9 kN m^{-3} (Tchobanoglous et al., 1993), plus 0.3 m of cover material with a unit weight of 20 kN m^{-3} , would result in a confining pressure of 23.7 kPa. Although confining pressures were not used in the current study, water boundary pressures of 36 - 48 kPa were generated because of the large hydraulic gradients (65 - 88). These pressures would be more representative of landfills in their initial stages of operation. These conditions would also be representative of surface impoundments. Further testing is recommended to better understand the effect of confining pressures on heavy metal permeated clay barriers.

a) Bentonite admix samples permeated with 0.01 M $\text{Ca}(\text{NO}_3)_2$ b) Forest soil admix sample permeated with 0.01 M $\text{Ca}(\text{NO}_3)_2$ c) Spruce Bark admix samples permeated with 0.01 M $\text{Ca}(\text{NO}_3)_2$

FIGURE 4.3.1. Hydraulic conductivity results for leachate blanks. (a) Bentonite admix. (b) Forest soil admix. (c) Spruce bark admix.

a) *Pb* permeants through bentonite admix samples b) *Cu* permeants through bentonite admix samples c) *Pb + Cu* permeants through bentonite admix samples d) *Pb + Cu + Cd* permeants through bentonite admix samples

FIGURE 4.3.2. Hydraulic conductivity results for bentonite admix samples.

(a) *Pb* permeant. (b) *Cu* permeant. (c) *Pb+Cu* permeant. (d) *Pb+Cu+Cd* permeant.

a) *Pb* permeants through Forest soil admix samples b) *Cu* permeants through Forest soil admix samples c) *Pb + Cu* permeants through Forest soil admix samples

Triplicate #		
× Test 1	□ Test 2	△ Test 3

FIGURE 4.3.3. Hydraulic conductivity results for Forest soil admix samples.

(a) *Pb* permeant. (b) *Cu* permeant. (c) *Pb+Cu* permeant.

a) *Pb* permeants through Spruce Bark admix samples b) *Cu* permeants through Spruce bark admix samples c) *Pb + Cu* permeants through Spruce bark admix samples

Triplicate #		
× Test 1	□ Test 2	△ Test 3

FIGURE 4.3.4. Hydraulic conductivity results for Spruce bark admix samples.
 (a) *Pb* permeant. (b) *Cu* permeant. (c) *Pb+Cu* permeant.

a) Bentonite admix - 100:8 of sand:bentonite

b) Forest soil admix - 100:7:1 of sand:bentonite:Forest soil

c) Spruce bark admix - 100:7:1 of sand:bentonite:Spruce bark

FIGURE 4.3.5. Averaged hydraulic conductivity results grouped by admix type.
(a) Bentonite admix. (b) Forest soil admix. (c) Spruce bark admix.

a) *Pb* Leachate b) *Cu* Leachate c) *Pb+Cu* Leachate

— Bentonite admix   — Forest soil admix   - - - Spruce bark admix

FIGURE 4.3.6. Averaged hydraulic conductivity results grouped by leachate type.

(a) *Pb* leachate. (b) *Cu* leachate. (c) *Pb+Cu* leachate

TABLE 4.3.3. Summary of hydraulic conductivity results from averaged data in Figures 4.3.5 & 4.3.6.

Admix	Leachate	Initial hydraulic conductivity	Hydraulic conductivity at 1200 ml of discharge
		m s^{-1}	m s^{-1}
Bentonite admix	Blank	2.4E-11 (test stopped before 1200 ml of discharge)	
	<i>Pb</i>	7.2E-11	4.7E-09
	<i>Cu</i>	5.0E-11	4.8E-09
	<i>Pb+Cu</i>	3.5E-10	4.3E-09
	<i>Pb+Cu+Cd</i>	3.1E-10	2.4E-09
Forest soil admix	Blank	2.8E-11 (test stopped before 1200 ml of discharge)	
	<i>Pb</i>	3.0E-09	5.0E-09
	<i>Cu</i>	8.0E-10	1.8E-09
	<i>Pb+Cu</i>	4.9E-10	3.3E-09
Spruce bark admix	Blank	1.4E-11 (test stopped before 1200 ml of discharge)	
	<i>Pb</i>	8.9E-11	6.4E-10
	<i>Cu</i>	8.4E-11	2.7E-09
	<i>Pb+Cu</i>	1.6E-10	3.4E-09

4.3.1.2 Mechanism of hydraulic conductivity increase

According to the Gouy-Chapman theory, solutions of increasing ionic strength causes increased flocculation of clay particles (Tan, 1998); thus, the higher the heavy metal concentration, the higher the degree of flocculation. However, the relationship between flocculation and changes in hydraulic conductivity remains uncertain. Figure 4.3.7 shows a proposed mechanism for hydraulic conductivity increase. The proposed mechanism was deduced from the shape of the hydraulic conductivity curves (Figures 4.2.3 - 4.3.4).

The characteristics of the hydraulic conductivity curves can be separated into three parts. In the initial portion, the hydraulic conductivity values were low. During this stage of initial permeation, the heavy metal solution was causing the bentonite particles to flocculate; however, the hydraulic conductivity remained low because of the resistance provided by the uncontaminated region in front of the heavy metal flow (Figure 4.3.7.a).

After the initial portion, a period of rapid hydraulic conductivity increase occurred. This rapid increase was probably initiated upon the full penetration of heavy metals (Figure 4.3.7.b). The breakthrough of heavy metals meant that complete heavy metal widened pathways had formed. The flow concentrated towards these preferential pathways, and further widened them.

The initial set of preferential pathways caused large increases in hydraulic conductivity. However, the impact of subsequent preferential pathways were limited by the structural fabric of the compacted sample. Thus, depending on the structural fabric of the compacted sample, and the size and number of preferential pathways formed, the hydraulic conductivity eventually reached an equilibrium value (Figure 4.3.7.c).

According to the proposed mechanism, hydraulic conductivity increase coincides with heavy metal breakthrough. Later, the presentation of heavy metal breakthrough results in Figures 4.3.8 - 4.3.10, (in section 4.3.3) will confirm this occurrence, giving additional credibility to the proposed mechanism.

4.3.1.3 Effect of heavy metals vs. calcium on hydraulic conductivity

The Leaching cell tests in this study were performed with the same set of experimental conditions. Also, all leachate solutions were set to the same initial pH, and similar ionic strengths. An important weakness in applying the Gouy-Chapman theory (Tan, 1998) to heavy metal contaminated soils was revealed through the current study. The Gouy-Chapman theory identifies cations only by their valence. Since the blank (Ca^{2+}) and heavy metal (Pb^{2+} , Cu^{2+} , Cd^{2+}) leachates all contain +2 cations, and possess similar ionic strengths, no differences in hydraulic conductivities should have been observed. However, the results in Figures 4.3.1 - 4.3.4 reveal that the heavy metal leachates had hydraulic conductivities over one magnitude greater than the blank

a) Initial permeation of heavy metals through Leaching cell

b) Initial penetration of heavy metals

c) Long-term flow pattern

FIGURE 4.3.7. Conceptual model for the mechanism of hydraulic conductivity increase in Leaching cells. (a) Initial permeation. (b) Initial heavy metal penetration. (c) Long-term flow pattern.

leachates. Specifically, *Pb* and *Cu* leachates caused significantly higher hydraulic conductivities than the *Ca* (blank) leachate. Hydraulic conductivity data for *Cd* was insufficient to make any conclusions. The current study showed that cations of the same valence may have wide ranging effects on hydraulic conductivity. Thus, valence is not a sufficient parameter in identifying the effect of cations.

Shown in Table 4.3.4, is a comparison between the sorption mechanisms of *Ca* and the heavy metals. In comparison to *Pb*, *Cu*, and *Cd*, *Ca* possesses a much lower potential for complexation, and precipitation. This comparison suggests that specific sorption characteristics may give indication to their effect on clay barrier hydraulic conductivity. Further research into calcium sorption capacities and characteristics would lead to stronger conclusions relating sorption characteristics and hydraulic conductivity. Furthermore, if flocculation is assumed to be the main mechanism that influences change in hydraulic conductivity, then one would need to investigate the relationship between sorption and flocculation, in order to bridge the gap of understanding.

TABLE 4.3.4. Comparison between the sorption mechanisms of *Ca* and the heavy metals.

Retention mechanism	Associated Reaction parameter *	Order from greatest to least potential
Cation exchange	Ionic radii	<i>Pb</i> > <i>Ca</i> > <i>Cd</i> > <i>Cu</i>
Complexation	1st hydrolysis constant	<i>Cu</i> > <i>Pb</i> > <i>Cd</i> > <i>Ca</i>
	2nd hydrolysis constant	
Precipitation	OH^- solubility constant	<i>Pb</i> > <i>Cu</i> > <i>Cd</i> > <i>Ca</i>

* See Table 4.2.7 for parameter values.

4.3.1.4 Importance of initial saturation

Barriers with high heavy metal retention capacities are preferable, because they are expected to retard the migration of heavy metals. However, Figures 4.3.1 - 4.3.4 show that the initial portions in the current study usually did not last more than 200 ml (≈ 1 pore volume), before large hydraulic conductivity increases occurred. Even though

the Batch adsorption tests showed that the clay barriers possessed high heavy metal sorption capacities, the short initial portions indicated that the barriers were not able to retard the migration of heavy metals.

In contrast, the results of Weber (1991), and Cabral (1992) were more in line with expectations. Each had one sample that did not show significant increases until after 7 and 5 pore volumes, respectively. Also, many of their samples did not show any increases for the duration of their tests.

The reason why the current study failed to delay hydraulic conductivity increases, may be due to initial saturation. The admix samples of Weber and Cabral were 100%, or near 100% saturated before *Pb* permeation. In contrast, the current study began heavy metal permeation on samples that were only $\approx 80\%$ saturated (Table 4.3.2). The presence of air voids would increase the heterogeneity of the soil/pore media; thus, increasing the likelihood of preferential channeling. Also, in comparison to water-filled voids, air voids would provide less resistance to structural changes within the compacted admixes. The structural changes brought about by seepage force and the flocculation of clay particles, may also lead to preferential channeling.

In actual field conditions, clay barriers require time to reach full saturation after construction. Thus, the current study represents the case in which clay barriers are required to perform, before full saturation is reached.

4.3.1.5 The effect of *Pb* and *Cu* on hydraulic conductivity

The Batch adsorption tests in section 4.2.2, showed that for bentonite, its *Pb* sorption capacity was higher than its *Cu* sorption capacity. The different sorption capacities of *Pb* and *Cu*, suggest that they also may cause different degrees of flocculation. However, the hydraulic conductivity results in Table 4.3.3 did not show any significant differences separating the effects of *Pb* and *Cu*. In addition, significant

differences could not be distinguished between the single and multi-heavy-metal results.

The fact that almost all heavy metal permeated samples attained hydraulic conductivity values between 1.8×10^{-9} - 5.0×10^{-9} m s⁻¹, indicated that the admixes were limited to a maximum hydraulic conductivity. This maximum hydraulic conductivity likely is determined by the structural fabric of the compacted samples. Apparently, all of the tested heavy metal concentrations were sufficient to bring the admixes to their maximum hydraulic conductivities. Further investigations are needed to determine the minimum heavy metal concentrations required to bring about hydraulic conductivity changes.

4.3.1.6 Uncertain factors influencing hydraulic conductivity

Further investigations are need to identify the effect of the following:

1. The high gradients used ($i = 65 - 88$) may cause particle migration. This phenomenon may decrease hydraulic conductivity by causing the clogging of pores, or increase hydraulic conductivity by causing the unplugging or erosion of pores. Since suspended solids were rarely detected in the discharge, increases in hydraulic conductivity due to particle migration, were unlikely.
2. Bacterial growth was observed in the discharge tubes leading from the Forest soil and Spruce bark admix barriers. Bacterial growth would decrease hydraulic conductivity, but its effect could not be isolated.
3. The heavy metal permeants dissolve certain components of Forest soil and Spruce bark. These may alter the viscosity of the permeants.

4.3.2 Heavy metal breakthrough results

The heavy metal breakthrough results gave insight into the migration and mobility of heavy metals. In addition, the breakthrough results were used to evaluate the usefulness of sorption capacities obtained from Batch adsorption tests. Finally, heavy metal breakthrough points (when heavy metal breakthrough concentration reached half the source concentration) were used to evaluate the performance of the admixes.

4.3.2.1 General observations

Similar to the hydraulic conductivity curves in Figures 4.3.2 - 4.3.4, the heavy metal breakthrough curves in Figures 4.3.8 - 4.3.10, show two distinct parts. Most of the tests started with an initial period of low heavy metal concentration, followed by a log-shaped increase. To facilitate the comparison of results, the triplicate breakthrough data was averaged together in Figures 4.3.11 - 4.3.12. Specific breakthrough concentrations taken from Figure 4.3.11 - 4.3.12 are summarized in Table 4.3.4. On average, the initial period concentrations ranged between 0 - 227 mg L⁻¹, and lasted between 50 - 350 ml of discharge (0 - 2.5 pore volumes). At a discharge volume of 1200 ml (7 pore volumes), breakthrough concentrations ranged between 269 - 506 mg L⁻¹ (54 - 100+ % of source concentration). The comparison point was chosen at a discharge volume of 1200 ml, because by this point, all breakthrough concentrations had reached near equilibrium.

a) *Pb* permeants through bentonite admix samples.

b) *Cu* permeants through bentonite admix samples.

c) *Pb+Cu* permeant - *Pb* data.

d) *Pb+Cu* permeant - *Cu* data.

e) *Pb+Cu+Cd* permeants - *Pb* data

f) *Pb+Cu+Cd* permeants - *Cu* data

g) *Pb+Cu+Cd* permeants - *Cd* data

Triplicate #
 × Test 1   □ Test 2   △ Test 3

FIGURE 4.3.8. Heavy metal breakthrough results for bentonite admix samples.

(a) *Pb* permeant. (b) *Cu* permeant. (c - d) *Pb+Cu* permeant.
 (e - g) *Pb+Cu+Cd* permeant.

a) *Pb* permeants through Forest soil admix samples. b) *Cu* permeants through Forest soil admix samples. c) *Pb + Cu* permeants - *Pb* data. d) *Pb + Cu* permeants - *Cu* data.

FIGURE 4.3.9. Heavy metal breakthrough results for Forest soil admix samples.

(a) *Pb* permeant. (b) *Cu* permeant. (c - d) *Pb+Cu* permeant.

a) *Pb* permeants through Spruce Bark admix samples. b) *Cu* permeants through Spruce bark admix samples. c) *Pb + Cu* permeants - *Pb* data. d) *Pb + Cu* permeants - *Cu* data.

FIGURE 4.3.10. Heavy metal breakthrough results for Spruce bark admix samples.

(a) *Pb* permeant. (b) *Cu* permeant. (c - d) *Pb + Cu* permeant.

a) *Pb* Leachate b) *Cu* Leachate c) *Pb+Cu* Leachate - *Pb* data d) *Pb+Cu* Leachate - *Cu* data

FIGURE 4.3.11. Averaged heavy metal breakthrough results grouped by leachate type. (a) *Pb* leachate. (b) *Cu* leachate. (c) *Pb+Cu* leachate.

FIGURE 4.3.12. Averaged heavy metal breakthrough results for bentonite admix permeated with *Pb+Cu+Cd* leachate.

TABLE 4.3.5. Summary of heavy metal breakthrough data from averaged data in Figures 4.3.11 & 4.3.12.

Admix	Leachate	Heavy metal analyzed	Initial breakthrough concentration	Heavy metal concentration at 1200 ml of discharge
			mg L ⁻¹	mg L ⁻¹
Bentonite admix	<i>Pb</i>	<i>Pb</i>	0	418
	<i>Cu</i>	<i>Cu</i>	0	429
	<i>Pb+Cu</i>	<i>Pb</i>	0	343
	<i>Pb+Cu</i>	<i>Cu</i>	1	398
	<i>Pb+Cu+Cd</i>	<i>Pb</i>	1	348
	<i>Pb+Cu+Cd</i>	<i>Cu</i>	1	449
	<i>Pb+Cu+Cd</i>	<i>Cd</i>	10	460
Forest soil admix	<i>Pb</i>	<i>Pb</i>	12	321
	<i>Cu</i>	<i>Cu</i>	227	439
	<i>Pb+Cu</i>	<i>Pb</i>	17	269
	<i>Pb+Cu</i>	<i>Cu</i>	104	474
Spruce bark admix	<i>Pb</i>	<i>Pb</i>	7	384
	<i>Cu</i>	<i>Cu</i>	3	410
	<i>Pb+Cu</i>	<i>Pb</i>	1	417
	<i>Pb</i>	<i>Cu</i>	2	506

4.3.2.2 Migration behavior - non-uniformity and fractured porous mediaNon-uniform flow

The conceptual mechanism for hydraulic conductivity increase presented in Figure 4.3.7, predicted the coincidental increase of breakthrough concentrations and hydraulic conductivities. A comparison of the breakthrough curves in Figures 4.3.11 - 4.3.12, with the hydraulic conductivity curves in Figures 4.3.2 - 4.3.4, show that at the point of breakthrough, the two curves increased as predicted.

According to contaminant transport theory, a uniformly migrating contaminant front would look like Figure 4.3.13 (Freeze & Cherry, 1979). Notice that both the retarded and non-retarded species, showed symmetric breakthrough profiles. Furthermore, their profiles increased smoothly from 0 - 100% of the source concentration. In contrast, most of the averaged breakthrough curves in Figure 4.3.11, approached zero slope at below 100% of the source concentration. Some of the curves reached to merely 60% of the source concentration. The studies performed by Weber (1991), and Cabral (1992), also showed the same phenomena. The conceptual model in Figure 4.3.7, is used to explain why the breakthrough concentrations did not reach 100% of the source concentration.

Figure 4.3.7.b, in section 4.3.2.2 showed that when heavy metals initially penetrate the entire cell, the flow concentrates towards the penetrated pathways. The higher volume of flow through these preferential channels results in higher heavy metal loading to the channel walls. In addition, the higher velocity of flow through these channels decreases the heavy metal migration time (or detention time) through the cell. As a result, the higher velocity and volume of heavy metals would quickly overwhelm the sorptive ability of the channel walls. A conceptual model for non-uniform heavy metal migration (Figure 4.3.14) shows that at the discharge end, the higher heavy metal concentrations from the preferential channels, would mix with the

lower heavy metal concentrations of the surrounding areas. This mixing of flows is what causes the breakthrough curve to reach near equilibrium at less than 100% of the source concentration.

FIGURE 4.3.13. Heavy metal concentration profiles of uniformly migrating plumes (Freeze & Cherry, 1979).

The mixing of flows results in temporarily stable breakthrough concentrations of less than 100% of the source concentration

FIGURE 4.3.14. Conceptual model for the mechanism of non-uniform heavy metal migration.

Fractured porous media

The breakthrough curves for the Spruce bark admixes (Figure 4.3.11) experienced greater concentration jumps than the other admixes. Assuming that significant short-circuiting was occurring, the compacted admix could be viewed as a porous media containing fractures (Freeze & Cherry, 1979). In this case, most of the leachate would be migrating through the fractures. According to contaminant transport theory for fractured media, the slope of breakthrough curves is determined by the degree in which the contaminant diffuses through the walls of the fractures into the surrounding porous media (Freeze & Cherry, 1979). Reasonably, penetration into the surrounding porous media may not be limited to diffusion, but could also be advective in nature. Greater degrees of diffusion, and advective flow from the fractures into the surrounding porous media results in flatter breakthrough curves. The steep breakthrough slopes for the Spruce bark admixes indicate a low degree of diffusion and advective flow into the general media. The specific reasons for this observation could not be determined from the breakthrough data; however, differences in the slopes of breakthrough curves are probably due to differences in the physical structures of the compacted admix samples.

4.3.2.3   Retention capacity versus breakthrough point

The main question related to clay barrier performance is ...

"when, if ever, will contaminant breakthrough occur?"

A second important question related to the first, is ...

"how much contaminant will get through?"

These two questions lead to two important points. Firstly, the main purpose of using highly sorptive materials in clay barriers is to delay the migration of heavy metals. Secondly, sorption capacities may be misleading, because in field conditions, a clay barrier may allow the breakthrough of large quantities of heavy metals, before its sorption capacities are reached. In the following analysis, the sorption capacities of Batch adsorption tests are evaluated for their ability to predict breakthrough points, and retention capacities of the Leaching cells.

Using the averaged data in Figures 4.3.11 - 4.3.12, the breakthrough points were determined for each curve, and summarized in Table 4.3.5. The breakthrough point for continuous sources was specified at one-half the source concentration (Freeze & Cherry, 1979). Table 4.3.5 shows that the breakthrough points ranged between 50 - 1100 ml (0.25 - 6.25 pore volumes) of discharge.

In addition, Table 4.3.5 summarizes for each curve, the heavy metal retention values up to the breakthrough point, as well as up to 1200 ml of discharge. The amount of each heavy metal retained, was calculated by determining the area above each breakthrough curve in Figures 4.3.11 - 4.3.12, minus one pore volume of clean discharge (see APPENDIX D.2 for calculations). The amount of heavy metals retained up to the breakthrough points ranged between 0 - 335 mg, and the amount of heavy metals retained after 1200 ml of discharge ranged between 0 - 359 mg.

Finally, shown in Table 4.3.5 are the predicted sorption capacities calculated from the Batch adsorption test results in section 4.2.1. Even after running the Leaching cell for 1200 ml of discharge (7 pore volumes), the amounts of heavy metals retained were still far less than the predicted capacities. Furthermore, the predicted capacities gave little indication to the timing of breakthrough points. For example, many of the *Cu* permeated samples showed zero retention up to the point of breakthrough even though according to the Batch adsorption tests, the samples were capable of sorbing 300 - 513 mg of *Cu*.

Following the same argument as in section 4.3.1.4, the discrepancy between the Leaching cell and Batch adsorption results may be due to under-saturation. Weber's (1991) and Cabral's (1992) samples, which were 100% saturated, had heavy metal breakthroughs at 5 - 7 pore volumes. In contrast, the breakthrough results in Table 4.3.5 show that most of the samples in the current study had breakthrough points at less than 2 pore volumes. The presence of air voids may have promoted preferential channeling within the admix samples.

These results show that sorption capacities from Batch tests were insufficient in predicting the breakthrough points and retention capacities of Leaching cells. In addition, these results show that for clay barriers, saturation may have been a significant factor in retarding the migration of heavy metals.

TABLE 4.3.6. Summary of heavy metal breakthrough points & retentions.

Admix	Leachate	HM* Type	Breakthrough point ml	Leaching Cells		Batch adsorption tests **	Percentage of predicted %
				HM retained up to break. pt. mg	HM retained up to 1200 ml mg	HM retention predicted mg	
Bentonite admix	Pb	Pb	370	82	239	1102	22%
	Cu	Cu	130	0	99	433	23%
	Pb+Cu	Pb	600	131	250	873	29%
		Cu	330	32	171	302	57%
	Pb+Cu+Cd	Pb	670	166	270	808	33%
		Cu	230	0	116	287	40%
Forest soil admix	Pb	Pb	850	244	318	1160	27%
		Cu	340	7	124	513	24%
	Pb+Cu	Pb	1100	335	359	919	39%
		Cu	290	12	114	355	32%
Spruce bark admix	Pb	Pb	320	44	192	1107	17%
	Cu	Cu	150	0	125	432	29%
	Pb+Cu	Pb	240	0	135	854	16%
		Cu	50	0	0	300	0%

* HM - Heavy metal

** Calculated from formulas in Table 4.2.5, in section 4.2.1.4.

4.3.2.4 Relative mobility of heavy metals

Figure 4.3.11 shows that for single and binary heavy metal systems involving *Pb* and *Cu*, *Cu* was always the first to breakthrough the soil column. In fact, an examination of the breakthrough points in Table 4.3.5, shows that *Cu* was ≈ 2.5 times more mobile than *Pb*. As for the relative mobilities amongst *Pb*, *Cu*, and *Cd*, the Leaching cell test involving these three metals, indicated that *Cd* was ≈ 1.5 times more mobile than *Cu*, and ≈ 4 times more mobile than *Pb*.

Using the sorption equations in section 4.2.1.4 (Table 4.2.5), heavy metal mobilities were calculated by dividing sorption concentrations with initial solution concentrations (Table 4.3.6). This was done to account for the differing molar concentrations of *Pb*, *Cu*, and *Cd*. Table 4.3.6 shows that the *Cd* sorption capacity for bentonite was ≈ 1.5 times less than the *Cu* sorption capacity, and ≈ 4.5 times less than the *Pb* capacity. Thus, a comparison between the Batch adsorption tests results with the breakthrough results, shows that the Batch adsorption tests are good indicators for the relative mobilities of *Pb*, *Cu*, and *Cd*.

TABLE 4.3.7. Heavy metal mobilities for bentonite.

Leachate	HM* analyzed	Relative HM Mobility for bentonite (from sorption equations in section 4.1.2.4) sorption/initial solution concentration
<i>Pb</i>	<i>Pb</i>	3.6
<i>Cu</i>	<i>Cu</i>	1.4
<i>Pb+Cu</i>	<i>Pb</i>	2.9
<i>Pb+Cu</i>	<i>Cu</i>	1.0
<i>Pb+Cu+Cd</i>	<i>Pb</i>	2.7
<i>Pb+Cu+Cd</i>	<i>Cu</i>	0.9
<i>Pb+Cu+Cd</i>	<i>Cd</i>	0.6

* HM - heavy metal

The Batch adsorption tests show that due to competition, the sorption capacity of heavy metals in single heavy metal systems are higher than in multi-heavy-metal systems. However, this competition effect could not be seen in the breakthrough results. The breakthrough points for individual heavy metals were similar between the single and multi-heavy-metal systems. The competition effect was probably overshadowed by the variability associated with the Leaching cell test. Earlier in this section, under-saturation was suggested to be a significant factor in causing early heavy metal breakthroughs. Since the initial saturations shown in Table 4.3.2 (section 4.3), broadly ranged between 74 - 86%, this may have had a significant impact on the variability of the breakthrough results. Further studies are required to determine whether the competition effect would be seen in samples that were 100% saturated before heavy metal permeation.

4.3.3 Performance of admixes

An objective of the Leaching cell tests was to determine whether the Forest soil and Spruce bark admixes would be an improvement compared to the bentonite admix. Improvements were identified by increased heavy metal retention capacity, and delayed heavy metal breakthrough, while causing little change to the hydraulic conductivity of the admix.

4.3.3.1 Performance based on hydraulic conductivity

After 1200 ml of discharge (≈ 7 pore volumes), most heavy metal permeated samples stabilized at hydraulic conductivity values between 1.8×10^{-9} - 5.0×10^{-9} m s⁻¹ (Table 4.3.3). In contrast, samples permeated with blank solutions of 0.01 M $\text{Ca}(\text{NO}_3)_2$ resulted in hydraulic conductivities between 1.4×10^{-11} - 2.8×10^{-11} m s⁻¹. This difference

of two orders of magnitude, shows that heavy metal compatibility is a significant design concern for clay barriers. The results from the current study show that for cases where significant concentrations of heavy metals are expected, Leaching cell testing is required to determine the hydraulic conductivity values caused by heavy metal permeation. Further investigation is recommended to determine specific values that constitute "significant" heavy metal concentrations.

The hydraulic conductivity curves in Figure 4.3.6, show that the initial portions of the Forest soil admix consistently averaged higher than the other admixes. This may be attributed to differences in pH, as observed in the discharge pH results in Figure 4.3.15. The discharge pH curves show that the Forest soil admix produced discharge pH values consistently lower than the other admixes. Since Forest soil possesses much lower initial pH (3.5 pH in CaCl_2) in comparison to bentonite (7.61 pH in CaCl_2), the presence of Forest soil would reduce the overall initial pH of the admix. The reduced initial pH may have several consequences:

1. Higher concentration of H^+ ions may cause a decrease in double layer thickness.
2. The reduced initial pH may reduce the potential for precipitation.

Both of these consequences could have been contributing factors to the higher initial hydraulic conductivities seen in the Forest soil admixes. Confirmation of these effects would require further investigation.

Regardless of the differences in initial hydraulic conductivity, almost all samples permeated with heavy metals eventually converged to a narrow range of values. Thus, in comparison to the bentonite admix, the other admixes performed equally well. The current study concludes that the substitution of one part bentonite from a 100:8 sand:bentonite admix, with one part of Forest soil or Spruce bark, does not cause significant increases in hydraulic conductivities.

a) *Pb* Leachate b) *Cu* Leachate c) *Pb+Cu* Leachate

◇ Bentonite admix   ▲ Forest soil admix   × Spruce bark admix

FIGURE 4.3.15. Discharge pH results grouped by leachate type. (a) *Pb* leachate. (b) *Cu* leachate. (c) *Pb+Cu* leachate.

4.3.3.2 Performance based on heavy metal breakthrough

As mentioned in section 4.3.2.3, the main concern in contaminant migration is not how much heavy metal would be retained, but how long a barrier could delay the breakthrough of heavy metals. According to the retention and breakthrough results in Table 4.3.5, the admixes rank as follows:

1. Forest soil admix
2. Bentonite admix
3. Spruce bark admix

Since Forest soil possessed the highest heavy metal sorption capacities (section 4.2.1.4), the Forest soil admix was predicted to have the highest heavy metal retentions, and latest heavy metal breakthrough points. Although the Forest soil admix performed the best, the results show that sorption capacity was not the only factor.

For this study, the initial saturation was suspected to have been a factor influencing heavy metal breakthrough. Another important factor that influenced breakthrough was the physical structures of the compacted admixes. Differences in structure were identified by variations in the slopes of the breakthrough curves. By visual inspection, the breakthrough slopes in Figure 4.3.11 had the following order of steepness:

Forest soil admix < Bentonite admix < Spruce bark admix.

The importance of admix structure is supported by similarities between the breakthrough point ranking and the breakthrough slope order.

4.3.4 Summary of Leaching cell results

Heavy metals' effect on hydraulic conductivity

1. In comparison to the blank solutions of 0.01 M $\text{Ca}(\text{NO}_3)_2$, the hydraulic conductivity increases due to heavy metal permeation, were approximately two orders of magnitude (from $\approx 2 \times 10^{-11} \text{ m s}^{-1}$ to $\approx 3 \times 10^{-9} \text{ m s}^{-1}$).
2. The current study shows that valence was not a sufficient parameter in identifying the effect of cations on hydraulic conductivity. A comparison of between Ca and the heavy metals suggests that their potential for specific sorption mechanisms such as complexation and precipitation may be factors in determining the hydraulic conductivity of clay barriers.
3. A conceptual mechanism describing hydraulic conductivity change and non-uniform heavy metal migration was presented in Figures 4.3.7 and 4.3.14.
4. The lack of confining pressures caused the hydraulic conductivities in the current study to increase much more than observed in other studies (Weber, 1991; Cabral, 1992).
5. Pb and Cu solutions produced similar hydraulic conductivities.
6. Single and multi-heavy metal solutions produced similar hydraulic conductivities.

The migration behavior of heavy metals

7. By comparing with the hydraulic conductivity, and heavy metal breakthrough results from Cabral (1992) and Weber (1991), under-saturation was suspected to be a factor in causing large hydraulic conductivity increases, and early heavy metal breakthroughs in the current study.

8. Batch adsorption tests were insufficient in predicting the breakthrough points and retention capacities of Leaching cell tests, but adequate in predicting relative heavy metal mobilities.
9. Based on the heavy metal breakthrough points, *Cd* is ≈ 1.5 times more mobile than *Cu*, and ≈ 4 times more mobile than *Pb*, respectively.

Performance of admixes

10. All three admixes produced similar hydraulic conductivity values (Table 4.3.3).
11. Based on heavy metal retention and breakthrough points, the admixes rank as follows:
  1. Forest soil admix
  2. Bentonite admix
  3. Spruce bark admix

4.4 SELECTIVE SEQUENTIAL EXTRACTION

The migration behavior and retention mechanisms of heavy metals were investigated using Selective Sequential Extractions (SSEs). SSE measures the amount of heavy metals sorbed onto the admixes in the form cation exchange (exchangeable component), precipitation (carbonate and hydroxide components), and complexation (hydroxide, and organic components). After the termination of a Leaching cell test, the admix sample was extruded and sliced into four layers. Two sampling procedures were used to collect material from each layer. For most extruded admix samples, the center and edge regions of each layer were sampled. For three sets of Leaching cell tests, each layer was remolded into uniform mixtures; then two composite samples were taken from each mixture to determine the average heavy metal concentration of each layer.

SSEs were also performed on a set of Batch adsorption samples. The purpose for these Batch adsorption tests was to examine the comparability between the Batch adsorption and Leaching cell tests, as well as determine the accuracy of the SSE procedure. The SSE test program is summarized in Table 4.4.1.

TABLE 4.4.1. Summary for the SSE tests.

Admix	HM* solution	Center & edge sampling	Composite sampling	Batch adsorption test samples
Bentonite	<i>Pb</i>	√		√
	<i>Cu</i>	√		√
	<i>Pb+Cu</i>	√		√
	<i>Pb+Cu+Cd</i>		√	√
Forest soil	<i>Pb</i>	√		√
	<i>Cu</i>		√	√
	<i>Pb+Cu</i>		√	√
Spruce bark	<i>Pb</i>	√		√
	<i>Cu</i>	√		√
	<i>Pb+Cu</i>			√

* HM - heavy metal

Note - all heavy metal solutions contained 500 mg L⁻¹ of each heavy metal specified.

4.4.1 SSE on a set of Batch adsorption tests

The SSE results for the Batch adsorption test samples are shown in Table 4.4.2. The SSE results for the Batch adsorption test samples were used for four types of comparisons:

1. The sorption characteristics of the three admixes were compared based on the Batch adsorption test samples.
2. The Batch adsorption tests in this section were performed on mixtures (bentonite, Forest soil, and Spruce bark admixes), while the Batch adsorption tests in section 4.2 were performed on individual materials. Comparing the two sets of Batch adsorption tests, showed whether the sorption capacities of mixtures could be predicted by adding their individual sorption capacities.
3. A comparison of the SSE results from the Batch adsorption and extruded Leaching cell samples showed the similarities between Batch adsorption and Leaching cell sorption capacities.
4. The SSE results on the Batch adsorption test samples were used to evaluate the accuracy of the SSE (see APPENDIX F.1)

TABLE 4.4.2. SSE results for Batch adsorption tests on admixes (see notes at bottom).

Admix	Heavy metal solution	HM analyzed	Exchangeable $\mu\text{g/g soil}$	Carbonates $\mu\text{g/g soil}$	Hydroxides $\mu\text{g/g soil}$	Organics $\mu\text{g/g soil}$	Residue $\mu\text{g/g soil}$	Total $\mu\text{g/g soil}$
Bentonite admix	Blank	Cu	n/a	1	1	0	0	3
	Blank	Pb	n/a	1	4	2	0	3
	Cu 1st	Cu	326	205	35	4	4	574
	Cu 2nd	Cu	325	196	35	4	5	565
	Pb 1st	Pb	817	584	178	17	7	1604
	Pb 2nd	Pb	970	637	138	12	4	1760
	Pb+Cu 1st	Cu	284	105	29	3	1	423
	Pb+Cu 1st	Pb	830	231	106	6	0	1174
	Pb+Cu 2nd	Cu	311	104	28	3	3	449
	Pb+Cu 2nd	Pb	852	264	106	12	5	1238
	Pb+Cu+Cd 1st	Cd	251	14	0	2	0.1	267
	Pb+Cu+Cd 1st	Cu	242	102	28	3	3	378
	Pb+Cu+Cd 1st	Pb	785	186	98	8	3	1079
	Pb+Cu+Cd 2nd	Cd	250	12	0	1	0.2	264
	Pb+Cu+Cd 2nd	Cu	244	90	28	3	2	367
	Pb+Cu+Cd 2nd	Pb	798	182	98	9	2	1090
Forest soil admix	Blank	Cu	n/a	1	0	1	2	3
	Blank	Pb	n/a	1	3	1	0	4
	Cu 1st	Cu	350	206	116	51	14	738
	Cu 2nd	Cu	332	206	122	46	16	721
	Pb 1st	Pb	832	753	255	67	5	1912
	Pb 2nd	Pb	826	790	398	70	4	2088
	Pb+Cu 1st	Cu	249	137	89	39	11	526
	Pb+Cu 1st	Pb	632	360	216	39	4	1252
	Pb+Cu 2nd	Cu	242	141	89	40	11	523
	Pb+Cu 2nd	Pb	642	377	220	40	1	1280
Spruce bark admix	Blank	Cu	n/a	1	0	0	1	2
	Blank	Pb	n/a	0	3	3	0	6
	Cu 1st	Cu	285	172	74	61	8	599
	Cu 2nd	Cu	285	163	74	22	9	552
	Pb 1st	Pb	592	423	189	60	4	1268
	Pb 2nd	Pb	606	436	194	61	1	1297
	Pb+Cu 1st	Cu	240	93	51	12	2	399
	Pb+Cu 1st	Pb	480	184	116	46	0	825
	Pb+Cu 2nd	Cu	228	96	43	14	8	389
	Pb+Cu 2nd	Pb	462	185	103	50	3	803

- Notes - Heavy metal solutions contain 500 mg L⁻¹ of each heavy metal specified.
 - Data rounded off to whole numbers.
 - Admix:solution ratio was 4 g of soil to 40 ml of solution.
 - n/a - not available

4.4.1.1 Sorption characteristics of the admixes

Table 4.4.3 displays the total amount of heavy metals extracted from each Batch sample using the SSE procedure. The Forest soil admix had an average sorptive advantage of 18% over the bentonite admix, while the Spruce bark admix had an average sorptive disadvantage of 16%. Figure 4.2.9 in section 4.2.2.1, showed that the heavy metal sorption capacities for bentonite and Spruce bark were approximately equal; thus, according to these individual sorption capacities, the bentonite and Spruce bark admixes should also be equal. These findings highlight the importance of testing potential barrier materials in clay barrier mixes rather than individually.

The 16% discrepancy may be related to the contrasting pHs of the two materials. In water, the initial pH of bentonite is 8.38, while for Spruce bark, it is 4.34 (Table 4.1.1). The low pH of the Spruce bark may inhibit the cation exchange and precipitation reactions associated with bentonite.

TABLE 4.4.3. Comparison of admixes based on SSE of Batch adsorption samples.

Heavy metal solution	HM analyzed	Total sorbed concentrations based on extractions				
		Bentonite admix	Forest s. admix	%	Spruce b. admix	%
		$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	Diff.	$\mu\text{g/g soil}$	Diff.
Cu	Cu	570	730	28%	576	1%
Pb	Pb	1682	2000	19%	1282	-24%
Pb+Cu	Cu	436	525	20%	394	-10%
	Pb	1206	1266	5%	814	-32%
Average				18%		-16%

The average percentages of *Pb* and *Cu* associated to each soil component of the three admixes are shown in Table 4.4.4. In comparison to the bentonite admix, the Forest soil and Spruce bark admixes retained more *Pb* within the carbonate, hydroxide, and organic components, and less within the exchangeable component. In addition, the Forest soil and Spruce bark admixes retained more *Cu* within the hydroxide and organic components, and less within the exchangeable component. These findings

show that the addition of Forest soil and Spruce bark into clay barrier mixes inhibited cation exchange, but promoted the retention mechanisms associated with the carbonate, hydroxide, and organic components.

TABLE 4.4.4. Averaged sorption characteristics for admixes based on SSE of Batch adsorption tests.

Heavy metal extracted	Admix type	Exchangeable	Carbonate	Hydroxide	Organic	Residue	Total μg/g soil
<i>Pb</i>	Bentonite	65%	25%	9%	1%	0%	1324
	Forest soil	46%	34%	17%	3%	0%	1633
	Spruce bark	52%	28%	14%	5%	0%	1048
<i>Cu</i>	Bentonite	63%	28%	7%	1%	1%	460
	Forest soil	47%	27%	17%	7%	2%	627
	Spruce bark	54%	27%	12%	5%	1%	485

4.4.1.2 Comparing sorption capacities of mixtures vs. individual materials

Shown in Table 4.4.5, are the total concentration of heavy metals extracted from the admix samples submitted to Batch adsorption tests. As well, Table 4.4.5 shows a predicted set of sorption capacities for the admixes (see APPENDIX F.2 for calculations). These predicted values were calculated from the sorption capacities of the individual admix materials (see section 4.2.1.4).

The comparison in Table 4.4.5, shows that most of the mixtures had higher sorption capacities than the summation of individual capacities. These results seem to suggest that the sorption capacities of individual materials were enhanced when the materials were mixed together. However, a more likely explanation is that the difference in sorption capacities was due to different soil:solution ratios. If the inert sand was excluded from the soil:solution ratio, then the ratio for the admixes would be 1 g of reactive material to 135 ml of heavy metal solution. The ratio for the individual materials was 1:50. This suggests that the soil:solution ratio used for the individual materials was not low enough to calculate the true heavy metal capacities.

TABLE 4.4.5. Sorption capacities of admixes.

Admix	Heavy metal solution	HM analyzed	Total extraction from admixes	Total sorption by summation of individual materials*	% Diff.
			$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	
Bentonite admix	Cu	Cu	570	528	-7%
	Pb	Pb	1682	1344	-20%
	Pb+Cu	Cu	436	368	-16%
		Pb	1206	1065	-12%
	Pb+Cu+Cd	Cd	265	229	-14%
		Cu	373	351	-6%
		Pb	1084	983	-9%
Forest soil admix	Cu	Cu	730	598	-18%
	Pb	Pb	2000	1376	-31%
	Pb+Cu	Cu	525	414	-21%
		Pb	1266	1089	-14%
Spruce bark admix	Cu	Cu	576	527	-8%
	Pb	Pb	1282	1350	5%
	Pb+Cu	Cu	394	366	-7%
		Pb	814	1041	28%

* Sorption capacities for individual materials calculated from formulas in Table 4.2.5.

4.4.1.3 Comparing the sorption capacities of Batch and Leaching cell samples

Yong et al. (1993), said that "because of the soil structure, and because of pore geometry and pore continuity, only a fraction of the total surface area of the soil particles [in Leaching cell samples] comes in direct contact with the permeating leachate". In addition, sorption capacities are affected by several other differences between the Batch and Leaching cell tests. The soil particles in a Batch container are exposed to a fixed amount of solution, while the soil particles in a Leaching cell are exposed to a continuous flow of fresh leachate. In terms of soil:solution ratio, the Batch adsorption test possesses a fixed ratio, while the ratio for the Leaching cell test varies with the volume of discharge. In terms of reaction time, the Batch adsorption test allows for enough time to bring about equilibrium, while the reaction time for the Leaching cell test may not allow for the completion of sorption reactions. Finally, in terms of heavy metal concentration, the Batch adsorption test possesses one

concentration for all soil particles, while for the Leaching cell test, the heavy metal concentration of the leachate changes as it permeates through the Leaching cell sample.

These differences raise concern over the applicability of Batch sorption capacities to Leaching cell results. A comparison of the sorption capacities of the influent end of Leaching cells, with the sorption capacities of the Batch adsorption tests is shown in Table 4.4.6. With the influent end samples, one was certain that exposure was to heavy metal concentrations of 500 mg L⁻¹. Because of sorption, the heavy metal leachate concentrations within the Leaching cells were unpredictable. Table 4.4.6 shows that the sorption capacities of the admix Batch adsorption tests were similar to that of the Leaching cells. This comparison shows that the 1:10 soil:solution ratio of the Batch adsorption tests was adequate to represent the conditions at the influent end of the Leaching cell samples.

TABLE 4.4.6. Comparing max. extractions of Leaching cell and Batch adsorption test samples.

Admix	Leachate solution	Sample region (1st layers only)	HM analyzed	Total heavy metals extracted		% Diff
				From Leaching cells	From Batch adsorption tests	
				µg/g soil	µg/g soil	
Bentonite	Cu	Center	Cu	534	570	7%
	Pb	Center	Pb	1569	1682	7%
	Pb+Cu	Edge	Cu	471	436	-7%
		Center	Pb	1175	1206	3%
	Pb+Cu+Cd	Composite	Cd	252	265	5%
		Composite	Cu	367	373	1%
		Composite	Pb	877	1084	24%
Forest soil	Cu	Composite	Cu	826	730	-12%
	Pb	Edge	Pb	1938	2000	3%
	Pb+Cu	Composite	Cu	568	525	-8%
		Composite	Pb	1069	1266	18%
Spruce bark	Cu	Center	Cu	651	576	-11%
	Pb	Center	Pb	1895	1282	-32%
	Pb+Cu	Center	Cu	404	394	-3%
		Edge	Pb	536	814	52%

4.4.2 SSEs on extruded Leaching cell samples

Selective sequential extractions (SSEs) were performed on extruded Leaching cell samples to investigate the migration behavior, and retention mechanisms of heavy metals. Since the Leaching cell tests were terminated well after heavy metal breakthrough, the SSEs only showed the heavy metal distributions after a significant amount of heavy metals have migrated through the samples. These heavy metal distributions indicated the uniformity of migration, as well as migration patterns. The insights gained on migration behavior are valuable in evaluating and developing heavy metal transport models through clay barriers.

The SSE results also were used to investigate the sorption characteristics of the various heavy metals (*Pb*, *Cu*, *Cd*) and admixes (bentonite, Forest soil, Spruce bark). This investigation was based on the broad range of sorption data ($0 - 1900 \mu\text{g g}^{-1}$) obtained by performing SSEs on different regions of the Leaching cell samples. The insights on reaction mechanisms were valuable in evaluating the performance of the admixes, as well as furthering the development of sorption models.

4.4.2.1 Heavy metal migration behavior

To determine the heavy metal distribution within the Leaching cell samples, the extruded cells were sliced into four layers, and each layer was submitted to the SSE. For most cell samples (Figures 4.4.1 - 4.4.7), the center and edge regions were tested separately to determine the heavy metal distribution within each layer. For three leaching cell runs (Figures 4.4.8 - 4.4.10), composite sampling was done to determine the average concentration of heavy metals sorbed onto each layer. A small diagram on the top right hand corner of each figure acts as a visual reference to the explain the graphs. For example, Figure 4.4.1.a shows the concentrations of *Pb* sorbed onto the center region of each layer. Layer 1 is the influent end of the cell sample, and the layer

numbers increase towards the discharge end.

Figures 4.4.1 - 4.4.7 show that heavy metal concentrations in the center regions varied significantly from the concentrations in the edge regions. In addition, layers 2 and 3 often contained very low concentrations compared to layers 1 and 4. Similarly, Figures 4.4.8 - 4.4.10 also frequently show low heavy metal concentrations in layers 2 and 3. These results indicate that short-circuiting occurred in many samples. This supports the findings in section 4.3.3.1, that heavy metals migrated non-uniformly through preferential channels.

Consistent sampling of high heavy metal concentrations in the 4th layer, was probably due to the decision in permeating the Leaching cell from bottom to top. Since the permeant exited at the top, it would sit for a period of time as a pool of leachate on top of the Leaching cell, before exiting through the discharge tube (see Figure 3.4.1). This probably resulted in an over-estimation of heavy metal sorption in the 4th layer. Since the sorption capacities of Leaching cell samples were already found to be much lower than predicted (section 4.3.2.3), this error would not significantly affect any of the previous findings. This error may have been mitigated by permeating from top to bottom, or by slicing a thin layer of admix off the top of the 4th layer before sampling.

Since only two regions (center and edge) in each layer were sampled, a detailed distribution of heavy metals could not be determined. From the graphs in Figures 4.4.1 - 4.4.10, no migration patterns could be identified. A recommendation for future research is to perform SSEs on an exhaustive sampling of the entire cell. If each layer was cut according to a grid pattern and SSEs were performed on each cube, then 3D heavy metal distribution graphs could be mapped.

The SSE results from this research emphasize the challenges in developing suitable transport models for the migration of heavy metals through clay barriers. The lack of uniformity discourages the application of simplistic transport models, since homogeneity is often an important assumption. The lack of migration patterns imposes a high degree of uncertainty to numerical transport modeling.

FIGURE 4.4.1. Distribution of heavy metals in bentonite admix samples leached with *Pb*.
 (a - b) Center & edge samples of 1st cell sample. (c - d) Center & edge samples of 2nd cell sample.

Admix type: Bentonite
 Leachate: *Cu*
 # of sample cells: 1
 Type of sampling: center & edge

a) Center sample

b) Edge sample

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS □ RESIDUE

FIGURE 4.4.2. Distribution of heavy metals in bentonite admix sample leached with *Cu*.
 (a) Center sample. (b) Edge sample.

Admix type: Bentonite
 Leachate: *Pb* + *Cu*
 # of sample cells: 1
 Type of sampling: center & edge

a) *Pb* extracted from center sample c) *Pb* extracted from edge sample b) *Cu* extracted from center sample d) *Cu* extracted from edge sample

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS □ RESIDUE

FIGURE 4.4.3. Distribution of heavy metals in bentonite admix samples leached with *Pb* & *Cu*.
 (a - b) *Pb* & *Cu* extracted from center sample. (c - d) *Pb* & *Cu* extracted from edge sample.

FIGURE 4.4.4. Distribution of heavy metals in Forest soil admix samples leached with *Pb*.
(a - b) Center & edge samples of 1st cell sample. (c - d) Center & edge samples of 2nd cell sample. (e - f) Center & edge samples of 3rd cell sample

Admix type: Spruce bark
 Leachate: *Pb*
 # of sample cells: 1
 Type of sampling: center & edge

a) *Pb* extracted from center b) *Pb* extracted from edge

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS ■ RESIDUE

FIGURE 4.4.5. Distribution of heavy metals in Spruce bark admix sample leached with *Pb*.
 (a) Center sample. (b) Edge sample.

Admix type: Spruce bark
 Leachate: *Cu*
 # of sample cells: 2
 Type of sampling: center & edge

a) *Cu* extracted from center of 1st cell

b) *Cu* extracted from edge of 1st cell

c) *Cu* extracted from center of 2nd cell

d) *Cu* extracted from edge of 2nd cell

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS □ RESIDUE

FIGURE 4.4.6. Distribution of heavy metals in Spruce bark admix sample leached with *Cu*.
 (a - b) *Cu* extracted from center & edge of 1st cell. (c - d) *Cu* extracted from center & edge of 2nd cell.

Admix type: Spruce bark
 Leachate: $Pb + Cu$
 # of sample cells: 3
 Type of sampling: center & edge

FIGURE 4.4.7. Distribution of heavy metals in Spruce bark admix samples leached with Pb & Cu .

(a - b) Pb & Cu extracted from center of 1st cell. (c - d) Pb & Cu extracted from edge of 1st cell.
 (e - f) Pb & Cu extracted from center of 2nd cell. (g - h) Pb & Cu extracted from edge of 2nd cell.
 (i - j) Pb & Cu extracted from center of 3rd cell. (k - l) Pb & Cu extracted from edge of 3rd sample.

Admix type: Bentonite
 Leachate: $Pb+Cu+Cd$
 # of sample cells: 2
 Type of sampling: composite

a) *Pb* extracted from 1st cell sample d) *Pb* extracted from 2nd cell sample b) *Cu* extracted from 1st cell sample e) *Cu* extracted from 2nd cell sample c) *Cd* extracted from 1st cell sample f) *Cd* extracted from 2nd cell sample

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS □ RESIDUE

FIGURE 4.4.8. Distribution of heavy metals in bentonite admix samples leached with *Pb*, *Cu*, & *Cd*.

(a - c) *Pb*, *Cu*, & *Cd* extracted from 1st cell sample. (d - e) *Pb*, *Cu*, & *Cd* extracted from 2nd cell sample.

Admix type: Forest soil
 Leachate: *Cu*
 # of sample cells: 1
 Type of sampling: composite

a) Composite sample of 1st cell

b) Composite sample of 2nd cell

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS ■ RESIDUE

FIGURE 4.4.9. Distribution of heavy metals in Forest soil admix samples leached with *Cu*.

(a) Composite sample of 1st cell. (b) Composite sample of 2nd cell.

Admix type: Forest soil
 Leachate: *Pb* + *Cu*
 # of sample cells: 3
 Type of sampling: composite

a) *Pb* extracted from 1st cell b) *Cu* extracted from 1st cell c) *Pb* extracted from 2nd cell d) *Cu* extracted from 2nd cell e) *Pb* extracted from 3rd cell f) *Cu* extracted from 3rd cell

□ EXCHANGEABLE ■ CARBONATES □ HYDROXIDES ■ ORGANICS ■ RESIDUE

FIGURE 4.4.10. Distribution of heavy metals in Forest soil admix samples leached with *Pb* & *Cu*.
 (a - b) *Pb* & *Cu* extracted from 1st cell sample. (c - d) *Pb* & *Cu* extracted from
 2nd cell sample. (e - f) *Pb* & *Cu* extracted from 3rd cell sample.

4.4.2.2 Heavy metal retention mechanisms

The Batch adsorption tests results presented in sections 4.2.1 and 4.4.1 produced a wide range of sorption capacities; however, they offered little insight on how the heavy metals were sorbed onto clay barriers. The SSE program of this study allowed the opportunity to examine the nature in which heavy metals were sorbed over a large range of sorption concentrations. Although only one concentration value (500 mg L^{-1}) was used for the leachate solutions, the permeation process produced soil samples that sorbed a wide range of heavy metal concentrations ($0 - 1900 \mu\text{g g}^{-1}$). By performing SSEs on these soil samples, one was able to identify distinct trends in which the heavy metals were sorbed. Because of the imprecision of the SSE procedure, the lower values ($< 100 \mu\text{g g}^{-1}$) were not included in the analysis.

Figures 4.4.11 - 4.4.12 show that a linear relationship exists between the percentages of *Pb* and *Cu* retained by the various soil components (exchangeable, carbonate, hydroxide, and organic), and the total amount of heavy metals sorbed by the admix samples. For clarification, to obtain the "total amount of heavy metals" for binary systems, the sorbed *Pb* and sorbed *Cu* quantities were added together. Because this calculation involves the addition of different types of heavy metals, molar quantities were used.

In comparison to *Pb* and *Cu*, very few SSEs were performed involving *Cd*. The data collected involving *Cd* sorption was not sufficient to create the same type of plots as seen in Figures 4.4.11 - 4.4.12. Instead, the *Cd* SSE data is presented in Table 4.4.7.

a) Exchangeable *Pb* component of total heavy metals sorbed.

b) Carbonate *Pb* component of total heavy metals sorbed.

c) Hydroxide *Pb* component of total heavy metals sorbed.

d) Organic *Pb* component of total heavy metals sorbed.

◆ Bentonite admix   × Forest soil admix   ○ Spruce bark admix

FIGURE 4.4.11. *Pb* sorption trends over a range of total sorption concentrations.

(a) Exchangeable component. (b) Carbonate component.
(c) Hydroxide component. (d) Organic component.

a) Exchangeable Cu component of total heavy metals sorbed.

b) Carbonate Cu component of total heavy metals sorbed.

c) Hydroxide Cu component of total heavy metals sorbed.

d) Organic Cu component of total heavy metals sorbed.

◆ Bentonite admix   × Forest soil admix   ○ Spruce bark admix

FIGURE 4.4.12. Cu sorption trends over a range of total sorption concentrations.

(a) Exchangeable component. (b) Carbonate component.
(c) Hydroxide component. (d) Organic component.

TABLE 4.4.7. SSE data for *Cd* from the bentonite admix.

Heavy metal extracted	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue	Total
							µg/g soil
<i>Cd</i>	1	96%	2%	1%	1%	0%	250
	2	94%	4%	1%	1%	0%	197
	3	96%	2%	1%	1%	0%	118
	4	96%	2%	1%	1%	0%	162
	1	96%	2%	1%	1%	0%	252
	2	96%	2%	1%	1%	0%	188
	4	96%	2%	1%	1%	0%	175

Sorption trends for *Pb*, *Cu*, and *Cd*

As shown in Figures 4.4.11 - 4.4.12, all three admixes had similar, linear sorption trends for *Pb* and *Cu*. At a sorption concentration of 2 mmol kg⁻¹, the exchangeable component accounted for only 10 - 40% of the total amount of heavy metals sorbed. As the sorption concentrations increased, the percentage for the exchangeable component increased, while the percentages for the other components decreased. At a sorption concentration of 12 mmol kg⁻¹, the exchangeable component accounted for 50 - 80% of the total amount of heavy metals sorbed.

In actual values, the amount of heavy metals sorbed onto the carbonate, hydroxide, and organic components increased with increasing sorption concentrations; however, the amount of heavy metals sorbed onto the exchangeable component increased at such a greater extent, that the heavy metal sorption of other components decreased in terms of percentage. In terms of retention mechanisms, Figures 4.4.11 - 4.4.12 show that precipitation and surface complexation dominated at low *Pb* and *Cu* sorption concentrations, while cation exchange dominated at higher sorption concentrations. The discussion in section 4.2.2.2, theorized that for *Cu* sorption, precipitation and complexation would dominate at low initial heavy metal solution concentrations, and cation exchange at high initial heavy metal concentrations. These findings are in agreement with the findings in section 4.2.2.2.

Table 4.4.7 shows that 96% of the *Cd* was sorbed by cation exchange. Compared to the *Pb* and *Cu* data, the *Cd* sorption concentration range of 1.0 - 2.2 mmol kg⁻¹ (118 - 250 µg g⁻¹), represents low values. Considering the sorption trends for *Pb* and *Cu*, cation exchange also would be expected to dominate at high *Cd* sorption concentrations. Further studies are needed to determine the dominant retention mechanisms for *Cd* sorption onto organic matter.

Information on the influence of various retention mechanisms for clay barriers shows that the desorption potential (future mobility) of heavy metals is dependent on the type of heavy metal, as well as the level of contamination. Because *Cd* sorption was mainly due to cation exchange, *Cd* possesses the highest desorption potential among the three heavy metals tested. For *Pb* and *Cu*, desorption potential was found to increase with increasing heavy metal sorption concentrations. This means that greater the contamination concentrations, greater the potential for heavy metals to desorb and re-enter into the groundwater.

The heavy metal sorption trends also provides direction in improving the sorption model developed in section 4.2. The sorption model in section 4.2, was not specific in identifying retention mechanisms, but used two parameters to empirically model the sorption data. Since *Cd* sorption was dominated by only one retention mechanism, the method used in section 4.2 was adequate; however, because *Pb* and *Cu* sorption involved many retention mechanisms, the model would be improved if cation exchange, complexation, and precipitation could be individually identified. Because the heavy metal solution concentrations within the different regions of Leaching cell samples were unknown, the SSE results could not be incorporated into the model developed in section 4.2. However, these results show that SSE may be a valuable tool in developing new sorption models. Further work in conducting extensive SSEs on Batch adsorption samples is recommended. The advantage of Batch adsorption samples is that their initial and equilibrium solution concentrations would be known.

Sorption differences between bentonite and other admixes

Figures 4.4.11 - 4.4.12, show that the Forest soil admix retained 13% more *Cu*, and 5% more *Pb*, within its organic component than the bentonite admix. Also, compared to the bentonite admix, the Spruce bark admix retained 5% more *Cu*, and 11% more *Pb*, within its organic component. These results correlate well with the compositions of the three admixes. Assuming that the silica sand made no contribution to the retention of heavy metals, the Forest soil and Spruce bark would constitute 12.5% of the reactive material in the Forest soil and Spruce bark admixes.

Compared to the bentonite admix, the Forest soil and Spruce bark admixes retained 33% less *Cu*, and 20% less *Pb*, within its exchangeable component. In addition, the Forest soil and Spruce bark admixes retained more heavy metals within their carbonate and hydroxide components. The retention mechanisms associated with these components include precipitation and complexation. These findings show that the presence of Forest soil and Spruce bark in clay barrier mixes promoted stronger retention mechanisms, agreeing with the findings in section 4.4.1.1.

Figure 4.3.15 in section 4.3.3.1, showed that the presence of Forest soil and Spruce bark resulted in lower discharge pHs. Since *Pb* and *Cu* precipitation is associated with higher pHs, surface complexation is probably the retention mechanism that was enhanced by the presence of Forest soil and Spruce bark.

Over the long term, one can assume that a clay barrier would be exposed to various chemical conditions; thus, sorbed heavy metals risk the chance of re-mobilization. Since *Pb* and *Cu* are bound more strongly by the Forest soil and Spruce bark admixes, these admixes hold an advantage over the bentonite admix. Based on the likelihood of re-mobilization, the admixes rank as follows:

Pb mobility - Spruce bark admix < Forest soil admix < Bentonite admix

Cu mobility - Forest soil admix < Spruce bark admix < Bentonite admix.

4.4.3 Summary of SSE results and the performance of the admixes

Migration behavior and sorption characteristics

1. Many admix samples from the 2nd and 3rd layers showed zero or near zero concentrations of heavy metals. The non-uniform and unpredictable migration behavior of heavy metals, presents a challenge to transport modeling.
2. The decision to permeate samples from bottom to top led to excess heavy metal sorption in the 4th (top) layer. Although this resulted in an overestimation of heavy metal sorption capacities for the Leaching cells, the error did not significantly change any conclusions made.
3. Sorption capacities of the admixes were greater than the sum of their individual materials. This was probably because the soil:solution ratio (1 g : 135 ml) of the admixes was lower than the soil:solution ratio (1 g : 30 ml) of the individual materials.
4. The SSE results showed that for all three admixes, precipitation and complexation dominated at low *Pb* and *Cu* concentrations, while cation exchange became dominant at higher concentrations. For the bentonite admix, 96% of the *Cd* was retained by cation exchange.
5. Amongst the three heavy metals tested, *Cd* was sorbed the weakest; thus *Cd* has the highest desorption potential. For *Pb* and *Cu*, desorption potential increased with increasing heavy metal sorption concentrations.
6. The SSE results showed that the sorption model developed *Pb* and *Cu*, in section 4.2.1 would be improved if cation exchange, surface complexation, and precipitation were individually identified. Since *Cd* was retained mainly by cation exchange for bentonite, the identification of individual mechanisms is unnecessary.

The applicability of Batch adsorption test results to the Leaching cell test

7. One came to the same conclusions regarding sorption characteristics using the SSE results for both the Batch and Leaching cell samples.
8. The heavy metal sorption capacities for Batch adsorption tests were comparable to that of Leaching cells.

Performance of admixes

9. The SSE results for Leaching cell samples, showed all three admixes experienced a significant amount of preferential channeling.
10. The SSE results for the Batch adsorption test samples showed that on average, Forest soil admix sorbed 18% more heavy metals, and Spruce bark admix sorbed 16% less heavy metals, than the bentonite admix.
11. The SSE results for the Leaching cell and Batch samples showed that the addition of Forest soil and Spruce bark into a typical bentonite admix likely inhibited cation exchange, but promoted surface complexation.
12. The SSE results showed that based on the likelihood of *Pb* and *Cu* re-mobilizing in the future, the admixes rank as follows:

Pb mobility - Spruce bark admix < Forest soil admix < Bentonite admix

Cu mobility - Forest soil admix < Spruce bark admix < Bentonite admix

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

Heavy metal sorption characteristics of the clay barrier materials

1. An empirical model based on the Freundlich equation was developed for the sorption of *Pb*, *Cu*, and *Cd*, onto bentonite, Forest soil, and Spruce bark. This model was capable of predicting single, binary, and ternary heavy metal systems. See Table 4.2.5 for the full set of equations.
2. The Batch adsorption tests results produced the following ranking of sorption capacities:

	Ranking
<i>Pb</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cu</i> sorption capacity	Forest soil > Bentonite $\approx$ Spruce bark
<i>Cd</i> sorption capacity	Forest soil > Bentonite > Spruce bark
Sorption onto Bentonite	$Pb > Cu > Cd$
Sorption onto Forest soil	$Cu > Pb > Cd$ (up to initial [metal] of 4 mmol/L, then $Pb > Cu$)
Sorption onto Spruce bark	$Pb > Cu > Cd$

3. Based on the competition functions in Table 4.2.7, the competition amongst heavy metals rank as follows: $Pb > Cu > Cd$.

Heavy metal sorption characteristics of the clay barrier admixes

4. The SSE results showed that for all three admixes, precipitation and complexation dominated at low *Pb* and *Cu* concentrations, while cation exchange became dominant at higher concentrations. For the bentonite admix, 96% of the *Cd* was retained by cation exchange.
5. The SSE results for the Batch test samples showed that on average, the Forest soil admix sorbed 18% more heavy metals, and the Spruce bark admix sorbed 16% less heavy metals, than the bentonite admix.
6. The SSE results for both Batch and Leaching cell samples showed that the addition of Forest soil and Spruce bark into a typical bentonite admix inhibited cation exchange, but likely promoted surface complexation.

Effect of heavy metals on hydraulic conductivity

7. In comparison to the blank solutions (only containing 0.01 M $\text{Ca}(\text{NO}_3)_2$), the hydraulic conductivities of the heavy metal (500 mg L⁻¹) permeated samples were greater by approximately two orders of magnitude (from $\approx 2 \times 10^{-11}$ m s⁻¹ to $\approx 3 \times 10^{-9}$ m s⁻¹).
8. The hydraulic conductivity results in the current study experienced much larger increases than those found in other studies. This discrepancy was probably due to the lack confining pressures used in the current study. This condition would represent that of a landfill at the beginning of operation.

9. The blank (Ca^{2+}) and heavy metal solutions (Pb^{2+} , Cu^{2+} , Cd^{2+} , Ca^{2+}), both contained cations of 2+ valence. Thus, valence was not sufficient in identifying the effect of cations on hydraulic conductivity. A comparison between Ca and the heavy metals suggests that their potential for specific sorption mechanisms, such as complexation and precipitation, may be factors in affecting the hydraulic conductivity of clay barriers.
10. Heavy metal solutions containing different combinations of Pb , Cu , and Cd , in 500 mg L⁻¹ concentrations, produced similar hydraulic conductivities. The results indicate that the attained hydraulic conductivities represent an upper limit determined by the soil structure of the admixes.

The migration and mobility of heavy metals through clay barriers

11. The breakthrough, hydraulic conductivity, and SSE results indicated that heavy metals migrated non-uniformly through the Leaching cell samples.
12. Early heavy metal breakthroughs, increases in hydraulic conductivity, and uneven distributions of heavy metals within the extruded Leaching cells, indicated that short-circuiting occurred.
13. A conceptual mechanism (Figures 4.3.7 & 4.3.15) for the increase in hydraulic conductivity and migration of heavy metals was developed based on the hydraulic conductivity and heavy metal breakthrough curves.
14. Based on breakthrough points, Cd was ≈ 1.5 times more mobile than Cu , and ≈ 4 times more mobile than Pb , respectively.

Prediction ability of Batch adsorption tests

15. The Batch adsorption tests were adequate indicators of relative heavy metal mobilities.
16. The SSE results showed that the Batch and Leaching cell samples had the same heavy metal sorption characteristics.
17. The Batch adsorption tests were insufficient at predicting the heavy metal breakthrough points and retention capacities of Leaching cell tests.

Performance of admixes

18. The three admixes produced similar hydraulic conductivity values (Table 4.3.3).
19. The Forest soil admix ranked the best in terms of retention capacity, points of breakthrough, and long-term immobilization of heavy metals.
20. The Bentonite admix was better than the Spruce bark admix in terms of retention capacity, and points of breakthrough.
21. The Spruce bark admix was better than the bentonite admix in terms of long-term immobilization of heavy metals.

5.2 RESEARCH CONTRIBUTIONS

The conclusions from this study are applied to the following areas:

1. *The design of landfill liners, surface impoundment liners, and vertical clay barriers*
  - a) The current study found that heavy metal compatibility studies are required when significant concentrations of heavy metals are expected. Leaching cell testing is recommended for determining the parameters for hydraulic conductivity, heavy metal breakthrough, and heavy metal retention.
  - b) The addition of Forest soil into a clay barrier mix, increased the heavy metal sorption capacity, and improved long-term heavy metal retention, without significantly increasing hydraulic conductivity values.
  - c) The addition of Spruce bark provided an improvement to the long-term heavy metal fixation, but reduced the sorption capacity of the clay barrier.
  - d) The clay barriers used in the study were under-saturated at the start of heavy metal permeation, and did not receive direct application of confining pressures. These conditions are comparable to those encountered early after barrier construction.
2. *Modeling the migration of heavy metals through soils.*
  - a) Sorption capacities attained from Batch adsorption testing, were insufficient for predicting the breakthrough points and retention capacities of Leaching cell tests, but adequately predicted the relative mobilities of *Pb*, *Cu*, and *Cd*.
  - b) The Batch adsorption and SSE results showed that the influence of different retention mechanisms vary with heavy metal type and sorption concentrations.

- c) This study found that heavy metal migration was non-uniform, and followed unpredictable pathways. These pose as challenges to transport modeling.

4. *Co-disposal of heavy metal contaminated soil*

This study found that the Forest soil admix possessed stronger heavy metal retention than the bentonite admix. These findings suggest the possibility of mixing heavy metal contaminated soils with Forest soil as a remedial measure.

5.3 RECOMMENDATIONS ON FURTHER RESEARCH

1. *Confirmation of proposed sorption model, and mechanism for hydraulic conductivity increase and heavy metal migration.*
  - a) The sorption model developed was able to describe binary and ternary systems of *Pb*, *Cu*, and *Cd* with bentonite, Forest soil, and Spruce bark. Recommended is further work with other cations and materials, and testing on quaternary and higher systems.
  - b) Conducting studies involving the scanning electron microscope would confirm the proposed mechanism for hydraulic conductivity increase. Also, a detailed mapping of heavy metal distribution using SSE, is recommended.
  - c) Further work is recommended in creating transport models based on the sorption model, and the proposed hydraulic conductivity increase mechanism.
2. *Leaching cell testing.*
  - a) The decision to permeate samples from bottom to top caused the contaminated leachate to pool at the top of the Leaching cell. For future studies, permeating the samples from top to bottom is recommended. This will prevent the over-adsorption of heavy metals at the discharge end. Another option would be to slice a thin layer of soil at the discharge end, before taking samples for Selective Sequential Extraction.
  - b) In simulating the conditions of a newly operating landfill, the current study did not apply confining pressures to the samples. Further research into the influence of confining pressures on heavy metal compatibility is recommended.

- c) Further investigation is recommended regarding the influence of cation sorption characteristics on the flocculation of clays, and the hydraulic conductivity of clay barriers.
- d) The high concentration (500 mg L^{-1}) of heavy metals used in the current study caused hydraulic conductivity values to reach an upper limit. Further research is recommended in investigating the minimum concentrations required to trigger increases in hydraulic conductivity.
- e) Further research is recommended in determining the influence of bacterial growth, and dissolved components of Forest soil and Spruce bark.

3. *Sorption studies.*

- a) In light of the current study, investigation into the sorption capacities and characteristics of calcium would be helpful in understanding the effects of heavy metals on clay barriers.
- b) Further research is required to determine why admixing Forest soil to bentonite appeared to promote greater precipitation and complexation.
- c) An extensive SSE and Batch adsorption testing program is recommended to develop a sorption model that distinguishes specific sorption mechanisms.

4. *Clay barrier studies.*

- a) Recommended, is further investigation on the mechanical (stress-strain) properties of the admixes used in the current study.

REFERENCES

- Acar, Y.B., Hamidon, A., Field, S.D., and Scott, L. 1985. The effect of organic fluids on hydraulic conductivity of compacted kaolinite. *In* Hydraulic Barriers in Soil and Rock, ASTM STP 874. Edited by A.I. Johnson, R.K. Frobels, N.J. Cavalli, and C.B. Pettersen. American Society for Testing Materials, Philadelphia, PA, pp. 171-187.
- Al-Asheh, S., and Duvnjak, Z., 1997. Sorption of cadmium and other heavy metals by pine bark. *Journal of Hazardous Materials*, **56**: 35-51.
- Allan, R.J. 1995. Impact of mining activities on the terrestrial and aquatic environment with emphasis on mitigation and remedial measures. *In* Heavy Metals: Problems and Solutions. Edited by W. Salomons, U. Forstner, and P. Mader. Springer-Verlag, Berlin Heidelberg, Germany, pp. 119-140.
- American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) 1995. Standard method 9081. *In* Standard Methods for the Examination of Water and Wastewater. Edited by M.A.H. Franson. APHA, Washington DC.
- Arnfolk, P., Wasay, A., Tokunaga, S. 1996. A comparative study of Cd, Cr(III), Cr(VI), Hg, and Pb uptake by minerals and soil materials. *Water, Air, and Soil Pollution*, **87**: 131-148.
- ASTM, (1995). Annual Book of ASTM Standards: Soil and Rock (I-II) **4.08-4.09**, American Society Testing and Materials, Philadelphia, PA.
- Bagchi, A. 1990. Design, Construction, and Monitoring of Sanitary Landfill. John Wiley & Sons, New York, USA.
- Barry, G.A., Chudek, P.J., Best, E.K., and Moody, P.W. 1995. Estimating sludge application rates to land based on heavy metal and phosphorus sorption characteristics of soil. *Water Research* **29**(9): 2031-2034.
- Bladel, R.V., Halen, H., Cloos, P. 1993. Calcium-zinc and calcium-cadmium exchange in suspensions of various types of clays. *Clay Minerals*, **28**: 33-38.
- Cabral, A.R. 1992. A study of clay compatibility to heavy metal transport in permeability testing, Ph.D. Thesis. Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Canada.

Carter, D.L., Mortland, M.M., and Kemper, W.D. 1986. Specific Surface. In *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods - Agronomy Monograph No. 9* (2nd Edition). American Society of Agronomy - Soil Science Society of America, Madison, WI, pp. 413-423.

Chapman, D.L. 1913. A contribution to the theory of electrocapillarity. *Phil. Mag.* **25**(6): 475-481.

Crosby, Donald G. 1998. *Environmental Toxicology and Chemistry*. Oxford University Press, Oxford, New York.

Daniel, D.E. 1995. State-of-the-art: laboratory hydraulic conductivity tests for saturated soils. In *Hydraulic Conductivity and Waste Contaminant Transport in Soil*, ASTM STP 1142. Edited by D.E. Daniel, and S.J. Trautwein. American Society for Testing and Materials, Philadelphia, PA.

Denham, W.T. 1999. The hydraulic conductivity and adsorptivity of clay barrier materials containing organoclay, M.A.Sc. Thesis. Department of Civil Engineering, University of British Columbia. Vancouver, BC.

Deshkar, A.M., Bokade, S.S., Dara, S.S. 1990. Modified Hardwickia Binata bark for adsorption of mercury (II) from water. *Water Research*, **24**(8): 1011-1016.

Dunn, J.R., Mitchell, J.K. 1984. Fluid conductivity testing of fine-grained soils. *Journal of Geotechnical Engineering*. **110**(11): 1648-1665.

Eltantawy, I.M., and Arnold, P.W. 1973. Reappraisal of ethylene glycol mono-ethyl ether (EGME) method for surface area estimations of clays. *Journal of Soil Science* **24**: 232-238.

EPA, 1987. Batch type adsorption procedures for estimating soil attenuation of chemicals. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA/530-SW-87-006, Washington, D.C.

Ernst, W.H.O. 1974. *Schwemetallvegetation der Erde*. Fischer, Stuttgart.

Ernst, W.H.O. 1990. Mine vegetation in Europe. In *Heavy Metal Tolerance in Plants: Evolutionary Aspects*. Edited by A.J. Shaw. CRC Press, Boca Raton, pp. 21-51.

Ernst, W.H.O. 1995. Decontamination or consolidation of metal-contaminated soils by biological means. In *Heavy Metals: Problems and Solutions*. Edited by W. Salomons, U. Forstner, and P. Mader. Springer-Verlag, Berlin Heidelberg, Germany.

- Ernst, W.H.O., Josse-van Damme E.N.G 1983. Umweltbelastung durch Mineralstoffe. Fischer, Jena.
- Ernst, W.H.O., Josse-van Damme E.N.G 1989. Zanieczyszczenie środowiska substancjami mineralnymi. Państwowe Wydawnictwo Rolnicze i Leśne, Warszawa.
- Evans, L.J. 1989. Chemistry of metal retention by soils. *Environmental Science and Technology*, **23**(9): 1046-1056.
- Fergusson, Jack E. 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon Press, Oxford, UK.
- Fernandez, F. and Quigley, R.M. 1985. Hydraulic conductivity of natural clays permeated with simple liquid hydrocarbons. *Canadian Geotechnical Journal* **22**: 205-214.
- Field, J.A., and Lettinga, G. 1991. Treatment and detoxification of aqueous spruce bark extracts by *Aspergillus Niger*. *Journal of Water Science and Technology* **24**(3/4): 127-137.
- Field, J.A., Leyendeckers, J.H., Alvarez, R.S., Lettinga, G., Habets, L.H.A. 1988. The methanogenic toxicity of bark tannins and the anaerobic biodegradability of water soluble bark matter. *Water, Science, and Technology*, **20**(1): 219-240.
- Fyfe, W.S. 1964. Geochemistry of Solids, An Introduction. McGraw-Hill, New York.
- Foreman, D.E., and Daniel, D.E. 1986. Permeation of compacted clay with organic chemicals. *Journal of Geotechnical Engineering*, **112**: 582-589.
- Freeze, R.A., and Cherry, J.A. 1979. Groundwater. Prentice-Hall, Eaglewood Cliffs, NJ.
- Gao, S., Walker, W.J., Dahlgren, R.A., Bold, J. 1997. Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. *Water, Air, and Soil Pollution*, **93**: 331-345.
- Gloaguen, V., and Morvan, H. 1997. Removal of heavy metal ions from aqueous solution by modified barks. *Journal of Environmental Science and Health*, **A32**(4): 901-912.
- Gouy, G. 1910. Sur la constitution de la charge électrique à la surface d'un électrolyte. *Ann. Phys. (Paris)*, Series 4, **9**: 457-468.
- Gutierrez, M., and Fuentes, H.R. 1993. Modeling adsorption in multicomponent systems using a Freundlich-type isotherm. *Journal of Contaminant Hydrology*, **14**: 247-260.

- Hatton, D., and Pickering, W.F. 1980. The effect of pH on the retention of Cu, Pb, Zn and Cd by clay-humic mixtures. *Water, Air, and Soil Pollution*, **14**: 13-21.
- Hayes, K.F. 1987. Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide/aqueous interface. Ph.D. Dissertation, Stanford University.
- Hayes, M.H.B., and Swift, R.S. (1978). The chemistry of soil organic colloids. In *The Chemistry of Soil Constituents*. Edited by D.J. Greenland, and M.H.B. Hayes. Wiley, New York, pp. 179-230.
- Haygreen, J.G., Bowyer, J.L. 1996. Forest Products and Wood Science. Iowa State University Press, Iowa.
- Hickey, M.G., and Kittrick, J.A. 1984. Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals. *Journal of Environmental Quality*, **13**(3): 372-376.
- Hinz, C., Buchter, B., and Selim, H.M. 1992. Heavy metal retention in soils: Application of multisite models to zinc sorption. In *Engineering Aspects of Metals-Waste Management*. Edited by I.K. Iskandar, H.M. Selim. Lewis Publishers, Boca Raton, pp. 141-157.
- Igloria, V.I., Hathhorn, W.E., and Yonge, D.R. 1998. Effects of natural organic matter on heavy metal transport during infiltration. *Transportation Research Record*, **1523**: 167-172.
- Irving, H., and Williams, R.J.P. 1953. The stability of transition-metal complexes. *Journal of the Chemical Society*, pp. 3192-3210.
- Lindsay, W.L. 1979. Chemistry Equilibria in Soils. John Wiley & Sons, New York.
- Livens, F.R. 1991. Chemical reactions of metals with humic material. *Environment Pollution*, **70**: 183-208.
- Lo, I.M-C., Liljestrand, H.M., Daniel, D.E. 1994. Hydraulic conductivity and adsorption parameters for pollutant transport through montmorillonite and modified montmorillonite clay liner materials. In *Hydraulic Conductivity and Waste Contaminant Transport in Soil*. ASTM STP 1142. Edited by David E. Daniel and Stephen J. Trautwein. American Society for Testing Materials, Philadelphia, 1994.
- Lu, J.C.S, Morrison, R.D., and Stearns, R.J. 1981. Leachate production municipal landfills: Summary and assessment. In *Land Disposal of Municipal Solid Waste*. Edited by W.D. Shultz. 7th Annu. Res. Symp., EPA-600/9-81/002a. 1-17. U.S. Environ. Prot. Agency, Cincinnati, Ohio.

McGinley, P.M., and Kmet, P. 1984. Formation, Characteristics, Treatment and Disposal of Leachate from Municipal Solid Waste Landfills. Bur. Solid Waste Manage., Wisconsin Dept. of Natural Resources, Madison.

McLean, E.O. 1982. Soil pH and lime requirement. *In* Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties. Edited by A.L. Page, R.H. Miller, and D.R. Keeney. American Society of Agronomy, Madison, WI, pp. 199-224.

McQuarrie, D.A., Rock, P.A. 1991. General Chemistry. W.H. Freeman, New York.

Meegoda, N.J. and Rajapakse, R.A. 1993. Short-term and long-term permeabilities of contaminated clays. *Journal of Environmental Engineering* **119**(4): 725-743.

Mitchell, J.K., Hooper, D.R., Campanella, R.G. 1965. Permeability of compacted clay. *Journal of the Soil Mechanics and Foundations Division, Proceedings of the ASCE*, **91**(SM4): 41-65.

Mohamed, A.M.O., and Antia, H.E. 1998. Geoenvironmental Engineering. Developments in Geotechnical Engineering, 82. Elsevier, Amsterdam, Netherlands.

Morely, G.F., and Gadd, G.M. 1995. Sorption of toxic metals by fungi and clay minerals. *Mycological Research*, **99**(12): 1429-1438.

Nriagu, J.O. 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature*, **279**(5712): 409-411.

Nriagu, J.O., and Pacyna, J.M. 1987. Worldwide contamination of air, water and soils with trace metals - quantitative assessment. *Nature*, 333.

Peirce, J.J., Sallfors, G., Peel, T.A., and Witter, K.W. 1987. Effects of selected inorganic leachates on clay permeability. *Journal of Geotechnical Engineering*, **113**(8): 915-919.

Phadungchewit, Y. 1989. The role of pH and soil buffer capacity in heavy metal retention in clay soils, Ph.D. Thesis. Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Canada.

Puls, R.W., and Bohn, H.L. 1988. Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. *Soil Science Society of America Journal* **52**: 1289-1292.

Ragaini, Richard C. 1994. Technologies for environmental cleanup: toxic and hazardous waste management. *In* Technologies for environmental cleanup: toxic and hazardous

waste management 1-15. Edited by A. Avogadro, R.C. Ragaini. ECSC, EEC, EAEC, Netherlands.

Ramos, L., Hernandez, L.M., and Gonzalez, M.J. 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park. *Journal of Environmental Quality*, **23**: 50-57.

Rose, S. 1989. The heavy-metal adsorption characteristics of Hawthorne formation (Florida, U.S.A.) sediments. *Chemical Geology*, **74**: 365-370.

Rousseaux, P., Navarro, and Vermande, P. 1989. Distribution of seven heavy metals in European household waste components. In *Heavy Metals in the Environment*. Edited by J.P. Vernet. CEP Consultants Ltd., Edinburgh, UK, **2**: 87-90.

Sharma, H.D., and Lewis, S.P. 1994. Waste Containment Systems, Waste Stabilization, and Landfills: Design and Evaluation. John Wiley & Sons, New York.

Sheindorf, Ch., Rebhun, M., and Sheintuch, M. 1981. A Freudlich-type multicomponent isotherm. *Journal of Colloid and Interface Science* **79**(1): 136-142.

Soldatini, G.F., Riffaldi, R., and Levi-Minzi, R. 1976. Pb adsorption by soils. *Water, Air, and Soil Pollution*, **6**: 111-118.

Sparks, D.L. 1995. Environmental Soil Chemistry. Academic Press, San Diego, California.

Stevenson, F.J. 1982. Humus Chemistry: Genesis, Composition, Reactions. Wiley, New York.

Tan, K.H. 1998. Principles of Soil Chemistry. Marcel Dekker, New York.

Tchobanoglous, G., Theisen, H., and Vigil, S. 1993. Integrated Solid Waste Management: Engineering Principles and Management Issues. McGraw-Hill, Inc., New York.

Uppot, J.O. and Stephenson, R.W. 1989. Permeability of clay under organic permants. *Journal of Geotechnical Engineering* **115**(1): 115-131.

U.S. Environmental Protection Agency (USEPA) 1984. Slurry Trench Construction for Pollution Migration Control, EPA-540/2-84-001. USEPA, Cincinnati, Ohio, p. 217.

U.S. Environmental Protection Agency (USEPA) 1989. Requirement for Hazardous Waste Landfill Design, Construction, and Closure, Seminar Publication, EPA/625/4-89/022. USEPA, Washington, D.C. p. 127.

Vazquez, G., Antorrena, G., Gonzalez, J., and Doval, M.D. 1994. Adsorption of heavy metal ions by chemically modified pinus pinaster bark. *Bioresource Technology*, **48**: 251-255.

Weber, L. 1991. The permeability and adsorption capability of kaolinite and bentonite clays under heavy metal leaching, M.A.Sc. Thesis. Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Canada.

Yanful, E.K., Quigley, R.M., Nesbitt, H.W. 1988. Heavy metal migration at a landfill site, Sarnia, Ontario, Canada - 2: metal partitioning and geotechnical implications. *Applied Geochemistry*, **3**: 623-629.

Yasumura, S., Vartsky, D., Ellis, K.J., and Cohn, S.H. 1980. Cadmuim in human beings. *In* Cadmium in the Environment Part 1: Ecological Cycling. *Edited by* Jerome O. Nriagu. John Wiley & Sons, New York.

Yong, R.N., Mohamed, A.M.O., and Warkentin, B.P. 1992. Principles of Contaminant Transport in Soils. *Developments in Geotechnical Engineering*, **73**. Elsevier, Amsterdam, Netherlands.

Yong, R.N., and Phadungchewit, Y. 1993. pH influence on selectivity and retention of heavy metals in some clay soils. *Canadian Geotechnical Journal*, **30**: 821-833.

APPENDIX A   PHYSICAL PROPERTIES OF CLAY BARRIER MATERIALS

A.1. PARTICLE SIZE DISTRIBUTION

A.2. SPECIFIC GRAVITY OF ADMIXES

A.3. SPECIFIC SURFACE AREA OF BENTONITE

**A.4. OPTIMUM MOISTURE CONTENT AND MAXIMUM DRY
DENSITY OF THE ADMIXES**

APPENDIX A.1. PARTICLE SIZE DISTRIBUTION

Methods

Dry sieving, performed according ASTM D422-63 (ASTM, 1995), was applied to particle sizes larger than 75 μm . The hydrometer analysis, adapted from ASTM D422-63 (ASTM, 1995), was performed to determine the size distribution of particles smaller than 75 μm . Dry sieving was performed for the sand, bentonite, Forest soil, and Spruce bark, while the hydrometer analysis was performed for the bentonite only.

Details of the hydrometer analysis

Five grams of dispersing agent (sodium hexametaphosphate) was added to approximately 700 ml of distilled water, and was stirred by a high-speed mixer. As the solution was stirred, 30.0 g of dry sample was slowly added. After 10 min. of mixing, the mixture was transferred to a 1.00 L sedimentation cylinder ($\approx$ 45 cm high and 56 cm in diameter). Additional distilled water was used to rinse all of the solids into the cylinder, and to fill the cylinder up to the 1.00 L mark. A second cylinder was filled with distilled water to store and rinse the hydrometer.

The following measurements were taken prior to the hydrometer test:

1. Internal diameter of the sedimentation cylinder
2. Volume of hydrometer bulb (measured using water volume displacement)
3. Distances between the bulb center and the bulb's graduation marks
4. Height of the meniscus on the hydrometer stem

Prior to starting the test, the sample was shaken for 30 s by using one hand to cover the open end of the cylinder, and continually inverting it upside-down and back. The start of the test was marked at the point where the cylinder was set on the table immediately after shaking. The hydrometer was inserted into the suspension to take readings at 0, 15, 30, 60, and 120 s. After each reading, the hydrometer was rinsed and stored in the water-filled cylinder. After the 2 min. reading, the mixture was hand shaken again, and the test was restarted. When a consistent pair of readings was obtained, the test was restarted again, but the first reading was not taken until the 2 min. mark. Subsequent readings were taken at 4, 8, 15 min., etc., until the elapsed time was large enough to give the minimum particle diameter. In addition to the hydrometer readings, the temperature was measured periodically. After the final reading, the mixture was transferred to a tared container, and dried for 24 hr. at 105 $^{\circ}\text{C}$ to determine the exact dry weight of the sample.

Calculations

Equation for particle diameter D (mm) is,

$$D = [(30nH_r)/(981)(G_s - 1)(\rho_w t)]^{1/2}$$

where t (mm) is the time after the start of sedimentation, G_s is the specific gravity of the particles (G_s taken from Denham, 1999), ρ_w (g/cm³) is the density of water at temperature T , n (g/cm·s) is the viscosity of water at temperature T , and H_r (cm) is the corrected depth of fall.

The corrected depth of fall H_r (cm) is,

$$H_r = H + C_m - (V_b/2A)$$

where H (cm) is the depth of fall measured from the meniscus to the center of the bulb, C_m (cm) is the meniscus correction, V_b (cm³) is the volume of the bulb, and A (cm²) is the cross-sectional area of the cylinder.

The percentage p by weight of particles with diameter smaller than D is,

$$p = (62.26/W_o)(R - C_d + m)[G_s/(G_s - 1)]$$

where W_o (g/L) is the oven-dried weight of material per liter of suspension, R (g/L) is the suspension unit weight reading from the hydrometer, C_d (g/L) is the dispersing agent correction, and m (g/L) is the temperature correction.

The dispersing agent correction C_d (g/L) is,

$$C_d = X_d V_s$$

where X_d (g) is the amount of sodium hexametaphosphate added, and V_s (L) is the volume of suspension.

The temperature correction m (g/L) is,

$$m = 1000\{0.99823 - \rho_w - [0.000025(T - 20)]\}$$

Results

The plot of particle size vs. percent finer is found in section 4.1 (Figure 4.1.1).

TABLE A.1.1. Particle size distribution of sand, bentonite, air-dried Forest soil, and Spruce bark (Dry sieving data unless otherwise indicated).

Sand		Air-dried Forest soil		Spruce bark		Bentonite		
Size (mm)	Percent Finer	Size (mm)	Percent Finer	Size (mm)	Percent Finer	Size (mm)	Percent Finer	
0.833	99.8%	6.35		6.35	99.9%	0.42	99.5%	Dry sieving
0.5	84.3%	2.38	99.9%	2.38	86.5%	0.3	99.2%	
0.42	64.1%	0.833	77.0%	0.833	43.5%	0.25	98.9%	
0.3	29.5%	0.5	58.8%	0.5	26.5%	0.149	98.0%	
0.25	17.4%	0.42	51.9%	0.3	15.4%	0.125	96.7%	
0.149	4.0%	0.3	41.7%	0.25	11.4%	0.104	95.2%	
0.125	1.4%	0.25	35.1%	0.125	3.8%	0.074	91.3%	
0.104	0.5%	0.125	16.9%	0.104	2.3%	0.0915	88.8%	Hydrometer
0.074	0.1%	0	0.0%	0	0.0%	0.0648	88.2%	
0	0.0%					0.0458	88.2%	
						0.0325	86.5%	
						0.0231	83.2%	
						0.0164	81.6%	
						0.0120	81.6%	
						0.0085	78.3%	
						0.0061	74.4%	
						0.0030	70.1%	
						0.0020	68.5%	
						0.0014	61.9%	
						0.0012	56.7%	
						0.0010	52.1%	

APPENDIX A.2. SPECIFIC GRAVITY OF ADMIXES

Specific gravities were measured for the admixes using the volume-displacement method described in ASTM D854-92 (ASTM, 1995).

Calculations

The equation for specific gravity G_s (mass material/mass water) is,

$$G_s = W_s / (W_s + W_{fs} + W_{fw})$$

where W_s is the weight of the dry admix, W_{fs} is the weight of the flask filled with admix and water, and W_{fw} is the weight of the flask filled with de-aired water only.

Results

TABLE A.2.1. Specific gravities of the admixes.

	Temperature (°C)	W_s (g)	W_{fw} (g)	W_{fs} (g)	G_s
Bentonite admix	18	123.4	699.9	777.0	2.67
Forest soil admix	18	128.5	666.0	746.1	2.65
Spruce bark admix	17.5	133.9	694.1	777.5	2.65

APPENDIX A.3. SPECIFIC SURFACE AREA OF BENTONITE

Method

The specific surface area was determined using an ethylene glycol monoethyl ether (EGME) method adapted from Eltantawy and Arnold (1973). This test was performed in cooperation with Denham (1999).

A samples of air-dried bentonite weighing 1.1 g was placed in a tared aluminum foil dish and dried at 60 °C for 48 hr. The dish was weighed before and after drying to determine moisture content and clay dry weight. Approximately 1.5 ml of EGME (Fisher) was added to the sample, which was then manually stirred to create a clay-EGME slurry. Clay which adhered to the stirring rod was returned to the slurry by dripping EGME onto the rod.

The sample was then placed in a dessicator over anhydrous CaCl_2 (granular, 20 mesh & finer, Fisher). A dish of EGME was also placed in the dessicator. The sample was left to equilibrate for 30 min. The dessicator was then evacuated with a vacuum pump. The pump was disconnected after 45 min., but the dessicator was kept under vacuum for 24 hr. After 24 hr., the vacuum was released through a drying trap.

The sample was weighed and returned to the dessicator. Then the dessicator was again evacuated for 45 min. and left for 24 hr. This procedure was repeated 8 more times until 240 hr. had passed, and a stable weight was achieved. In theory, the difference in the weight of the clays before and after the elapsed time represents a monomolecular layer of EGME covering the internal and external surfaces of the sample.

Calculations

The equation for the specific surface area in m^2/g is provided by Carter et al. (1986):

$$A = W_a / (W_s \cdot 2.86)$$

where A is the specific surface, in m^2/g , W_a is the weight of EGME retained by the sample, in g, W_s is the weight of the dry clay, in g, and 0.000286 g is the weight of EGME required to form a monomolecular layer on 1 m^2 of surface.

Results**TABLE A.3.1. Specific surface of bentonite.**

Sample	W_s (g)	W_a (g)	A (m ² /g)
Bentonite (duplicate 1)	1.0654	0.1414	464.1
Bentonite (duplicate 2)	1.0600	0.1397	460.8
Average			462.4

APPENDIX A.4. OPTIMUM MOISTURE CONTENT AND MAXIMUM DRY DENSITY OF THE ADMIXES

The optimum moisture contents and maximum dry densities of the admixes were determined according to ASTM D1557-91 (ASTM, 1995), except for changes in the mold size, the number of compaction lifts, and the number of blows per lift (Table A.4.1). The changes were made to reflect the conditions used in the Leaching cell test.

TABLE A.4.1. Changes made to the modified Proctor method.

Test	Cell size	# of layers	# of blows per layer	Compactive energy per volume, ft-lb/cu ft
Modified Proctor	4.6 in x 4 in dia.	5	25	56300
Current study	2.2 in x 4 in dia.	3	12, 12, 13	34700

Results

The compaction curves are shown in Figures A.4.1 - A.4.3. Table A.4.2 summarizes the results for each admix.

TABLE A.4.2. Optimum water contents and maximum dry densities of the bentonite, Forest soil, and Spruce bark admixes.

Admix	Optimum water content	Maximum dry density (kg/m ³)
Bentonite admix	12.7 %	1860
Forest soil admix	12.8 %	1830
Spruce bark admix	12.7 %	1815

FIGURE A.4.1. Compaction curves for the admixes.

APPENDIX B CHEMICAL PROPERTIES OF CLAY BARRIER MATERIALS

B.1. SOIL pH

B.2. CATION EXCHANGE CAPACITY OF BENTONITE AND SAND

APPENDIX B.1. SOIL pH

The pH of the bentonite and sand was measured according to a method adapted from McLean (1982). Soil pH measurements are performed usually with a 1:1 soil material:water ratio, or a 1:2 soil material:0.01 M calcium chloride (CaCl_2) ratio. These ratios were lowered because more liquid was needed to sufficiently wet the soil materials and to allow for settlement.

The materials were measured into 100 ml beakers. After adding the water or 0.01 M CaCl_2 , the suspensions were stirred occasionally for 30 minutes. Then, the suspensions were allowed to settle for the next 30 minutes. The pH was measured by placing the pH probe in the partially settled suspension. Table B.1.1 summarizes the type and quantity of materials used for the pH measurement.

TABLE B.1.1. The type and quantity of materials submitted to soil pH measurement.

Material	Liquid added	Mass (oven-dried) of material (g)	Volume of liquid added (ml)	Ratio
Bentonite	water	2	20	1:10
Bentonite	0.01 M CaCl_2	2	20	1:10
Sand	water	5	5	1:1
Sand	0.01 M CaCl_2	5	10	1:2

Results

TABLE B.1.2. The soil pH results for bentonite and sand.

Type of Liquid	Bentonite pH	Sand pH
Water	8.38	4.72
0.01 M CaCl_2	7.61	7.67

APPENDIX B.2. CATION EXCHANGE CAPACITY OF BENTONITE AND SAND

The cation exchange capacity (CEC) of bentonite and sand was measured using the sodium acetate method adapted from Standard methods 9081 (APHA, AWWA, WEF, & 1995). The sodium acetate method is applicable for both calcareous and non-calcareous materials, but not acidic materials.

Method

Sodium saturation of exchange sites

Two to four grams (dry mass) of material was placed into a centrifuge tube. After adding 33 ml of 1.0 NaOAc solution to the material, the suspension was shaken in a mechanical wrist-shaker for approximately 5 min. The centrifuge tube was then centrifuged at 3500 rpm for 15 min. After decanting the liquid, this procedure was repeated two more times. Thirty-three milliliters of 2-propanol was then added to wash the sample, and was again shaken in a mechanical wrist-shaker for approximately five minutes. After decanting the liquid, this washing procedure was repeated two more times. The 2-propanol rinse was for removing all the Na in solution, without affecting the Na sorbed onto exchange sites.

Displacement of the sodium with ammonium

To displace the Na from the exchange sites, 33 ml of NH_4OAc was added to the sample, and the was shaken in a mechanical shaker for approximately 5 min. The liquid then was decanted into a 100 ml volumetric flask. This procedure was repeated two more times. Each time, the liquid was decanted into the same flask. Next, the 100 ml flask containing the decanted solution was filled to the 100 ml mark with NH_4OAc , and the Na concentration of the solution was determined using Atomic Absorption Spectrophotometry.

Calculations

CEC in centimoles of positive charge per kilogram (cmol/kg) was calculated from the following equation:

$$\text{CEC} = C_{\text{Na}} \cdot V_{\text{fl}} \cdot 1 \text{ g}/1000 \text{ mg} \cdot 1000 \text{ g}/1 \text{ kg} \cdot 1 \text{ mol}/23 \text{ g} \cdot 100 \text{ cmol}/1 \text{ mol}$$

where C_{Na} is the concentration of Na (mg/L) in the volumetric flask, and V_{fl} (L) is the volume of the flask.

Results**TABLE B.2.1.** The cation exchange capacity of bentonite and sand.

	Na concentration (mg/L)	CEC (cmol/kg)	Average
Bentonite (triplicate 1)	272.9	59.3	
Bentonite (triplicate 2)	273.9	59.5	
Bentonite (triplicate 3)	276.9	60.2	59.7
Sand (triplicate 1)	0		
Sand (triplicate 2)	0		
Sand (triplicate 3)	0		0

APPENDIX C METHODS SUPPLEMENT

C.1. EQUIPMENT LISTS AND DESCRIPTIONS

C.2. COMPACTION PROCEDURE FOR THE LEACHING CELL TEST

APPENDIX C.1. EQUIPMENT LISTS AND DESCRIPTIONS

For the Batch adsorption test

Listed below are some important items required for the Batch adsorption test. The equipment was made of materials that are non-reactive with heavy metals.

- 50 ml polypropylene centrifuge test tube
- rotator or shaker
- centrifuge (Beckman GS-6 model)
- test tubes and test tube pre-filters (for Forest soil and Spruce bark)

for dilutions

- 1 each - 25 ml, 50 ml, and 100 ml volumetric flasks
- 1 each - 1 ml, 2 ml, 4 ml, 6 ml, and 10 ml pipettes

For the Leaching cell test

The following are important items needed for the Leaching cell test. Figures C.1.1 - C.1.2, show schematics for the compaction hammer, compaction mold, and the Leaching cell. These equipment were made of materials that are non-reactive with heavy metals:

Compaction apparatus - compaction hammer, compaction mold, paper disk, saran wrap, ruler, knife

Leaching cell apparatus - leaching cell, 100 ml graduated cylinder (discharge collector), leachate reservoir, pressure gauge

dilution equipment - (see equipment for Batch adsorption test)

FIGURE C.1.1. Diagrams of compaction hammer and mold.

Note: Everything except for porous stones are made of Plexiglas

FIGURE C.1.2. Diagrams of Leaching cell.

For the Selective Sequential Extraction test

The list below outlines some important items needed to perform one SSE extraction. All items are non-reactive with heavy metals:

- wire saw
- ruler
- small spoon
- centrifuge
- 50 ml centrifuge polypropylene test tube
- 250 ml glass flask
- glass reflux cap
- dilution equipment (see equipment for Batch adsorption test)

APPENDIX C.2. COMPACTION PROCEDURE FOR THE LEACHING CELL TEST

The compaction procedure was modified from the modified Proctor procedure used in ASTM 1557-91 (ASTM, 1995). Figure C.2.1 illustrates the compaction procedure.

To improve the seal between the cell wall and the compacted sample, the inner wall of the Leaching cell was smeared with a thin layer of bentonite/water paste. Then, a paper disk (cut out from regular plain loose-leaf paper) was fitted into the bottom mold piece. Next, saran wrap was placed over the paper disk; the cell was fitted onto the bottom mold piece; and the entire assembly was weighed. The paper disk was there to prevent the compacted sample from sticking to the mold, and the purpose of the saran wrap was to keep the paper disk dry. Saran wrap used by itself ripped too easily during compaction. The rest of the mold was attached to the cell; then the admix was compacted into the cell in 3 lifts. The purpose of the mold is to prevent the cell from deformation during compaction. Twelve blows were used for the first 2 lifts, and 13 blows were used for the last lift. For consistency, the same pattern of blows were applied for every test (Figure C.2.2). After compaction, the top portion of the mold was removed, and the top of the sample was leveled using a ruler. The sample, leaching cell, and bottom mold piece were weighed together to obtain the wet mass of the sample. At this point, a small sample was taken from the admix container for water content analysis.

The bottom mold piece, paper disk, and saran wrap were then removed from the Leaching cell. A knife was used to scarify the bottom of the sample, and then the top and bottom lids were attached onto the cell. Finally, the cell was attached to the rest of the Leaching cell apparatus, by connecting it to the reservoir, and discharge collection container. Dry density, water content, and saturation were calculated for the Leaching cell samples.

FIGURE C.2.1. Diagrams of the compaction procedure.

FIGURE C.2.2. Striking pattern for compaction hammer.

APPENDIX D BATCH ADSORPTION TEST CALCULATIONS AND DATA

D.1. CALCULATION FOR CONVERTING MASS UNITS INTO MOLAR UNITS

D.2. BATCH ADSORPTION DATA FOR SINGLE HEAVY METAL LEACHATES

D.3. BATCH ADSORPTION DATA FOR BINARY HEAVY METAL LEACHATES

D.4. BATCH ADSORPTION DATA FOR TERNARY HEAVY METAL LEACHATES

APPENDIX D.1. CALCULATION FOR CONVERTING MASS UNITS INTO MOLAR UNITS

The equations for converting from [mg/L] to [mmol/L] are,

$$[\text{mmol/L}] \text{ of } Pb = \frac{[\text{mg/L}] \text{ of } Pb}{207.2}$$

$$[\text{mmol/L}] \text{ of } Cu = \frac{[\text{mg/L}] \text{ of } Cu}{63.55}$$

$$[\text{mmol/L}] \text{ of } Cd = \frac{[\text{mg/L}] \text{ of } Cd}{112.4}$$

The equations for converting from [mg/g] to [cmol/kg] are,

$$[\text{cmol of } Pb/\text{kg of material}] = [\text{mg of } Pb/\text{g of material}] \cdot \frac{1 \text{ g}}{1000 \text{ mg}} \cdot \frac{1 \text{ mol}}{207.2 \text{ g}} \cdot \frac{100 \text{ cmol}}{1 \text{ mol}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$[\text{cmol of } Cu/\text{kg of material}] = [\text{mg of } Cu/\text{g of material}] \cdot \frac{1 \text{ g}}{1000 \text{ mg}} \cdot \frac{1 \text{ mol}}{63.55 \text{ g}} \cdot \frac{100 \text{ cmol}}{1 \text{ mol}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$[\text{cmol of } Cd/\text{kg of material}] = [\text{mg of } Cd/\text{g of material}] \cdot \frac{1 \text{ g}}{1000 \text{ mg}} \cdot \frac{1 \text{ mol}}{112.4 \text{ g}} \cdot \frac{100 \text{ cmol}}{1 \text{ mol}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}}$$

APPENDIX D.2. BATCH ADSORPTION DATA FOR SINGLE HEAVY METAL LEACHATES

Pb sorption of bentonite

Initial <i>Pb</i> conc.		Final <i>Pb</i> conc.		Sorbed <i>Pb</i> concentration		Final
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg <i>Pb</i> per g bentonite	cmol <i>Pb</i> per kg bentonite	solution pH
0.0	0.0	0.0	0.0	0.0	0.0	7.44
0.0	0.0	0.0	0.0	0.0	0.0	7.42
50.0	0.2	0.1	0.0	2.5	1.2	6.84
50.0	0.2	0.2	0.0	2.5	1.2	6.94
100.0	0.5	4.4	0.0	4.8	2.3	6.57
100.0	0.5	4.7	0.0	4.8	2.3	6.53
200.0	1.0	32.7	0.2	8.4	4.0	6.17
200.0	1.0	34.5	0.2	8.3	4.0	6.18
500.0	2.4	108.4	0.5	19.6	9.5	5.87
500.0	2.4	106.2	0.5	19.7	9.5	5.89
1000.0	4.8	412.2	2.0	29.4	14.2	5.30
1000.0	4.8	417.9	2.0	29.1	14.0	5.38
2000.0	9.7	1219.0	5.9	39.1	18.8	5.12
2000.0	9.7	1210.5	5.8	39.5	19.1	5.13
3000.0	14.5	2071.0	10.0	46.5	22.4	4.99
3000.0	14.5	2083.5	10.1	45.8	22.1	5.00

Cu sorption of bentonite

Initial Cu conc.		Final Cu conc.		Sorbed Cu concentration		Final
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cu per g bentonite	cmol Cu per kg bentonite	solution pH
0.0	0.0	0.0	0.0	0.0	0.0	7.46
0.0	0.0	0.0	0.0	0.0	0.0	7.44
46.1	0.7	6.0	0.1	2.0	3.2	6.45
46.1	0.7	6.5	0.1	2.0	3.1	6.50
92.9	1.5	32.6	0.5	3.0	4.7	5.94
92.9	1.5	30.6	0.5	3.1	4.9	5.87
183.8	2.9	94.3	1.5	4.5	7.0	5.48
183.8	2.9	96.3	1.5	4.4	6.9	5.50
462.5	7.3	324.8	5.1	6.9	10.8	5.23
462.5	7.3	325.8	5.1	6.8	10.8	5.21
932.5	14.7	736.5	11.6	9.8	15.4	4.99
932.5	14.7	740.3	11.6	9.6	15.1	5.00
1862.0	29.3	1615.0	25.4	12.4	19.4	4.81
1862.0	29.3	1622.0	25.5	12.0	18.9	4.83
2792.5	43.9	2516.0	39.6	13.8	21.8	4.72
2792.5	43.9	2490.0	39.2	15.1	23.8	4.74
3748.0	59.0	3403.8	53.6	17.2	27.1	4.59
3748.0	59.0	3452.5	54.3	14.8	23.2	4.61

Cd sorption of bentonite

Initial Cd conc.		Final Cd conc.		Sorbed Cd concentration		Final
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cd per g bentonite	cmol Cd per kg bentonite	solution pH
0.0	0.0	0.0	0.0	0.0	0.0	7.23
0.0	0.0	0.0	0.0	0.0	0.0	7.23
49.4	0.4	24.3	0.2	1.3	1.1	6.85
49.4	0.4	24.2	0.2	1.3	1.1	6.84
98.3	0.9	53.9	0.5	2.2	2.0	6.74
98.3	0.9	53.4	0.5	2.2	2.0	6.71
194.7	1.7	121.2	1.1	3.7	3.3	6.57
194.7	1.7	121.9	1.1	3.6	3.2	6.56
498.7	4.4	351.0	3.1	7.4	6.6	6.38
498.7	4.4	355.3	3.2	7.2	6.4	6.37
1018.6	9.1	761.0	6.8	12.9	11.5	6.22
1018.6	9.1	765.6	6.8	12.7	11.3	6.25
2050.4	18.2	1648.6	14.7	20.1	17.9	6.07
2050.4	18.2	1656.2	14.7	19.7	17.5	6.12
3053.0	27.2	2618.3	23.3	21.7	19.3	6.04
3053.0	27.2	2631.2	23.4	21.1	18.8	6.05
3984.5	35.4	3482.3	31.0	25.1	22.3	5.95
3984.5	35.4	3569.7	31.8	20.7	18.5	6.05
4923.6	43.8	4367.1	38.9	27.8	24.8	5.98
4923.6	43.8	4326.5	38.5	29.9	26.6	5.97

Pb sorption of Forest soil

Initial Pb conc.		Final Pb conc.		Sorbed Pb concentration		Final
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Pb per g Forest soil	cmol Pb per kg Forest soil	solution pH
0.0	0.0	0.1	0.0	0.0	0.0	3.32
0.0	0.0	0.2	0.0	0.0	0.0	3.31
50.0	0.2	4.1	0.0	7.2	3.5	3.26
50.0	0.2	4.1	0.0	7.2	3.5	3.26
100.0	0.5	13.0	0.1	13.6	6.6	3.21
100.0	0.5	11.4	0.1	13.8	6.7	3.21
200.0	1.0	38.3	0.2	25.2	12.2	3.13
200.0	1.0	40.1	0.2	24.9	12.0	3.13
500.0	2.4	188.5	0.9	48.6	23.5	2.99
500.0	2.4	187.3	0.9	48.8	23.5	2.99
1000.0	4.8	559.0	2.7	68.8	33.2	2.88
1000.0	4.8	556.8	2.7	69.1	33.4	2.88
2000.0	9.7	1405.0	6.8	92.8	44.8	2.79
2000.0	9.7	1451.5	7.0	85.6	41.3	2.79
3000.0	14.5	2325.0	11.2	105.3	50.8	2.75
3000.0	14.5	2314.0	11.2	107.0	51.6	2.75
4000.0	19.3	3230.0	15.6	120.1	58.0	2.70
4000.0	19.3	3311.7	16.0	107.4	51.8	2.71

Cu sorption of Forest soil

NOTE: w/c = 212%; weighed sample is 0.8385 g; dry mass is 0.2688 g (other Batch tests used 0.5 g dry mass)

Initial Cu conc.		Final Cu conc.		Sorbed Cu concentration		Final pH
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cu per g Forest soil	cmol Cu per kg Forest soil	solution
0.0	0.0	0.0	0.0	0.0	0.0	3.17
0.0	0.0	0.0	0.0	0.0	0.0	3.19
46.1	0.7	8.0	0.1	3.5	5.6	3.07
46.1	0.7	7.8	0.1	3.6	5.6	3.09
92.9	1.5	26.0	0.4	6.2	9.8	3.01
92.9	1.5	25.8	0.4	6.2	9.8	3.01
183.8	2.9	79.4	1.3	9.7	15.3	2.92
183.8	2.9	80.3	1.3	9.6	15.1	2.92
462.5	7.3	299.2	4.7	15.2	23.9	2.80
462.5	7.3	298.2	4.7	15.3	24.0	2.80
932.5	14.7	720.0	11.3	19.7	31.1	2.71
932.5	14.7	728.5	11.5	19.0	29.8	2.72
1832.0	28.8	1583.7	24.9	23.1	36.3	2.63
1832.0	28.8	1608.2	25.3	20.8	32.7	2.64
2758.0	43.4	2419.6	38.1	31.4	49.5	2.58
2758.0	43.4	2458.8	38.7	27.8	43.8	2.60
3666.0	57.7	3421.7	53.8	22.7	35.7	2.56
3666.0	57.7	3420.0	53.8	22.9	36.0	2.57

Cd sorption of Forest soil

Initial Cd conc.		Final Cd conc.		Sorbed Cd concentration		Final pH
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cd per g Forest soil	cmol Cd per kg Forest soil	solution
0.0	0.0	0.0	0.0	0.0	0.0	7.23
0.0	0.0	0.0	0.0	0.0	0.0	3.17
0.0	0.0	0.0	0.0	0.0	0.0	3.18
49.4	0.4	30.2	0.3	1.8	1.6	3.15
49.4	0.4	30.9	0.3	1.7	1.5	3.16
98.3	0.9	64.4	0.6	3.2	2.8	3.15
98.3	0.9	63.9	0.6	3.2	2.8	3.15
194.7	1.7	136.0	1.2	5.5	4.9	3.12
194.7	1.7	136.9	1.2	5.4	4.8	3.13
498.7	4.4	380.1	3.4	11.0	9.8	3.06
498.7	4.4	382.7	3.4	10.8	9.6	3.07
1018.6	9.1	839.4	7.5	16.7	14.8	2.99
1018.6	9.1	821.1	7.3	18.4	16.3	3.01
2050.4	18.2	1764.6	15.7	26.6	23.6	2.92
2050.4	18.2	1766.6	15.7	26.4	23.5	2.94
3053.0	27.2	2760.5	24.6	27.2	24.2	2.88
3053.0	27.2	2792.6	24.8	24.2	21.5	2.88
3984.5	35.4	3675.1	32.7	28.8	25.6	2.85
3984.5	35.4				0.0	2.86

Pb sorption of Spruce bark

Initial Pb conc.		Final Pb conc.		Sorbed Pb concentration		Final pH
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Pb per g Spruce bark	cmol Pb per kg Spruce bark	solution
0.0	0.0	0.1	0.0	0.0	0.0	4.02
0.0	0.0	0.1	0.0	0.0	0.0	3.72
50.0	0.2	1.4	0.0	2.4	1.2	3.96
50.0	0.2	1.4	0.0	2.4	1.2	4.01
100.0	0.5					
100.0	0.5					
200.0	1.0					
200.0	1.0					
500.0	2.4	106.9	0.5	19.7	9.5	3.68
500.0	2.4	106.5	0.5	19.7	9.5	3.68
1000.0	4.8	420.3	2.0	29.0	14.0	3.5
1000.0	4.8	421.3	2.0	28.9	14.0	3.49
2000.0	9.7	1277.0	6.2	36.2	17.4	3.33
2000.0	9.7	1270.0	6.1	36.5	17.6	3.33
3000.0	14.5	2183.0	10.5	40.9	19.7	3.24
3000.0	14.5	2187.0	10.6	40.7	19.6	3.24
4000.0	19.3	3148.3	15.2	42.6	20.6	3.18
4000.0	19.3	3093.3	14.9	45.3	21.9	3.18

Cu sorption of Spruce bark

Initial Cu conc.		Final Cu conc.		Sorbed Cu concentration		Final pH
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cu per g Spruce bark	cmol Cu per kg Spruce bark	solution
0.0	0.0	0.0	0.0	0.0	0.0	3.98
0.0	0.0	0.0	0.0	0.0	0.0	4.00
46.1	0.7	11.9	0.2	1.7	2.7	3.95
46.1	0.7	12.0	0.2	1.7	2.7	3.96
92.9	1.5	28.2	0.4	3.2	5.1	3.88
92.9	1.5	27.9	0.4	3.2	5.1	3.92
183.8	2.9	82.1	1.3	5.1	8.0	3.77
183.8	2.9	81.8	1.3	5.1	8.0	3.74
462.5	7.3	318.7	5.0	7.2	11.3	3.56
462.5	7.3	315.2	5.0	7.4	11.6	3.56
932.5	14.7	755.0	11.9	8.9	14.0	3.41
932.5	14.7	750.0	11.8	9.1	14.4	3.42
1832.0	28.8	1640.5	25.8	9.6	15.1	3.28
1832.0	28.8	1621.9	25.5	10.5	16.5	3.29
2758.0	43.4	2558.8	40.3	10.0	15.7	3.21
2758.0	43.4	2492.1	39.2	13.3	20.9	3.22
3666.0	57.7	3516.0	55.3	7.5	11.8	3.16
3666.0	57.7	3490.0	54.9	8.8	13.8	3.17
4728.0	74.4	4536.0	71.4	9.6	15.1	3.12
4728.0	74.4	4472.0	70.4	12.8	20.1	3.13

Cd sorption of Spruce bark

Initial Cd conc.		Final Cd conc.		Sorbed Cd concentration		Final pH
mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	mg Cd per g Spruce bark	cmol Cd per kg Spruce bark	solution
0.0	0.0	0.0	0.0	0.0	0.0	4.04
0.0	0.0	0.0	0.0	0.0	0.0	4.07
49.4	0.4	28.6	0.3	1.0	0.9	3.93
49.4	0.4	28.8	0.3	1.0	0.9	3.94
98.3	0.9	58.6	0.5	2.0	1.8	3.92
98.3	0.9	59.0	0.5	2.0	1.7	3.92
194.7	1.7	125.1	1.1	3.5	3.1	3.89
194.7	1.7	127.4	1.1	3.4	3.0	3.89
498.7	4.4	373.1	3.3	6.3	5.6	3.84
498.7	4.4	370.1	3.3	6.4	5.7	3.84
1018.6	9.1	808.8	7.2	10.5	9.3	3.74
1018.6	9.1	809.9	7.2	10.4	9.3	3.74
2050.4	18.2	1711.0	15.2	17.0	15.1	3.65
2050.4	18.2	1726.8	15.4	16.2	14.4	3.67
3053.0	27.2	2743.5	24.4	15.5	13.8	3.61
3053.0	27.2	2763.0	24.6	14.5	12.9	3.61
3984.5	35.4	3630.6	32.3	17.7	15.7	3.57
3984.5	35.4	3642.7	32.4	17.1	15.2	3.58
4923.6	43.8	4420.9	39.3	25.1	22.4	3.55
4923.6	43.8	4409.5	39.2	25.7	22.9	3.55

APPENDIX D.3 BATCH ADSORPTION DATA FOR BINARY HEAVY METAL LEACHATES

Pb and Cu sorption of bentonite

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cu</i> conc.	Final <i>Cu</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cu</i>	Final pH
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g bentonite	mg <i>Cu</i> per g bentonite	
242.1	46.2	0.0	0.0	9.8	0.0	5.68
242.1	45.1	0.0	0.0	9.9	0.0	5.75
239.7	56.9	50.8	23.8	9.1	1.4	5.4
239.7	56.7	50.8	23.4	9.2	1.4	5.42
237.9	59.3	100.0	57.8	8.9	2.1	5.31
237.9	61.9	100.0	58.0	8.8	2.1	5.32
238.0	69.9	250.0	171.0	8.4	4.0	5.18
238.0	70.7	250.0	171.6	8.4	3.9	5.2
238.0	84.9	500.0	393.0	7.7	5.4	5.06
238.0	83.7	500.0	385.5	7.7	5.7	5.08
238.0	102.1	1000.0	865.0	6.8	6.8	4.9
238.0	103.4	1000.0	858.0	6.7	7.1	4.98
982.6	408.5	0.0	0.0	28.7	0.0	5.36
982.6	409.1	0.0	0.0	28.7	0.0	5.36
982.4	438.9	51.5	31.4	27.2	1.0	5.24
982.4	431.0	51.5	31.1	27.6	1.0	5.25
987.4	449.9	104.2	67.7	26.9	1.8	5.19
987.4	455.8	104.2	68.5	26.6	1.8	5.2
985.0	499.2	250.0	185.1	24.3	3.2	5.09
985.0	496.2	250.0	184.5	24.4	3.3	5.1
985.0	527.5	500.0	401.5	22.9	4.9	5.01
985.0	539.0	500.0	403.5	22.3	4.8	5.02
985.0	578.0	1000.0	877.0	20.4	6.2	4.91
985.0	577.0	1000.0	887.0	20.4	5.7	4.92

Pb and Cu sorption of bentonite

in molar units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cu</i> conc.	Final <i>Cu</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cu</i>	Final pH
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol <i>Pb</i> per kg bentonite	cmol <i>Cu</i> per kg bentonite	
1.2	0.2	0.0	0.0	4.7	0.0	5.68
1.2	0.2	0.0	0.0	4.8	0.0	5.75
1.2	0.3	0.8	0.4	4.4	2.1	5.40
1.2	0.3	0.8	0.4	4.4	2.2	5.42
1.1	0.3	1.6	0.9	4.3	3.3	5.31
1.1	0.3	1.6	0.9	4.2	3.3	5.32
1.1	0.3	3.9	2.7	4.1	6.2	5.18
1.1	0.3	3.9	2.7	4.0	6.2	5.20
1.1	0.4	7.9	6.2	3.7	8.4	5.06
1.1	0.4	7.9	6.1	3.7	9.0	5.08
1.1	0.5	15.7	13.6	3.3	10.6	4.90
1.1	0.5	15.7	13.5	3.2	11.2	4.98
4.7	2.0	0.0	0.0	13.9	0.0	5.36
4.7	2.0	0.0	0.0	13.8	0.0	5.36
4.7	2.1	0.8	0.5	13.1	1.6	5.24
4.7	2.1	0.8	0.5	13.3	1.6	5.25
4.8	2.2	1.6	1.1	13.0	2.9	5.19
4.8	2.2	1.6	1.1	12.8	2.8	5.20
4.8	2.4	3.9	2.9	11.7	5.1	5.09
4.8	2.4	3.9	2.9	11.8	5.2	5.10
4.8	2.5	7.9	6.3	11.0	7.7	5.01
4.8	2.6	7.9	6.3	10.8	7.6	5.02
4.8	2.8	15.7	13.8	9.8	9.7	4.91
4.8	2.8	15.7	14.0	9.8	8.9	4.92

Pb and Cu sorption of Forest soil

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cu</i> conc.	Final <i>Cu</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cu</i>	Final
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g Forest soil	mg <i>Cu</i> per g Forest soil	pH
242.1	14.8	0.0	0.0	11.4	0.0	3.20
242.1	15.2	0.0	0.0	11.3	0.0	3.20
239.7	20.4	50.8	5.9	11.0	2.2	3.13
239.7	20.7	50.8	5.8	11.0	2.3	3.13
237.9	26.0	100.0	19.1	10.6	4.0	3.08
237.9	23.7	100.0	19.1	10.7	4.0	3.07
238.0	36.8	250.0	90.1	10.1	8.0	2.96
238.0	36.2	250.0	89.4	10.1	8.0	2.96
238.0	53.0	500.0	265.0	9.3	11.8	2.86
238.0	60.0	500.0	261.0	8.9	12.0	2.87
238.0	81.0	1000.0	688.0	7.9	15.6	2.77
238.0	91.0	1000.0	680.0	7.4	16.0	2.77
982.6	205.2	0.0	0.0	38.9	0.0	2.97
982.6	207.0	0.0	0.0	38.8	0.0	2.97
982.4	234.5	51.5	13.7	37.4	1.9	2.93
982.4	232.8	51.5	13.7	37.5	1.9	2.92
987.4	257.0	104.2	35.6	36.5	3.4	2.89
987.4	259.2	104.2	36.1	36.4	3.4	2.89
985.0	328.8	250.0	124.4	32.8	6.3	2.83
985.0	326.0	250.0	125.2	33.0	6.2	2.83
985.0	382.0	500.0	308.0	30.2	9.6	2.77
985.0	382.5	500.0	310.0	30.1	9.5	2.78
985.0	489.0	1000.0	751.0	24.8	12.5	2.71
985.0	494.0	1000.0	746.0	24.6	12.7	2.72

Pb and Cu sorption of Forest soil

in molar units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cu</i> conc.	Final <i>Cu</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cu</i>	Final
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol <i>Pb</i> per kg Forest soil	cmol <i>Cu</i> per kg Forest soil	pH
1.2	0.1	0.0	0.0	5.5	0.0	3.20
1.2	0.1	0.0	0.0	5.5	0.0	3.20
1.2	0.1	0.8	0.1	5.3	3.5	3.13
1.2	0.1	0.8	0.1	5.3	3.5	3.13
1.1	0.1	1.6	0.3	5.1	6.4	3.08
1.1	0.1	1.6	0.3	5.2	6.4	3.07
1.1	0.2	3.9	1.4	4.9	12.6	2.96
1.1	0.2	3.9	1.4	4.9	12.6	2.96
1.1	0.3	7.9	4.2	4.5	18.5	2.86
1.1	0.3	7.9	4.1	4.3	18.8	2.87
1.1	0.4	15.7	10.8	3.8	24.5	2.77
1.1	0.4	15.7	10.7	3.5	25.2	2.77
4.7	1.0	0.0	0.0	18.8	0.0	2.97
4.7	1.0	0.0	0.0	18.7	0.0	2.97
4.7	1.1	0.8	0.2	18.0	3.0	2.93
4.7	1.1	0.8	0.2	18.1	3.0	2.92
4.8	1.2	1.6	0.6	17.6	5.4	2.89
4.8	1.3	1.6	0.6	17.6	5.4	2.89
4.8	1.6	3.9	2.0	15.8	9.9	2.83
4.8	1.6	3.9	2.0	15.9	9.8	2.83
4.8	1.8	7.9	4.8	14.6	15.1	2.77
4.8	1.8	7.9	4.9	14.5	14.9	2.78
4.8	2.4	15.7	11.8	12.0	19.6	2.71
4.8	2.4	15.7	11.7	11.8	20.0	2.72

Pb and Cu sorption of Spruce bark

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cu</i> conc.	Final <i>Cu</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cu</i>	Final
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g Spruce bark	mg <i>Cu</i> per g Spruce bark	pH
242.1	26.2	0.0	0.0	10.8	0.0	4.16
242.1	25.9	0.0	0.0	10.8	0.0	4.14
239.7	38.0	50.8	20.4	10.1	1.5	3.98
239.7	36.9	50.8	20.2	10.1	1.5	4.00
237.9	47.4	100.0	48.5	9.5	2.6	3.87
237.9	47.9	100.0	49.0	9.5	2.6	3.86
238.0	78.0	250.0	170.2	8.0	4.0	3.72
238.0	76.4	250.0	165.8	8.1	4.2	3.71
238.0	101.0	500.0	392.5	6.9	5.4	3.59
238.0	108.0	500.0	389.5	6.5	5.5	3.61
238.0	157.0	1000.0	873.0	4.1	6.4	3.47
238.0	141.0	1000.0	865.0	4.9	6.8	3.49
982.6	429.8	0.0	0.0	27.6	0.0	3.68
982.6	414.7	0.0	0.0	28.4	0.0	3.69
982.4	478.2	51.5	35.4	25.2	0.8	3.65
982.4	470.1	51.5	35.3	25.6	0.8	3.70
987.4	493.6	104.2	71.5	24.7	1.6	3.63
987.4	481.9	104.2	70.9	25.3	1.7	3.63
985.0	581.1	250.0	193.5	20.2	2.8	3.55
985.0	574.8	250.0	193.5	20.5	2.8	3.56
985.0	634.5	500.0	411.0	17.5	4.5	3.49
985.0	630.0	500.0	412.5	17.8	4.4	3.50
985.0	730.0	1000.0	919.0	12.8	4.1	3.41
985.0	715.0	1000.0	913.0	13.5	4.4	3.42

Pb and Cu sorption of Spruce bark

in molar units

Initial Pb conc.	Final Pb conc.	Initial Cu conc.	Final Cu conc.	Sorbed Pb	Sorbed Cu	Final
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol Pb per kg Spruce bark	cmol Cu per kg Spruce bark	pH
1.2	0.1	0.0	0.0	5.2	0.0	4.16
1.2	0.1	0.0	0.0	5.2	0.0	4.14
1.2	0.2	0.8	0.3	4.9	2.4	3.98
1.2	0.2	0.8	0.3	4.9	2.4	4.00
1.1	0.2	1.6	0.8	4.6	4.1	3.87
1.1	0.2	1.6	0.8	4.6	4.0	3.86
1.1	0.4	3.9	2.7	3.9	6.3	3.72
1.1	0.4	3.9	2.6	3.9	6.6	3.71
1.1	0.5	7.9	6.2	3.3	8.5	3.59
1.1	0.5	7.9	6.1	3.1	8.7	3.61
1.1	0.8	15.7	13.7	2.0	10.0	3.47
1.1	0.7	15.7	13.6	2.3	10.6	3.49
4.7	2.1	0.0	0.0	13.3	0.0	3.68
4.7	2.0	0.0	0.0	13.7	0.0	3.69
4.7	2.3	0.8	0.6	12.2	1.3	3.65
4.7	2.3	0.8	0.6	12.4	1.3	3.70
4.8	2.4	1.6	1.1	11.9	2.6	3.63
4.8	2.3	1.6	1.1	12.2	2.6	3.63
4.8	2.8	3.9	3.0	9.7	4.4	3.55
4.8	2.8	3.9	3.0	9.9	4.4	3.56
4.8	3.1	7.9	6.5	8.5	7.0	3.49
4.8	3.0	7.9	6.5	8.6	6.9	3.50
4.8	3.5	15.7	14.5	6.2	6.4	3.41
4.8	3.5	15.7	14.4	6.5	6.8	3.42

Pb and Cd sorption of bentonite

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g bentonite	mg <i>Cd</i> per g bentonite	pH
250.0	44.9	0.0	0.0	10.3	0.0	6.13
250.0	42.1	0.0	0.0	10.4	0.0	6.17
250.0	45.6	50.0	32.1	10.2	0.9	6.11
250.0	44.6	50.0	35.0	10.3	0.8	6.10
250.0	45.9	100.0	75.4	10.2	1.2	6.07
250.0	49.3	100.0	72.0	10.0	1.4	6.06
250.0	52.3	250.0	186.3	9.9	3.2	6.02
250.0	53.6	250.0	182.5	9.8	3.4	6.01
250.0	63.0	500.0	395.2	9.4	5.2	5.96
250.0	61.4	500.0	390.8	9.4	5.5	5.95
250.0	78.4	1000.0	806.9	8.6	9.7	5.88
250.0	79.4	1000.0	811.3	8.5	9.4	5.87
1000.0	430.7	0.0	0.3	28.5	0.0	5.45
1000.0	422.5	0.0	-1.6	28.9	0.1	5.44
1000.0	432.7	50.0	38.7	28.4	0.6	5.42
1000.0	424.6	50.0	40.9	28.8	0.5	5.42
1000.0	433.7	100.0	82.3	28.3	0.9	5.41
1000.0	439.0	100.0	83.9	28.1	0.8	5.40
1000.0	442.7	250.0	198.5	27.9	2.6	5.39
1000.0	432.0	250.0	195.9	28.4	2.7	5.39
1000.0	460.3	500.0	410.6	27.0	4.5	5.28
1000.0	465.7	500.0	415.3	26.7	4.2	5.35
1000.0	496.7	1000.0	840.3	25.2	8.0	5.35
1000.0	499.4	1000.0	846.6	25.0	7.7	5.35

Pb and Cd sorption of bentonite

in molar units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol <i>Pb</i> per kg bentonite	cmol <i>Cd</i> per kg bentonite	pH
1.2	0.2	0.0	0.0	5.0	0.0	6.13
1.2	0.2	0.0	0.0	5.0	0.0	6.17
1.2	0.2	0.4	0.3	4.9	0.8	6.11
1.2	0.2	0.4	0.3	5.0	0.7	6.10
1.2	0.2	0.9	0.7	4.9	1.1	6.07
1.2	0.2	0.9	0.6	4.8	1.2	6.06
1.2	0.3	2.2	1.7	4.8	2.8	6.02
1.2	0.3	2.2	1.6	4.7	3.0	6.01
1.2	0.3	4.4	3.5	4.5	4.7	5.96
1.2	0.3	4.4	3.5	4.6	4.9	5.95
1.2	0.4	8.9	7.2	4.1	8.6	5.88
1.2	0.4	8.9	7.2	4.1	8.4	5.87
4.8	2.1	0.0	0.0	13.7	0.0	5.45
4.8	2.0	0.0	0.0	13.9	0.1	5.44
4.8	2.1	0.4	0.3	13.7	0.5	5.42
4.8	2.0	0.4	0.4	13.9	0.4	5.42
4.8	2.1	0.9	0.7	13.7	0.8	5.41
4.8	2.1	0.9	0.7	13.5	0.7	5.40
4.8	2.1	2.2	1.8	13.4	2.3	5.39
4.8	2.1	2.2	1.7	13.7	2.4	5.39
4.8	2.2	4.4	3.7	13.0	4.0	5.28
4.8	2.2	4.4	3.7	12.9	3.8	5.35
4.8	2.4	8.9	7.5	12.1	7.1	5.35
4.8	2.4	8.9	7.5	12.1	6.8	5.35

Pb and Cd sorption of Forest soil

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g Forest soil	mg <i>Cd</i> per g Forest soil	pH
250.0	12.1	0.0	0.0	11.9	0.0	3.07
250.0	11.8	0.0	0.0	11.9	0.0	3.08
250.0	13.8	50.0	30.0	11.8	1.0	3.07
250.0	14.2	50.0	27.5	11.8	1.1	3.07
250.0	15.3	100.0	60.8	11.7	2.0	3.05
250.0	14.8	100.0	62.7	11.8	1.9	3.06
250.0	17.9	250.0	161.7	11.6	4.4	3.02
250.0	17.7	250.0	164.6	11.6	4.3	3.03
250.0	21.6	500.0	348.4	11.4	7.6	2.98
250.0	20.7	500.0	347.5	11.5	7.6	2.98
250.0	28.7	1000.0	757.5	11.1	12.1	2.91
250.0	28.2	1000.0	748.6	11.1	12.6	2.93
1000.0	208.6	0.0	-2.4	39.6	0.1	2.78
1000.0	204.8	0.0	-0.3	39.8	0.0	2.81
1000.0	213.0	50.0	38.6	39.4	0.6	2.81
1000.0	216.7	50.0	40.6	39.2	0.5	2.81
1000.0	219.4	100.0	83.8	39.0	0.8	2.81
1000.0	227.8	100.0	83.7	38.6	0.8	2.81
1000.0	230.3	250.0	203.7	38.5	2.3	2.79
1000.0	228.4	250.0	198.5	38.6	2.6	2.8
1000.0	248.3	500.0	419.5	37.6	4.0	2.77
1000.0	249.3	500.0	418.6	37.5	4.1	2.78
1000.0	280.6	1000.0	844.3	36.0	7.8	2.74
1000.0	284.1	1000.0	853.6	35.8	7.3	2.75

Pb and Cd sorption of Forest soil

in molar units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol <i>Pb</i> per kg Forest soil	cmol <i>Cd</i> per kg Forest soil	pH
1.2	0.1	0.0	0.0	5.7	0.0	3.07
1.2	0.1	0.0	0.0	5.7	0.0	3.08
1.2	0.1	0.4	0.3	5.7	0.9	3.07
1.2	0.1	0.4	0.2	5.7	1.0	3.07
1.2	0.1	0.9	0.5	5.7	1.7	3.05
1.2	0.1	0.9	0.6	5.7	1.7	3.06
1.2	0.1	2.2	1.4	5.6	3.9	3.02
1.2	0.1	2.2	1.5	5.6	3.8	3.03
1.2	0.1	4.4	3.1	5.5	6.7	2.98
1.2	0.1	4.4	3.1	5.5	6.8	2.98
1.2	0.1	8.9	6.7	5.3	10.8	2.91
1.2	0.1	8.9	6.7	5.4	11.2	2.93
4.8	1.0	0.0	0.0	19.1	0.1	2.78
4.8	1.0	0.0	0.0	19.2	0.0	2.81
4.8	1.0	0.4	0.3	19.0	0.5	2.81
4.8	1.0	0.4	0.4	18.9	0.4	2.81
4.8	1.1	0.9	0.7	18.8	0.7	2.81
4.8	1.1	0.9	0.7	18.6	0.7	2.81
4.8	1.1	2.2	1.8	18.6	2.1	2.79
4.8	1.1	2.2	1.8	18.6	2.3	2.80
4.8	1.2	4.4	3.7	18.1	3.6	2.77
4.8	1.2	4.4	3.7	18.1	3.6	2.78
4.8	1.4	8.9	7.5	17.4	6.9	2.74
4.8	1.4	8.9	7.6	17.3	6.5	2.75

Pb and Cd sorption of Spruce bark

in mass units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg <i>Pb</i> per g Spruce bark	mg <i>Cd</i> per g Spruce bark	pH
250.0	23.3	0.0	0.0	11.3	0.0	3.95
250.0	23.9	0.0	0.0	11.3	0.0	3.94
250.0	25.6	50.0	38.2	11.2	0.6	3.96
250.0	26.2	50.0	35.2	11.2	0.7	4.01
250.0	27.8	100.0	78.0	11.1	1.1	3.90
250.0	27.5	100.0	78.4	11.1	1.1	3.95
250.0	31.4	250.0	202.6	10.9	2.4	3.84
250.0	31.7	250.0	200.1	10.9	2.5	3.85
250.0	38.1	500.0	422.9	10.6	3.9	3.86
250.0	37.4	500.0	423.5	10.6	3.8	3.79
250.0	46.5	1000.0	868.0	10.2	6.6	3.71
250.0	47.1	1000.0	879.5	10.1	6.0	3.73
1000.0	444.6	0.0	-1.9	27.8	0.1	3.53
1000.0	437.6	0.0	-0.1	28.1	0.0	3.51
1000.0	430.0	50.0	43.7	28.5	0.3	3.53
1000.0	432.4	50.0	47.3	28.4	0.1	3.54
1000.0	444.7	100.0	97.7	27.8	0.1	3.53
1000.0	448.3	100.0	96.5	27.6	0.2	3.53
1000.0	453.8	250.0	233.2	27.3	0.8	3.52
1000.0	451.5	250.0	235.0	27.4	0.8	3.52
1000.0	474.1	500.0	478.4	26.3	1.1	3.50
1000.0	488.4	500.0	478.6	25.6	1.1	3.50
1000.0	507.4	1000.0	962.7	24.6	1.9	3.48
1000.0	513.8	1000.0	962.8	24.3	1.9	3.49

Pb and Cd sorption of Spruce bark

in molar units

Initial <i>Pb</i> conc.	Final <i>Pb</i> conc.	Initial <i>Cd</i> conc.	Final <i>Cd</i> conc.	Sorbed <i>Pb</i>	Sorbed <i>Cd</i>	Final
mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	cmol <i>Pb</i> per kg Spruce bark	cmol <i>Cd</i> per kg Spruce bark	pH
1.2	0.1	0.0	0.0	5.5	0.0	3.95
1.2	0.1	0.0	0.0	5.5	0.0	3.94
1.2	0.1	0.4	0.3	5.4	0.5	3.96
1.2	0.1	0.4	0.3	5.4	0.7	4.01
1.2	0.1	0.9	0.7	5.4	1.0	3.90
1.2	0.1	0.9	0.7	5.4	1.0	3.95
1.2	0.2	2.2	1.8	5.3	2.1	3.84
1.2	0.2	2.2	1.8	5.3	2.2	3.85
1.2	0.2	4.4	3.8	5.1	3.4	3.86
1.2	0.2	4.4	3.8	5.1	3.4	3.79
1.2	0.2	8.9	7.7	4.9	5.9	3.71
1.2	0.2	8.9	7.8	4.9	5.4	3.73
4.8	2.1	0.0	0.0	13.4	0.1	3.53
4.8	2.1	0.0	0.0	13.6	0.0	3.51
4.8	2.1	0.4	0.4	13.8	0.3	3.53
4.8	2.1	0.4	0.4	13.7	0.1	3.54
4.8	2.1	0.9	0.9	13.4	0.1	3.53
4.8	2.2	0.9	0.9	13.3	0.2	3.53
4.8	2.2	2.2	2.1	13.2	0.7	3.52
4.8	2.2	2.2	2.1	13.2	0.7	3.52
4.8	2.3	4.4	4.3	12.7	1.0	3.50
4.8	2.4	4.4	4.3	12.3	1.0	3.50
4.8	2.4	8.9	8.6	11.9	1.7	3.48
4.8	2.5	8.9	8.6	11.7	1.7	3.49

APPENDIX D.4. BATCH ADSORPTION DATA FOR TERNARY HEAVY METAL LEACHATES

Pb, Cu, and Cd sorption of bentonite

in mass units

Initial Pb conc. mg/L	Initial Cu conc. mg/L	Initial Cd conc. mg/L	Final Pb conc. mg/L	Final Cu conc. mg/L	Final Cd conc. mg/L	Sorbed mg Pb / g bentonite	Sorbed mg Cu / g bentonite	Sorbed mg Cd / g bentonite	Final pH
201.6	199.6	192.0	58.6	130.1	157.3	7.2	3.5	1.7	5.21
802.3	202.2	193.8	340.4	143.2	164.0	23.1	2.9	1.5	5.08
199.0	779.5	190.7	84.0	632.5	165.3	5.8	7.4	1.3	4.94
802.3	779.4	190.0	412.8	641.0	171.2	19.5	6.9	0.9	4.87
197.2	200.9	771.8	79.2	140.0	631.9	5.9	3.0	5.6	5.25
802.3	198.8	757.8	366.5	148.9	642.4	21.8	2.5	5.2	5.10
195.0	774.1	734.3	99.4	653.0	655.7	4.8	6.1	3.9	4.92
802.3	773.3	753.5	430.9	669.0	666.0	18.6	5.2	3.8	4.86
-0.6	494.2	466.2	0.3	369.8	400.1	0.0	6.2	3.3	5.15
949.2	488.6	464.1	533.9	392.0	408.1	20.8	4.8	2.8	4.92
484.5	0.6	473.0	123.1	0.0	372.3	18.1	0.0	5.0	5.65
480.2	983.1	461.3	216.3	847.5	411.5	13.2	6.8	2.5	4.85
477.1	489.2	-2.9	173.1	378.5	2.8	15.2	5.5	-0.3	4.92
480.4	491.8	936.3	201.4	403.8	827.7	14.0	4.4	5.4	4.92
487.2	498.1	474.5	194.1	394.5	399.2	14.7	5.2	3.8	4.94
487.2	498.1	474.5	197.5	396.0	397.3	14.5	5.1	3.9	4.94
194.4	480.3	194.8	70.9	375.8	164.5	6.2	5.2	1.5	5.00
194.3	201.2	470.1	65.6	135.8	378.1	6.4	3.3	4.6	5.22

Pb, Cu, and Cd sorption of bentonite

in molar units

Initial Pb conc. mmol/L	Initial Cu conc. mmol/L	Initial Cd conc. mmol/L	Final Pb conc. mmol/L	Final Cu conc. mmol/L	Final Cd conc. mmol/L	Sorbed Pb / kg bentonite	Sorbed Cu / kg bentonite	Sorbed Cd / kg bentonite
0.97	3.14	1.71	0.28	2.05	1.40	3.45	5.47	1.55
3.87	3.18	1.72	1.64	2.25	1.46	11.15	4.64	1.33
0.96	12.27	1.70	0.41	9.95	1.47	2.78	11.57	1.13
3.87	12.26	1.69	1.99	10.09	1.52	9.40	10.89	0.84
0.95	3.16	6.87	0.38	2.20	5.62	2.85	4.79	4.98
3.87	3.13	6.74	1.77	2.34	5.71	10.52	3.92	4.65
0.94	12.18	6.53	0.48	10.28	5.83	2.31	9.53	3.50
3.87	12.17	6.70	2.08	10.53	5.92	8.96	8.21	3.34
0.00	7.78	4.15	0.00	5.82	3.56	0.00	9.79	2.94
4.58	7.69	4.13	2.58	6.17	3.63	10.02	7.60	2.49
2.34	0.01	4.21	0.59	0.00	3.31	8.72	0.05	4.48
2.32	15.47	4.10	1.04	13.34	3.66	6.37	10.67	2.22
2.30	7.70	-0.03	0.84	5.96	0.00	7.34	8.71	0.00
2.32	7.74	8.33	0.97	6.35	7.36	6.73	6.92	4.83
2.35	7.84	4.22	0.94	6.21	3.55	7.07	8.15	3.35
2.35	7.84	4.22	0.95	6.23	3.53	6.99	8.04	3.43
0.94	7.56	1.73	0.34	5.91	1.46	2.98	8.23	1.35
0.94	3.17	4.18	0.32	2.14	3.36	3.11	5.15	4.09

Pb, Cu, and Cd sorption of Spruce bark

in mass units

Initial Pb conc. mg/L	Initial Cu conc. mg/L	Initial Cd conc. mg/L	Final Pb conc. mg/L	Final Cu conc. mg/L	Final Cd conc. mg/L	Sorbed mg Pb / g Spruce bark	Sorbed mg Cu / g Spruce bark	Sorbed mg Cd / g Spruce bark	Final pH
201.6	199.6	192.0	46.9	115.2	168.5	7.7	4.2	1.2	3.56
802.3	202.2	193.8	378.0	148.8	182.2	21.2	2.7	0.6	3.38
199.0	779.5	190.7	97.8	645.5	181.8	5.1	6.7	0.4	3.31
802.3	779.4	190.0	497.3	662.5	182.7	15.2	5.8	0.4	3.27
197.2	200.9	771.8	58.1	128.1	756.5	7.0	3.6	0.8	3.50
802.3	198.8	757.8	400.5	148.5	700.9	20.1	2.5	2.8	3.39
195.0	774.1	734.3	97.1	668.5	722.3	4.9	5.3	0.6	3.31
802.3	773.3	753.5	508.6	688.5	750.6	14.7	4.2	0.1	3.27
-0.6	494.2	466.2	-0.2	349.3	457.0	0.0	7.2	0.5	3.47
949.2	488.6	464.1	594.5	406.0	467.6	17.7	4.1	-0.2	3.32
484.5	0.6	473.0	128.9	0.3	433.7	17.8	0.0	2.0	3.63
480.2	983.1	461.3	310.8	865.0	476.8	8.5	5.9	-0.8	3.24
477.1	489.2	-2.9	254.7	387.5	2.5	11.1	5.1	0.0	3.40
480.4	491.8	936.3	262.8	395.0	887.0	10.9	4.8	2.5	3.35
487.2	498.1	474.5	253.7	398.0	464.6	11.7	5.0	0.5	3.34
487.2	498.1	474.5	255.0	392.8	463.6	11.6	5.3	0.5	3.36
194.4	480.3	194.8	76.9	368.0	182.2	5.9	5.6	0.6	3.44
194.3	201.2	470.1	51.9	122.6	435.1	7.1	3.9	1.8	3.55

Pb, Cu, and Cd sorption of Spruce bark

in molar units

Initial Pb conc. mmol/L	Initial Cu conc. mmol/L	Initial Cd conc. mmol/L	Final Pb conc. mmol/L	Final Cu conc. mmol/L	Final Cd conc. mmol/L	Sorbed		Sorbed	
						Spruce bark	cmol Pb / kg Spruce bark	cmol Cu / kg Spruce bark	cmol Cd / kg Spruce bark
0.97	3.14	1.71	0.23	1.81	1.50	3.73	6.64	1.05	
3.87	3.18	1.72	1.82	2.34	1.62	10.24	4.20	0.52	
0.96	12.27	1.70	0.47	10.16	1.62	2.44	10.55	0.39	
3.87	12.26	1.69	2.40	10.42	1.63	7.36	9.20	0.33	
0.95	3.16	6.87	0.28	2.02	6.73	3.36	5.73	0.68	
3.87	3.13	6.74	1.93	2.34	6.24	9.70	3.95	2.53	
0.94	12.18	6.53	0.47	10.52	6.43	2.36	8.31	0.53	
3.87	12.17	6.70	2.45	10.83	6.68	7.09	6.67	0.13	
0.00	7.78	4.15	0.00	5.50	4.07	-0.01	11.40	0.41	
4.58	7.69	4.13	2.87	6.39	4.16	8.56	6.50	-0.16	
2.34	0.01	4.21	0.62	0.00	3.86	8.58	0.03	1.75	
2.32	15.47	4.10	1.50	13.61	4.24	4.09	9.29	-0.69	
2.30	7.70	-0.03	1.23	6.10	0.02	5.37	8.00	0.00	
2.32	7.74	8.33	1.27	6.22	7.89	5.25	7.61	2.19	
2.35	7.84	4.22	1.22	6.26	4.13	5.63	7.88	0.44	
2.35	7.84	4.22	1.23	6.18	4.12	5.60	8.29	0.49	
0.94	7.56	1.73	0.37	5.79	1.62	2.84	8.84	0.56	
0.94	3.17	4.18	0.25	1.93	3.87	3.44	6.19	1.56	

APPENDIX E LEACHING TEST CALCULATIONS AND DATA

- E.1. AVERAGING THE HYDRAULIC CONDUCTIVITY, HEAVY METAL BREAKTHROUGH, AND DISCHARGE pH DATA**
- E.2. CALCULATIONS FOR THE HEAVY METAL RETENTION OF A LEACHING CELL SAMPLE BASED ON BREAKTHROUGH CURVES**
- E.3. HYDRAULIC CONDUCTIVITY, HEAVY METAL BREAKTHROUGH, AND DISCHARGE pH DATA**

APPENDIX E.1. AVERAGING THE HYDRAULIC CONDUCTIVITY, HEAVY METAL BREAKTHROUGH, AND DISCHARGE pH DATA

Method

Figure E.1.1 shows the hydraulic conductivity data for the permeation of *Pb* leachate through the bentonite admix. The hydraulic conductivities of each sample in the triplicate experienced erratic increases and decreases, but all three followed the same trend: they started at low values; increased over an order of magnitude between 175 ml and 400 ml of discharge (1 - 2.5 pore volumes); and then showed little change after 400 ml of discharge (≈ 2.5 pore volumes). The hydraulic conductivity data in Figure E.1.1 represents the typical difficulties in averaging the triplicate data.

FIGURE E.1.1. Hydraulic conductivity results for permeating *Pb* leachate through bentonite admix samples

In order to combine the triplicate data, the hydraulic conductivity curve was split into two parts. The initial portion of the curve was near horizontal, so a simple mean was calculated for that group of data. The rest of the curve beyond the initial portion resembled a log curve; thus, a best-fit log curve was iterated from that group of data. The curve-fitting was done by the "trendline" feature in EXCEL 5.0 (Microsoft). Figure E.1.1 shows the averaged curve plotted with the triplicate data. The method used to combine the triplicate data in Figure E.1.1 was applied to all the hydraulic conductivity and heavy metal breakthrough curves. As for the discharge pH curves, the initial portions were left in raw form. Beyond the initial portions, straight lines were used to fit the rest of the data. Table E.1.1 summarizes the best-fit parameters used for averaging the hydraulic conductivity, heavy metal breakthrough, and discharge pH data.

TABLE E.1.1. Best-fit parameters for average curves of hydraulic conductivity, heavy metal breakthrough, and discharge pH.

		Hydraulic Conductivity				Heavy metal breakthrough					pH		
Admix	Leachate type	Initial Hyd. Conductivity (m/s)	Start of log portion (ml)	m _k	b _k	HM* type	Initial HM conc. (mg/L)	Start of log portion (ml)	m _c	b _c	Start of line (ml)	m _{pH}	b _{pH}
Bentonite admix	Pb	7.16E-11	200	2.6212	-13.892	Pb	0.4	200	226.29	-1186.2	200	-0.0003	6.2644
	Cu	5.03E-11	50	1.4092	-5.1606	Cu	0.0	50	81.309	-147.07	200	-0.0004	5.7016
	Pb+Cu	3.51E-10	100	1.6322	-7.256	Pb	0.0	100	134.72	-612.41	1000	-0.0001	5.4139
						Cu	0.6	100	113.51	-406.36			
	Pb+Cu+Cd	3.07E-10	100	0.9542	-4.3307	Pb	1.5	150	166.31	-831.54	700	-0.0002	5.297
						Cu	1.5	50	121.04	-408.95			
						Cd	10.5	50	107.91	-304.68			
Forest soil admix	Pb	2.96E-09	300	2.8837	-15.406	Pb	11.7	300	202.48	-1114.7	400	-0.0011	6.242
	Cu	7.97E-10	200	0.8047	-3.878	Cu	227.2	200	149.69	-622.05	400	-5.00E-05	4.4523
	Pb+Cu	4.91E-10	300	2.4621	-14.136	Pb	17.4	300	193.53	-1103.6	400	-0.0002	4.328
						Cu	104.3	100	156	-632.48			
Spruce bark admix	Pb	8.89E-11	200	0.1733	-0.5922	Pb	6.9	200	100.49	-328.57	500	2.00E-05	5.9047
	Cu	8.43E-11	150	1.1623	-5.5045	Cu	3.4	150	59.382	-11.168	400	-0.0002	5.6896
	Pb+Cu	1.57E-10	50	0.9884	-3.6373	Pb	1.3	50	103.24	-314.68	200	-0.0003	5.4016
						Cu	2.1	50	55.637	111.27			

* HM - heavy metal

Calculations

The best-fit equation used to calculate the log-shaped portion of the hydraulic conductivity curves is,

$$k = [m_k \cdot \ln(D_v) + b_k] \cdot 0.000000001$$

where k (m/s) is hydraulic conductivity, m_k and b_k are best-fit parameters, D_v (ml) is the discharge volume, and 0.000000001 is a scaling factor.

The best-fit equation used to calculate the log-shaped portion of the heavy metal breakthrough curves is,

$$C = m_c \cdot \ln(D_v) + b_c$$

where C (mg/L) is the heavy metal breakthrough concentration, and m_c and b_c are best-fit parameters.

The best-fit equation used to calculate the straight-line portion of the discharge pH curves is,

$$\text{pH} = m_{\text{pH}} \cdot D_v + b_{\text{pH}}$$

where m_{pH} and b_{pH} are best-fit parameters.

APPENDIX E.2. CALCULATIONS FOR THE HEAVY METAL RETENTION OF A LEACHING CELL SAMPLE BASED ON BREAKTHROUGH CURVES

Figure E.2.1 shows a labeled diagram of a typical heavy metal breakthrough curve.

FIGURE E.2.1. Diagram of heavy metal breakthrough curve.

The amount, Q (mg), of heavy metal retained by the Leaching cell sample represented by Figure E.2.1, is calculated from the following equation:

$$Q_b = Q_T - Q_a - Q_{ab}$$

where Q_b (mg) is the amount of heavy metal retained after D_b of discharge, Q_T (mg) is the total input of heavy metal after D_b of discharge, Q_a (mg) is the amount of heavy metal discharged after D_a of discharge, and Q_{ab} (mg) is the amount of heavy metal discharged between D_a and D_b of discharge.

The equation for calculating Q_T (mg) is,

$$Q_T = \frac{500 \cdot (D_b - 175)}{1000}$$

where 500 (mg/L) is heavy metal concentration of the leachate, 175 (ml) is one pore volume of the Leaching cell sample, and 1000 is a scaling factor.

The equation for calculating Q_a (mg) is,

$$Q_a = \frac{C_a \cdot D_a}{1000}$$

where C_a (mg/L) is the breakthrough concentration of the initial portion, and D_a (ml) is the discharge volume in which the log-shaped portion begins.

The equation for calculating Q_{ab} (mg) is,

$$Q_{ab} = \frac{[m_c \cdot D_b \cdot \ln(D_b) - m_c \cdot D_b + b_c \cdot D_b] - [m_c \cdot D_a \cdot \ln(D_a) - m_c \cdot D_a + b_c \cdot D_a]}{1000}$$

where m_c and b_c (see Table E.1.1) are best-fit parameters for the log-shaped portion.

APPENDIX E.3. HYDRAULIC CONDUCTIVITY, HEAVY METAL BREAKTHROUGH, AND DISCHARGE pH DATA

Blank (0.01 M calcium nitrate ($\text{Ca}(\text{NO}_3)_2$)) leachates

Bentonite admix permeated with blank (0.01 M ($\text{Ca}(\text{NO}_3)_2$) leachate

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Discharge pH
	ml	hr	m/s	
Test 1	2.2	125	2.12E-11	
	11.2	231	3.12E-11	8.49
	19.6	314	9.11E-12	
	26.1	409	2.54E-11	
	32.1	527	4.13E-12	
	34.4	578	1.18E-11	8.51
	44.9	653	5.99E-11	8.52
	66.7	805	3.99E-11	8.50
	86.5	961	2.29E-11	8.53
	95.4	1038	9.25E-12	
	97.4	1061	1.30E-11	
	101.7	1104	4.14E-11	
Test 2	5.4	76	3.06E-11	8.31
	11.3	125	3.85E-11	
	20.3	231	2.54E-11	
	27.8	314	1.03E-11	
	31.5	409	1.13E-11	8.51
	38.6	526	3.80E-11	8.53
	53.3	578	2.79E-11	8.51
	67.7	653	1.74E-11	8.56
	74.6	805	8.29E-12	
	76.5	961	1.18E-11	
	80.3	1038	3.64E-11	

Forest soil admix permeated with blank (0.01 M (Ca(NO₃)₂) leachate

Triplicate #	Cumulative discharge	Time	Hydraulic conductivity	Discharge pH
	volume			
	ml	hr	m/s	
Test 1	3.5	188	8.79E-11	
	9.2	264	3.08E-11	
	11.4	338		
	15.4	422	4.28E-11	8.24
	21.7	505	2.46E-11	
	26.2	583	2.22E-11	8.33
	30.0	649	2.59E-11	8.42
	32.9	695	2.59E-11	8.42
	36.4	764	1.98E-11	8.43
	39.8	832	3.47E-11	

Spruce bark admix permeated with (0.01 M (Ca(NO₃)₂) leachate

Triplicate #	Cumulative discharge	Time	Hydraulic	Discharge
	volume		conductivity	
	ml	hr	m/s	pH
Test 1	5.6	281	2.21E-11	
	11.8	369	1.46E-11	8.51
	17.1	469	1.28E-11	
	22.1	593	2.54E-11	8.60
	26.5	643	1.93E-11	
	31.6	748	1.45E-11	8.58
	35.7	831	5.24E-12	
	39.0	926	1.26E-11	
	45.6	1044	1.72E-11	
	50.0	1095	2.33E-12	8.48
	53.2	1170	1.92E-11	
	60.5	1323	1.38E-11	8.41
	67.4	1479	8.07E-12	8.59
	70.6	1556	3.71E-12	
	71.4	1578	5.28E-12	
	73.4	1622	1.87E-11	
Test 2	1.5	135	1.51E-11	
	6.1	207	2.06E-11	
	12.8	281	2.37E-11	
	19.6	369	1.69E-11	8.56
	25.6	469	1.41E-11	
	31.4	593	3.12E-11	8.65
	36.6	643	2.21E-11	
	43.0	748	1.91E-11	8.57
	48.4	831	6.66E-12	
	52.7	926	1.60E-11	8.65
	57.9	1044	8.63E-12	
	60.3	1095	3.16E-12	8.44
	64.3	1170	2.36E-11	
	73.4	1323	1.74E-11	8.38
	82.2	1479	1.04E-11	8.68
	86.2	1556	4.58E-12	
	87.3	1578	7.40E-12	
	89.7	1622	2.26E-11	

Single heavy metal leachates - lead (Pb) & copper (Cu)*Bentonite admix permeated with 500 mg/L of Pb leachate*

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Pb conc.	Discharge pH
	ml	hr	m/s	mg/L	
Test 1	2.0	16	3.57E-11		
	5.4	42	6.68E-11	0.1	8.20
	9.9	93	5.00E-11	0.0	8.45
	16.0	139	4.98E-11	0.0	
	21.8	186	4.88E-11	0.0	8.55
	32.1	308	4.84E-11	0.0	8.61
	49.8	476	4.66E-11	0.0	8.70
	66.9	626	4.56E-11	0.0	
	79.8	757	4.34E-11	0.0	8.72
	95.3	968	4.32E-11	0.0	8.60
	118.1	1083	7.47E-11	0.0	8.60
	148.8	1202	1.83E-10	0.0	8.50
	179.8	1285	1.60E-10	0.0	8.11
	206.3	1363	1.48E-10	0.0	8.56
	225.8	1436	1.10E-10	0.0	8.54
	242.6	1492	2.77E-10	0.0	8.48
	446.3	1544	1.76E-09	185.0	6.18
	746.2	1601	6.82E-09	315.3	5.89
	874.7	1610	3.91E-09	337.5	5.94
	916.5	1615	4.19E-09	346.1	6.06
Test 2	959.7	1619	4.32E-09	362.1	6.02
	1021.2	1625	4.39E-09	372.3	6.01
	1092.7	1633	4.20E-09	372.3	5.98
	1163.0	1640	4.55E-09	384.3	5.91
	2.5	34	4.47E-11		
	6.2	60	5.49E-11	0.0	8.18
	10.2	111	4.67E-11	0.0	8.39
	15.9	156	4.65E-11	0.3	
	21.4	203	4.79E-11	0.4	8.53
	31.6	308	4.81E-11		8.61
	49.0	476	4.52E-11	0.0	8.61
	65.4	626	4.27E-11	0.0	
	77.9	757	4.34E-11	0.0	8.72
	93.4	968	3.53E-11	0.0	8.64
	112.4	1083	5.35E-11	0.0	8.76
	129.7	1202	8.11E-11	0.0	8.72
	141.0	1298	6.30E-11	0.0	8.65
	150.0	1363	6.26E-11	0.0	8.86
	159.1	1436	6.03E-11	0.0	8.84
	167.3	1492	1.27E-10	0.0	8.79
	266.2	1544	8.57E-10	30.9	6.90

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Pb conc.	Discharge pH
	ml	hr	m/s	mg/L	
Test 2					
continued	420.7	1601	3.87E-09	146.0	6.16
	493.6	1610	2.22E-09	218.9	6.16
	517.1	1615	2.33E-09	223.0	6.13
	541.6	1619	2.48E-09	226.8	6.13
	578.1	1625	2.66E-09	256.6	6.10
	621.9	1633	2.60E-09	269.8	6.07
	666.6	1640	2.97E-09	286.4	5.98
Test 3	12.0	9	5.39E-11	0.0	8.09
	14.5	34	4.00E-11		
	17.7	59	7.88E-11	0.0	8.29
	23.2	79	1.36E-10	0.0	8.37
	29.3	110	6.58E-11	0.0	8.40
	36.6	155	8.46E-11	0.1	8.50
	45.5	203	6.74E-11	0.7	8.46
	64.3	326	9.58E-11		
	98.2	476	8.67E-11	0.0	8.61
	167.2	693	2.07E-10	12.0	
	233.7	774	3.30E-10	70.7	6.32
	335.2	846	6.13E-10	253.7	6.11
	497.9	930	1.95E-09	295.4	6.08
	680.7	968	2.54E-09	330.1	6.02
	860.2	998	3.08E-09	357.6	5.90
	1198.0	1044	3.52E-09		6.01

Bentonite admix permeated with 500 mg/L of Cu leachate

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Cu conc.	Discharge pH
	ml	hr	m/s	mg/L	
Test 1	5.2	87	4.63E-11	0.0	8.49
	13.6	194	5.43E-11		
	51.2	214	1.44E-09	181.9	6.07
	93.8	223	2.58E-09	246.6	5.54
	212.9	261	2.11E-09	290.2	5.60
	308.7	288	1.48E-09	288.7	5.58
	354.9	302	2.63E-09	303.4	5.61
	412.2	314	2.91E-09	337.7	5.54
	471.4	326	2.68E-09	340.9	5.53
	539.2	338	3.17E-09	364.7	5.46
	591.2	347	2.96E-09	366.7	5.45
	653.8	358	3.12E-09	387.3	5.43
	723.5	370	3.33E-09	383.0	5.42
	757.5	376	3.58E-09	392.5	5.40
	816.5	385	3.78E-09	395.2	5.37
	871.0	393	3.93E-09	396.0	5.36
	1006.5	407	5.51E-09	432.9	5.30
	1179.3	424	6.74E-09	448.0	5.24
	1260.1	430	7.68E-09	448.0	5.21
	1735.6	482	7.41E-09		

Forest soil admix permeated with 500 mg/L of Pb leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Discharge pH
Test 1	1.5	3	2.03E-09	0.0	
	5.5	6	2.92E-09	0.0	7.04
	13.5	10	1.82E-09	0.0	7.13
	25.5	15	2.26E-09	0.2	6.31
	42.5	20	2.18E-09	0.2	6.31
	68.0	29	1.21E-09	3.8	6.29
	95.0	40	1.79E-09	15.5	6.06
	114.5	47	1.28E-09	14.0	6.69
	134.5	56	1.16E-09	26.8	6.48
	156.5	67	9.77E-10	31.2	6.48
	176.5	79	8.76E-10	15.4	6.70
	202.5	98	6.85E-10	13.5	7.16
	228.5	120	5.95E-10	11.6	7.13
	245.5	137	5.53E-10	8.7	7.33
	262.0	153	6.09E-10	9.5	7.37
	284.0	173	5.98E-10	15.4	7.26
	304.5	191	7.54E-10	21.2	7.08
	324.3	204	9.04E-10	41.4	6.50
	358.3	222	1.16E-09	79.6	6.32
	391.0	237	1.28E-09	94.9	6.43
	430.3	249	1.97E-09	149.9	6.34
	515.5	264	4.50E-09	248.4	5.79
	618.8	277	4.16E-09	270.2	5.45
	694.3	287	4.41E-09	281.5	5.38
	783.8	296	6.30E-09	306.0	5.65
	905.5	306	7.10E-09	345.6	4.85
	1023.5	318	6.93E-09	349.2	
Test 2	5.0	0	3.42E-08		
	16.5	3	8.80E-09		
	39.0	6	1.87E-08	3.4	6.13
	69.5	10	4.81E-09	17.3	5.95
	91.5	15	2.61E-09	17.3	
	106.5	20	1.56E-09	17.3	6.14
	126.8	29	1.03E-09	12.4	6.03
	147.5	40	1.20E-09	14.7	6.05
	164.0	47	1.46E-09	18.4	6.60
	187.5	56	1.39E-09	42.2	6.32
	215.5	67	1.34E-09	39.3	6.35
	246.5	79	1.50E-09	49.8	6.26
	298.3	98	1.49E-09	67.0	6.41
	359.5	120	1.56E-09	94.1	6.31
	411.8	137	2.10E-09	121.7	6.19
	466.5	153	1.83E-09	142.5	6.13
	536.0	173	1.97E-09	153.6	5.49
	600.5	191	2.22E-09	159.4	5.54

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Discharge pH
Test 2					
continued	660.5	204	2.81E-09	180.9	5.35
	753.0	222	2.92E-09	206.2	5.45
	833.8	237	2.97E-09	217.2	5.56
	903.3	249	3.12E-09	229.0	5.35
	1003.0	264	4.30E-09	266.4	5.21
	1123.0	277	5.86E-09	301.8	4.94
	1223.3	287	5.27E-09	313.6	4.87
	1304.5	296	4.88E-09	322.5	4.87
	1390.5	306	4.52E-09	320.3	4.70
	1468.0	318	4.70E-09	325.3	
	1536.0	326	4.69E-09	320.1	
	1608.5	335	4.77E-09	326.3	
Test 3					
	1.0	0	6.77E-09		
	3.5	3	2.01E-09		
	9.0	6	4.63E-09	0.1	6.95
	17.0	10	1.31E-09	0.2	7.18
	25.0	15	1.38E-09	0.2	
	37.5	20	1.75E-09	0.2	6.63
	66.8	29	1.66E-09	0.2	6.29
	100.0	40	1.85E-09	0.3	6.24
	122.0	47	1.61E-09	0.0	7.00
	143.0	56	1.05E-09	0.0	7.00
	166.0	67	1.17E-09	0.0	6.96
	184.5	79	5.79E-10	0.0	7.18
	209.0	98	7.67E-10	0.0	7.54
	246.8	120	1.14E-09	0.3	7.33
	277.8	137	9.06E-10	0.2	7.51
	302.5	153	8.44E-10	2.2	7.36
	328.0	173	5.68E-10	3.6	7.28
	347.0	191	6.59E-10	4.1	7.17
	370.5	204	1.28E-09	25.0	6.46
	431.8	222	2.28E-09	111.2	6.19
	496.5	237	2.47E-09	133.1	6.50
	553.0	249	2.47E-09	151.0	6.25
	655.0	264	5.18E-09	205.4	5.74
	776.0	277	4.89E-09	260.6	5.35
	861.5	287	4.56E-09	280.3	5.21
	934.0	296	4.38E-09	287.1	5.25
	1015.3	306	4.45E-09	304.6	4.98
	1089.3	318	4.27E-09	298.5	
	1151.0	326	4.17E-09	306.0	
	1215.0	335	4.13E-09	312.1	

Forest soil admix permeated with 500 mg/L of Cu leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Discharge pH
Test 1	4.5	32	3.24E-10	0.9	4.41
	24.5	39	1.10E-09	123.0	4.55
	68.5	46	2.25E-09	315.2	4.41
	125.0	58	1.22E-09	293.0	4.44
	172.0	70	8.79E-10	250.8	4.59
	242.0	88	1.47E-09	266.1	4.63
	325.0	111	7.29E-10	282.5	4.48
	387.0	129	8.97E-10	267.4	4.51
	473.5	153	1.27E-09	299.4	4.53
	578.0	177	1.05E-09	350.8	4.32
	704.7	200	1.80E-09	385.0	4.42
	865.2	225	1.73E-09	411.7	4.38
	1023.7	246	1.91E-09	427.9	4.34
	1119.9	258	8.56E-10	419.8	4.17
	1244.3	270	4.67E-09	452.5	4.34
	1734.1	344	3.90E-09	467.0	4.32
Test 2	7.5	39	5.33E-10	106.8	4.43
	36.8	46	1.71E-09	334.9	4.36
	72.0	58	5.86E-10	299.5	4.44
	92.3	70	3.12E-10	191.2	4.65
	118.0	88	5.46E-10	165.6	4.85
	148.0	111	2.51E-10	162.0	4.88
	176.0	129	5.08E-10	190.9	4.76
	199.5	177	1.44E-10	172.7	4.86
	211.0	200	1.17E-10	78.6	5.44
	222.5	225	1.41E-10	68.8	5.57
	239.0	246	2.56E-10	141.4	4.98
	255.0	267	1.51E-10	132.2	5.18
	289.5	292	6.32E-10		
	368.0	321	9.20E-10	337.9	4.53
	468.5	350	9.22E-10	357.1	4.57
	575.5	375	1.17E-09	392.4	4.40
	728.1	423	1.05E-09	430.9	4.53
	870.1	467	5.48E-10	430.9	4.36
	957.9	485	1.28E-09	419.6	4.34
	1179.6	522	2.53E-09	480.5	4.53
	1834.6	648	1.98E-09	503.8	4.46
	2484.6	782	6.91E-10	479.2	4.36
	3024.6	890	1.78E-09	480.5	4.30

Spruce bark admix permeated with 500 mg/L of Pb leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Discharge pH
Test 1	1.0	35	3.05E-11		
	5.0	61	2.17E-10		
	10.5	76	2.88E-10	0.6	8.17
	15.9	132	5.30E-11	0.5	8.64
	27.3	144	1.47E-09	2.4	8.18
	38.3	159	1.43E-10	11.4	8.41
	43.9	233	4.59E-11	9.5	8.54
	49.8	306	2.09E-11	11.0	8.87
	54.8	406	1.12E-11	7.8	8.63
	59.3	466	8.91E-12	6.3	8.70
	72.6	549	3.58E-11	4.2	7.41
	102.1	595	6.29E-11	9.0	7.03
	129.4	613	3.47E-11	13.5	7.33
	156.6	639	9.24E-11	49.0	6.46
	183.6	664	1.10E-10	73.3	6.42
	196.1	701	3.52E-11	3.2	8.15
	205.0	807	3.88E-11	5.9	8.44
	213.7	890	4.00E-11	4.3	8.59
	258.9	970	3.35E-10	122.0	6.20
	334.3	989	2.99E-10	264.0	6.32
	412.5	1002	3.66E-10	317.7	6.27
	549.5	1025	8.06E-10	357.1	6.12
	944.9	1090	1.82E-09	397.7	6.09
	1393.1	1156	7.97E-10	440.8	5.93
	1883.8	1222	1.40E-09	466.7	5.90
	2310.2	1284	3.15E-10	423.4	5.86
	2461.5	1307	2.63E-10	436.4	5.88
	2620.7	1332	3.43E-10	427.8	5.85
	2846.9	1372	6.22E-10	440.8	5.73
	3065.4	1399	4.18E-10	424.8	5.63
	3268.0	1438	7.00E-10	406.0	5.90
	3565.7	1530	7.19E-10	429.5	5.98
	3785.3	1610	1.83E-10	358.3	6.01
	3878.8	1641	2.22E-10	349.1	6.08
	3985.0	1688	2.08E-10	351.4	6.12
	4067.6	1723	1.22E-10	358.3	6.09
	4115.6	1742	1.45E-10	361.8	6.10
	4177.6	1765	2.70E-10	360.6	5.93
	4260.6	1795	2.54E-10	372.2	6.03
	4417.4	1854	5.79E-10	369.9	6.06
	4607.1	1927	3.62E-10	372.2	6.06
Test 2	1.9	68	2.77E-11	0.0	8.45
	6.6	140	2.09E-11	0.1	8.63
	11.6	240	1.12E-11	0.3	8.61
	16.3	301	9.49E-12	0.1	8.30

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Pb conc.	Discharge pH
	ml	hr	m/s	mg/L	
Test 2					
continued	21.0	430	7.82E-12	0.4	8.19
	26.3	536	2.69E-11	0.3	8.51
	31.3	642	1.54E-11	0.3	8.67
	35.5	725	2.45E-11	4.1	8.37
	41.0	860	2.77E-11	0.7	8.36
	47.0	925	1.66E-11	0.6	8.36
	52.5	1041	1.03E-11	0.5	8.78
	57.8	1207	8.35E-12	0.9	8.84
	64.1	1365	1.53E-11	0.3	8.89
	70.9	1577	2.17E-11	0.4	8.42
	76.8	1689	1.41E-11	0.6	8.60
	82.0	1824	9.76E-12	0.6	8.89
	88.4	2017	9.67E-12		

Spruce bark admix permeated with 500 mg/L of Cu leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Cu conc. mg/L	Discharge pH
Test 1	3.2	104	2.41E-11	0.3	8.22
	7.8	204	3.32E-11	0.3	8.56
	12.8	264	2.13E-11	0.2	8.33
	17.6	394	2.89E-11	0.1	8.58
	41.4	499	3.05E-10	2.0	7.66
	69.0	560	1.70E-10	5.8	8.35
	78.0	606	9.18E-11	4.4	8.55
	151.0	689	1.81E-09	385.1	5.69
	280.4	725	9.18E-10	356.0	5.62
	372.8	749	7.56E-10	367.0	5.62
	470.1	769	1.96E-09	395.7	5.61
	608.9	800	3.09E-09	391.8	5.60
	777.2	823	2.26E-09	404.5	5.50
	1026.1	888	1.29E-09	363.2	5.58
	1303.2	954	9.84E-10	421.5	5.46
	1991.6	1021	4.49E-09	446.4	5.33
	2732.9	1082	1.57E-09	434.5	5.20
Test 2	3083.7	1105	4.11E-09	454.8	5.17
	3492.1	1131	4.85E-09	457.9	5.12
	4174.3	1170	5.78E-09	475.2	5.08
	1.9	183	2.08E-11	0.2	8.37
	6.2	283	3.32E-11	0.3	8.68
	11.0	344	2.00E-11	0.2	8.26
	15.7	473	2.89E-11	0.1	8.24
	38.3	578	2.87E-10	1.0	7.91
	61.8	685	9.79E-11	2.2	8.62
	67.6	768	6.72E-11	1.9	8.42
	75.9	848	1.66E-10	2.3	7.97
	87.4	902	1.41E-10	5.0	8.50
Test 3	100.7	968	6.11E-11	2.5	8.46
	113.8	1083	2.61E-11	4.2	8.71
	136.7	1161	1.22E-10	32.6	6.85
	186.3	1184	7.60E-10	274.1	5.74
	256.3	1210	7.82E-10	316.9	5.75
	5.3	67	3.70E-11	3.9	8.61
	10.9	167	3.11E-11	1.0	8.65
	15.6	228	2.00E-11	0.4	8.54
	20.2	357	2.70E-11	0.1	8.47
	35.8	463	1.91E-10	0.5	7.71
	52.5	523	8.92E-11	2.7	8.50
	58.7	569	9.49E-11	2.4	8.30
	67.2	652	1.42E-10	3.2	8.55
	76.4	713	8.17E-11	3.6	8.02
	83.6	786	8.83E-11	1.7	8.71
	96.4	852	7.64E-11	1.3	8.02

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Cu conc. mg/L	Discharge pH
Test 3 continued	109.3	917	2.99E-11	1.6	8.37
	120.9	984	6.22E-11	3.7	8.63
	143.9	1046	1.36E-10	21.0	6.49
	173.4	1068	3.33E-10	202.5	5.71
	197.6	1094	2.09E-10	139.6	5.96
	319.0	1134	1.43E-09	372.6	5.66
	489.2	1161	1.12E-09	439.1	5.68

Binary heavy metal leachates - lead (Pb) & copper (Cu)*Bentonite admix permeated with 500 mg/L of Pb & Cu leachate*

Triplicate #	Cumulative discharge volume	Time	Hydraulic conductivity	Pb conc.	Cu conc.	Discharge pH
	ml	hr	m/s	mg/L	mg/L	
Test 1	18.0	13	5.00E-10	0.1		8.15
	31.5	38	2.83E-10	0.0	0.1	8.27
	43.5	64	2.74E-10	0.0	0.6	8.28
	52.3	85	2.13E-10	0.0	0.8	8.28
	63.9	115	3.15E-10	0.0	0.7	8.23
	78.4	133	3.61E-10	0.0		
	89.7	148	5.13E-10	0.1	1.1	8.26
	102.6	161	5.90E-10	0.0	5.8	8.06
	127.3	176	1.38E-09	8.8	52.6	6.21
	162.1	189	1.64E-09	49.0	159.8	
	191.6	199	1.65E-09	85.9	203.1	
	219.3	208	1.62E-09	109.1	230.7	
	249.3	218	1.56E-09	136.5	246.0	5.74
	277.3	230	1.88E-09	161.1	269.7	5.63
	304.3	238	2.02E-09	184.4	282.0	5.58
	333.6	246	1.83E-09	204.1	296.0	5.58
	371.3	257	2.06E-09	213.6	313.2	5.48
	449.3	276	2.41E-09	181.5	319.0	5.48
	575.8	305	2.47E-09	243.0	332.0	5.40
	686.8	329	2.72E-09	269.0	345.0	5.35
	798.8	349	3.36E-09	289.5	367.0	5.21
	931.8	370	3.50E-09	306.5	380.0	5.30
	1035.8	387	3.68E-09	319.0	378.5	5.27
	1159.3	405	4.07E-09	356.0	415.6	5.30
	1306.8	425	4.33E-09	368.0	418.0	5.25
	1415.6	439	4.26E-09	380.8	422.4	5.26
	1515.6	452	4.88E-09	391.6	432.0	5.27
	1634.8	466	4.99E-09	398.4	440.0	5.23
	2019.8	505	5.80E-09	414.0	448.8	5.17
	2420.7	545	5.96E-09			
	2571.7	559	5.96E-09	438.5	459.0	5.09
	2715.2	572	5.78E-09	444.0	464.0	5.11
	2975.2	615	6.18E-09	436.0	459.5	5.06
	3153.7	648	2.14E-09	442.0	465.5	5.08
	2840.7	588	2.99E-09	443.5	469.5	5.08

Forest soil admix permeated with 500 mg/L of Pb & Cu leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Cu conc. mg/L	Discharge pH
Test 1	10.3	32	7.91E-10	21.1	113.3	4.70
	25.5	39	3.77E-10	14.0	141.4	4.77
	46.8	46	1.28E-09	48.6	198.5	4.66
	74.5	58	4.99E-10	23.0	175.4	4.73
	93.0	70	3.24E-10	18.9	155.0	4.76
	120.5	88	5.95E-10	24.3	146.6	4.82
	153.5	111	2.90E-10	26.1	140.6	4.91
	178.0	129	3.66E-10	25.3	139.5	4.94
	212.8	153	5.23E-10	4.4	140.2	5.03
	250.5	177	3.36E-10	4.6	149.4	5.06
	297.5	200	7.54E-10	8.6	208.2	4.68
	357.3	225	6.02E-10	16.7	253.2	4.50
	409.0	246	6.15E-10	15.7	285.5	4.39
	460.5	267	6.93E-10	18.8	302.0	4.34
	522.5	292	7.65E-10	35.2	312.1	4.26
	613.0	321	1.05E-09	151.0	342.0	4.24
	707.5	350	7.23E-10	200.5	350.7	4.23
	797.5	375	1.09E-09	258.7	433.4	4.20
	893.5	408	7.31E-10	330.4	403.1	4.12
Test 2	28.0	32	9.95E-10	12.5	67.3	4.38
	42.5	39	1.13E-10	13.5	85.9	4.91
	51.5	46	5.91E-10	11.8	85.0	5.04
	66.8	58	3.37E-10	20.6	86.1	5.05
	81.5	70	3.24E-10	13.9	95.3	4.93
	115.0	88	7.69E-10	18.4	164.5	4.65
	161.5	111	4.64E-10	35.5	242.4	4.52
	206.5	129	7.62E-10	58.1	290.1	4.34
	276.0	153	1.02E-09	21.0	339.1	4.23
	353.5	177	7.38E-10	30.9	357.3	4.19
	465.9	200	1.87E-09	65.4	421.1	4.10
	643.2	225	2.13E-09	99.8	462.1	4.09
	834.4	246	2.39E-09	112.7	473.1	4.06
	956.1	258	1.29E-09	117.2	471.8	4.01
	1084.8	270	4.59E-09	116.8	480.1	4.06
	1535.0	321	6.54E-09	482.0	480.6	4.14
Test 3	11.0	46	8.85E-10	12.5	81.6	4.50
	37.5	88	4.48E-10	13.4	74.6	5.22
	58.8	111	1.34E-10	13.2	83.7	5.40
	70.0	129	1.68E-10	8.6	61.0	5.58
	86.5	153	2.53E-10	2.1	60.1	5.66
	113.0	177	3.47E-10	4.4	135.6	5.16
	140.5	200	2.83E-10	7.9	118.6	5.25
	163.0	225	2.28E-10	5.7	109.6	5.37
	185.5	246	3.07E-10	7.7	142.5	5.17
	216.0	267	4.66E-10			4.79

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Cu conc. mg/L	Discharge pH
Test 3 continued	255.5	292	4.65E-10		223.9	4.78
	293.0	321	3.08E-10	64.3	245.6	4.71
	320.5	350	2.07E-10	46.4	202.8	4.84
	344.8	375	2.82E-10	44.5	204.2	4.86
	371.8	408	2.26E-10	67.2	249.8	4.66

Spruce bark admix permeated with 500 mg/L of Pb & Cu leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Cu conc. mg/L	Discharge pH
Test 1	4.0	53		0.9	0.4	6.72
	15.3	89	1.79E-10	1.9	1.6	7.17
	26.7	150	1.39E-10	1.3	3.1	7.83
	33.0	196	7.29E-11	1.5	2.7	8.44
	61.6	257	9.00E-10	462.2	499.9	5.21
	201.8	279	2.78E-09	406.2	463.0	5.29
	399.8	315	1.28E-09	293.7	467.6	5.19
	513.7	340	6.43E-10	357.1	457.5	5.19
	595.3	359	1.52E-09	375.4	438.6	5.20
	709.0	391	2.57E-09	308.7	453.6	5.22
	837.2	413	1.59E-09	375.4	461.1	5.16
Test 2	6.5	89	1.61E-10	1.0	1.0	7.40
	17.1	150	1.35E-10	1.2	2.6	7.95
	26.3	196	1.76E-10	1.2	2.5	8.16
	55.0	210	9.39E-10	13.6	134.7	5.82
	105.5	224	1.08E-09	57.6	420.4	5.32
	202.7	242	2.15E-09	308.7	481.4	5.30
	326.9	258	1.84E-09	187.9	446.6	5.35
	646.9	279	6.65E-09	468.5	498.0	5.10
	1187.8	315	4.17E-09	474.8	513.8	4.95
	1551.8	340	1.94E-09	471.6	520.3	4.85
	1773.4	359	3.89E-09	446.6	496.7	4.84
	2063.5	391	6.56E-09	474.8	510.4	4.82
	2287.4	413	1.59E-09			
Test 3	6.5	89	1.61E-10	1.0	0.7	7.12
	18.6	150	1.87E-10	1.3	2.2	8.01
	27.7	196	1.19E-10	1.6	2.8	8.33
	38.7	241	2.37E-10	1.6	3.8	8.50
	91.2	279	1.10E-09	16.3	252.6	5.57
	197.2	315	9.24E-10	79.8	402.6	5.36
	283.1	340	5.45E-10	153.3	428.7	5.40
	366.5	359	1.71E-09	176.3	434.6	5.37
	424.8	378		296.7	465.7	5.33
	512.5	413	2.10E-09	372.4	475.2	5.26

Ternary heavy metal leachate - lead (Pb), copper (Cu), & cadmium (Cd)

Bentonite admix permeated with 500 mg/L of Pb, Cu, & Cd leachate

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Cu conc. mg/L	Cd conc. mg/L	Discharge pH
Test 1	5.0	50	4.31E-10	0.0	1.2	4.6	8.00
	13.3	61	1.68E-10	0.0	1.1	1.9	8.09
	34.5	84	3.88E-10	0.0	2.1	20.7	7.76
	69.7	112	3.23E-10	2.6	47.2	114.9	6.22
	109.3	132	5.48E-10	40.4	162.1	215.1	5.83
	140.8	144	3.55E-10	82.0	232.9	267.9	5.71
	167.6	160	5.74E-10	104.0	244.7	283.4	5.68
	210.8	174	9.34E-10	77.2	286.0	315.3	5.54
	267.8	184	1.78E-09	40.4	330.0	354.4	5.49
	313.8	195	6.58E-10	54.4	319.0	344.5	5.45
	349.8	204	1.21E-09	52.6	319.0	345.9	5.45
	394.3	215	1.09E-09	63.7	333.7	360.1	5.35
	454.3	229	1.40E-09	82.4	352.1	371.5	5.22
	512.3	242	8.85E-10	120.0	363.1	385.2	5.14
	582.8	255	1.93E-09	153.2	374.1	392.4	5.09
	701.0	279		262.3	381.5	401.8	5.16
	807.1	299	9.76E-10	305.3	399.9	411.3	5.11
	891.1	311	2.04E-09	320.5	399.9	417.9	5.06
	999.1	326	2.23E-09	352.4	407.2	422.4	5.08
	1082.5	337	1.08E-09	379.0	407.2	424.6	5.11
Test 2	1196.2	350	3.71E-09	397.0	418.3	434.2	5.07
	1775.3	417	3.79E-09	461.8	469.8	480.7	4.94
	6.0	44		0.0	1.0	1.9	7.90
	14.0	50		0.0	1.2	7.1	7.97
	23.6	61	2.35E-10	0.0	2.2	26.6	7.63
	44.6	84	3.56E-10	0.4	7.9	52.7	6.76
	74.4	112	2.49E-10	10.3	64.9	112.0	6.12
	105.1	132	4.26E-10	25.1	101.8	143.8	6.01
	131.4	144	3.45E-10	47.9	150.4	195.5	5.85
	158.9	160	6.06E-10	68.5	176.9	219.8	5.80
	206.1	174	1.04E-09	91.6	244.7	283.9	5.66
	266.6	184	1.81E-09	33.7	315.3	341.7	5.55
	313.1	195	6.58E-10	38.5	315.3	338.9	5.53
	347.1	204	1.10E-09	46.9	319.0	343.8	5.54
	390.1	215	1.12E-09	95.7	330.0	351.6	5.42
	450.1	229	1.39E-09	124.0	344.7	364.4	5.38
	507.1	242	8.64E-10	165.4	359.4	378.0	5.30
	573.6	255	1.80E-09	158.3	370.4	390.2	5.21
	708.1	279	1.94E-09	267.7	392.5	407.0	5.24
	838.0	299	1.08E-09	324.9	414.6	427.5	5.20
	931.5	311	2.28E-09	338.0	414.6	424.6	5.20
	1051.1	326	2.46E-09	385.7	418.3	427.5	5.18

Triplicate #	Cumulative discharge volume ml	Time hr	Hydraulic conductivity m/s	Pb conc. mg/L	Cu conc. mg/L	Cd conc. mg/L	Discharge pH
Test 2							
continued	1149.7	337	1.52E-09	408.2	422.0	433.4	5.12
	1285.0	350	4.23E-09	408.2	425.6	441.6	5.12
	1809.3	417	3.27E-09	453.8	469.8	484.5	5.05

APPENDIX F SELECTIVE SEQUENTIAL EXTRACTION CALCULATIONS AND DATA

F.1. ACCURACY OF THE SELECTIVE SEQUENTIAL EXTRACTION PROCEDURE

**F.2. CALCULATIONS FOR SORPTION CAPACITIES OF ADMIXES BASED ON
BATCH ADSORPTION RESULTS FOR INDIVIDUAL MATERIALS**

F.3. SELECTIVE SEQUENTIAL EXTRACTION DATA

APPENDIX F.1. ACCURACY OF THE SELECTIVE SEQUENTIAL EXTRACTION PROCEDURE

Since the sorbed amount of heavy metals were calculated for the admix samples submitted to Batch adsorption tests, heavy metal recoveries could be calculated after submitting the same samples to Selective Sequential Extraction (SSE). The heavy metal recoveries are shown in Table F.1.1. Excluding two outliers, the average recovery of the SSE procedure was 91%. The systematically low recovery probably was due to the loss of sample during the washing and decanting steps of the SSE procedure. Since the recoveries were relatively consistent, the two outliers were probably caused by an error in the Batch adsorption test procedure. Large dilution factors were required to bring some Batch adsorption samples to within measurable range. Large dilution factors coupled with low sorption quantities result in large random errors.

TABLE F.1.1. Recovery results for the Selective Sequential Extraction procedure.

Admix	HM* solution	HM* analyzed	Total conc. of HM sorbed $\mu\text{g/g soil}$	Total conc. HM extracted using SSE $\mu\text{g/g soil}$	Recovery
Bentonite admix	<i>Cu 1st</i>	<i>Cu</i>	567	574	101%
	<i>Cu 2nd</i>	<i>Cu</i>	541	565	105%
	<i>Pb 1st</i>	<i>Pb</i>	1803	1604	89%
	<i>Pb 2nd</i>	<i>Pb</i>	1687	1760	104%
	<i>Pb+Cu 1st</i>	<i>Cu</i>	439	423	96%
	<i>Pb+Cu 1st</i>	<i>Pb</i>	1166	1174	101%
	<i>Pb+Cu 2nd</i>	<i>Cu</i>	455	449	99%
	<i>Pb+Cu 2nd</i>	<i>Pb</i>	1354	1238	91%
	<i>Pb+Cu+Cd 1st</i>	<i>Cd</i>	487	267	55%**
	<i>Pb+Cu+Cd 1st</i>	<i>Cu</i>	861	378	44%**
	<i>Pb+Cu+Cd 1st</i>	<i>Pb</i>	1211	1079	89%
	<i>Pb+Cu+Cd 2nd</i>	<i>Cd</i>	469	264	56%**
	<i>Pb+Cu+Cd 2nd</i>	<i>Cu</i>	958	367	38%**
	<i>Pb+Cu+Cd 2nd</i>	<i>Pb</i>	1140	1090	96%
Forest soil admix	<i>Cu 1st</i>	<i>Cu</i>	859	738	86%
	<i>Cu 2nd</i>	<i>Cu</i>	936	721	77%
	<i>Pb 1st</i>	<i>Pb</i>	2146	1912	89%
	<i>Pb 2nd</i>	<i>Pb</i>	2163	2088	97%
	<i>Pb+Cu 1st</i>	<i>Cu</i>	710	526	74%
	<i>Pb+Cu 1st</i>	<i>Pb</i>	1337	1252	94%
	<i>Pb+Cu 2nd</i>	<i>Cu</i>	619	523	85%
Spruce bark admix	<i>Pb+Cu 2nd</i>	<i>Pb</i>	1356	1280	94%
	<i>Cu 1st</i>	<i>Cu</i>	591	599	101%
	<i>Cu 2nd</i>	<i>Cu</i>	642	552	86%
	<i>Pb 1st</i>	<i>Pb</i>	n/a	1268	n/a
	<i>Pb 2nd</i>	<i>Pb</i>	n/a	1297	n/a
	<i>Pb+Cu 1st</i>	<i>Cu</i>	412	399	97%
	<i>Pb+Cu 1st</i>	<i>Pb</i>	756	825	109%
	<i>Pb+Cu 2nd</i>	<i>Cu</i>	554	389	70%
	<i>Pb+Cu 2nd</i>	<i>Pb</i>	846	803	95%

* HM - Heavy metal

** outliers

n/a - not available

APPENDIX F.2. CALCULATIONS FOR SORPTION CAPACITIES OF ADMIXES BASED ON BATCH ADSORPTION RESULTS FOR INDIVIDUAL MATERIALS

The calculations for the sorption capacities of the admixes are,

$$Q_{\text{Bentonite admix}} = Q_{\text{Bentonite}}$$

$$Q_{\text{Forest soil admix}} = Q_{\text{Bentonite}} \cdot 7/8 + q_{\text{Forest soil}} \cdot 1/8$$

$$Q_{\text{Spruce bark admix}} = Q_{\text{Bentonite}} \cdot 7/8 + q_{\text{Spruce bark}} \cdot 1/8$$

where $q_{\text{bentonite admix}}$, $q_{\text{Forest soil admix}}$, and $q_{\text{Spruce bark admix}}$, are the sorption capacities for the Bentonite, Forest soil, and Spruce bark admixes, $Q_{\text{Bentonite}}$, $Q_{\text{Forest soil}}$, and $Q_{\text{Spruce bark}}$ are the sorption capacities for Bentonite, Forest soil, and Spruce bark, and the number fractions are based on the compositions of the admixes.

The calculations for the sorption capacities of bentonite, Forest soil, and Spruce bark are,

where the sorption equations are taken from section 4.2.1.4.

The compositions of the admixes are,

Bentonite admix = 100:8 sand and bentonite

Forest soil admix = 100:7:1 sand, bentonite, and Forest soil

Spruce bark admix = 100:7:1 sand, bentonite, and Spruce bark

APPENDIX F.3. SSE DATA

Single heavy metal leachates of Pb and Cu

Bentonite admix permeated with 500 mg/L of Pb leachate

TEST 1

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Center	1	804	638	96	25	6
	2	76	257	18	3	0
	3	476	402	74	10	0
	4	470	363	71	12	2
Edge	1	679	401	83	11	0
	2	2	23	7	5	29
	3	1	2	1	0	0
	4	1	3	3	0	0

TEST 2

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Center	1	7	290	286	20	10
	2	6	68	82	6	4
	3	4	18	167	6	7
	4	3	55	24	2	1
Edge	1	13	151	111	9	4
	2	0	1	1	0	1
	3	3	0	1	0	1
	4	1	1	9	1	2

Bentonite admix permeated with 500 mg/L of Cu leachate

TEST 1

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Center	1	378	116	30	5	5
	2	372	142	24	4	
	3	308	146	23	3	5
	4	339	133	24	5	8
Edge	1	220	112	24	3	4
	2	0	7	5	1	1
	3	146	19	11	3	3
	4	69	90	20	3	1

*Forest soil admix permeated with 500 mg/L of Pb leachate***TEST 1**

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$
Center	1	7	131	34	15	
	2	2	16	11	3	
	3	14	238	64	31	
	4	3	5	6	2	
Edge	1	32	302	61	41	
	2	1	0	1	0	
	3	1	0	1	0	
	4	5	89	26	16	

TEST 2

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$
Center	1	241	695	192	68	
	2	48	377	96	49	
	3	1	4	0	0	
	4	127	493	122	54	
Edge	1	403	999	215	109	
	2	0	2	1	0	
	3	3	4	1	2	
	4	15	206	64	34	

TEST 3

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$	$\mu\text{g/g soil}$
Center	1	494	754	143	60	2
	2	1	1	1	2	0
	3	1	1	1	1	0
	4	1	2	3	1	0
Edge	1	769	885	209	75	0
	2	64	411	78	37	0
	3	1	1	1	2	0
	4	23	285	55	23	0

*Forest soil admix permeated with 500 mg/L of Cu leachate***TEST 1**

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Composite	1	295	243	100	42	23
	2	3	48	26	29	11
	3	1	23	16	21	12
	4	30	125	49	37	16

TEST 2

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Composite	1	391	237	124	49	25
	2	102	n/a	119	40	23
	3	1	29	16	21	11
	4	44	149	56	39	18

*Spruce bark admix permeated with 500 mg/L of Pb leachate***TEST 1**

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Center	1	156	1533	56	150	
	2	1	4	3	0	
	3	2	54	7	22	
	4	56	534	55	59	
Edge	1	25	396	47	61	
	2	25	351	39	58	
	3	7	180	20	44	
	4	147	823	109	73	

*Spruce bark admix permeated with 500 mg/L of Cu leachate***TEST 1**

Location	Layer	Exchangeable	Carbonates	Hydroxides	Organics	Residue
		µg/g soil	µg/g soil	µg/g soil	µg/g soil	µg/g soil
Center	1	205	361	30	47	7
	2	3	49	12	12	6
	3	1	4	1	3	1
	4	80	137	42	21	5
Edge	1	156	271	32	43	5
	2	52	154	25	28	7
	3	33	108	21	19	6
	4	162	144	56	33	4

TEST 2

Location	Layer	Exchangeable		Carbonates		Hydroxides		Organics		Residue	
		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$	
Center	1	182		150		201		29		4	
	2	0		3		1		3		2	
	3	0		1		0		1		0	
	4	1		2		0		5		2	
Edge	1	67		229		41		23		9	
	2	0		2		1		2		0	
	3	0		3		1		2		1	
	4	1		13		3		4		2	

*Binary heavy metal leachates of Pb and Cu**Bentonite admix permeated with 500 mg/L of Pb & Cu leachate***TEST 1**

Location	Layer	Exchangeable		Carbonates		Hydroxides		Organics		Residue	
		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Center	1	703	280	335	97	115	25	14	5	7	2
	2	191	154	99	100	57	24	6	4	3	3
	3	19	24	40	79	19	21	1	2	2	3
	4	520	182	260	120	85	31	10	5	5	3
Edge	1	519	334	135	99	123	30	12	4	5	4
	2	75	92	59	92	38	26	2	3	3	2
	3	359	231	126	94	98	27	8	3	2	1
	4	257	177	120	115	72	29	6	4	3	2

*Forest soil admix permeated with 500 mg/L of Pb & Cu leachate***TEST 1**

Location	Layer	Exchangeable		Carbonates		Hydroxides		Organics		Residue	
		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Composite	1	540	274	361	167	139	74	29	37	0	16
	2	29	20	117	84	37	39	14	30	0	13
	3	2	15	37	85	17	37	9	32	0	10
	4	17	1	91	19	27	11	13	19	0	8

TEST 2

Location	Layer	Exchangeable µg/g soil		Carbonates µg/g soil		Hydroxides µg/g soil		Organics µg/g soil		Residue µg/g soil	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Composite	1	293	154	282	143	77	52	18	35	4	19
	2	4	2	54	30	19	17	5	21	1	10
	3	3	1	37	14	15	8	3	17	1	8
	4	52	34	154	106	46	41	14	36	1	12

TEST 3

Location	Layer	Exchangeable µg/g soil		Carbonates µg/g soil		Hydroxides µg/g soil		Organics µg/g soil		Residue µg/g soil	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Composite	1	212	151	216	151	72	61	19	37	0	13
	2	1	0	13	14	8	7	4	16	0	9
	3	1	1	12	6	9	3	6	11	0	7
	4	4	3	41	44	18	23	9	25	0	10

Spruce bark admix permeated with 500 mg/L of Pb & Cu leachate

TEST 1

Location	Layer	Exchangeable µg/g soil		Carbonates µg/g soil		Hydroxides µg/g soil		Organics µg/g soil		Residue µg/g soil	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Center	1	121	114	208	193	29	35	53	13		
	2	1	1	0	1	1	0	0	2		
	3										
	4	36	37	110	117	18	40	38	13		
Edge	1	23	28	120	121	6	16	36	11		
	2	1	0	0	0	1	0	0	1		
	3										
	4	54	39	179	134	11	23	47	11		

TEST 2

Location	Layer	Exchangeable µg/g soil		Carbonates µg/g soil		Hydroxides µg/g soil		Organics µg/g soil		Residue µg/g soil	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Center	1	158	143	232	181	36	32	57	13		
	2	2	1	1	3	2	1	0	2		
	3	2	1	1	2	2	4	0	1		
	4	58	44	150	130	9	20	39	15		
Edge	1	212	158	228	145	36	23	61	12		
	2	92	53	163	109	13	16	42	11		
	3	56	25	157	81	8	15	40	9		
	4	178	99	253	152	26	31	53	14		

TEST 3

Location	Layer	Exchangeable		Carbonates		Hydroxides		Organics		Residue	
		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$		$\mu\text{g/g soil}$	
		Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Center	1	163	140	177	196	78	36	38	21	6	12
	2	1	0	1	0	0	0	0	1	0	1
	3	1	1	1	0	1	0	0	1	0	1
	4	1	1	18	16	5	9	3	5	1	3
Edge	1	77	64	192	136	34	25	40	20	0	3
	2	7	6	120	61	11	21	33	7	2	4
	3	9	11	108	61	9	20	28	8	0	2
	4	53	38	183	104	23	31	39	11	4	8

*Ternary heavy metal leachate of Pb, Cu, and Cd**Bentonite admix permeated with 500 mg/L of Pb, Cu, and Cd leachate***TEST 1**

Location	Layer	Exchangeable			Carbonates			Hydroxides			Organics			Residue		
		$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$		
		Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
Composite	1	592	250	239	168	82	5	93	27	3	24	7	3	0	2	0
	2	122	119	186	68	72	7	40	22	2	12	6	2	0	4	0
	3	69	45	113	60	48	2	25	16	2	6	3	1	1	3	0
	4	152	103	156	78	69	4	34	19	2	9	5	1	0	3	0

TEST 2

Location	Layer	Exchangeable			Carbonates			Hydroxides			Organics			Residue		
		$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$			$\mu\text{g/g soil}$		
		Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
Composite	1	521	244	243	133	80	4	83	27	2	32	7	2	0	3	0
	2	87	97	181	63	67	5	27	20	1	9	4	1	0	3	0
	3	45	29	90	56	42	5	19	14	1	7	4	1	0	2	0
	4	182	108	168	91	73	4	34	21	1	15	4	1	0	3	0