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ASPECTS OF COMPETITIVE ADSORPTION

AND PRECIPITATION OF HEAVY METALS

BY A CLAY SOIL

by

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April, 1994

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Engineering

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ASPECTS OF RETENTION OF HEAVY METALS BY A CLAY SOIL

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ABSTRACT

This thesis examines the retention of three heavy metals (Pb, Cu, Zn) on a predominantly illite clay soil initially saturated with calcium and magnesium. The heavy metal retention mechanisms were examined both experimentally, using batch equilibrium and precipitation tests, and analytically, using the geochemical equilibrium speciation model MINTEQA2. Heavy metal retention was examined in both non-competitive (single metal) situations and competitive (multi-metal) situations. A definite adsorption selectivity order of Pb>Cu>>Zn was established, as has been found by many other researchers. Retention by ion exchange adsorption was observed by comparing the total amount of heavy metals retained to the total amount of initially adsorbed calcium and magnesium released. In most cases, it was found that ion exchange was the dominant retention mechanism, even at neutral equilibrium pH values. The effect of initial heavy metal solution pH on heavy metal retention was explored. A comparison was made between batch equilibrium tests performed with metal solutions adjusted to an initial pH of 3 and tests performed with metal solutions that were not adjusted and thus at a higher initial pH. In many cases it was found that greater overall retention occurred when initial metal solutions were at a pH of 3 as opposed to a higher initial pH. The speciation modelling, when compared to the experimental results, was found to adequately predict heavy metal retention in simple single metal batch equilibrium tests but in more complicated multimetal scenarios the modelling had limited success.

RESUMÉ

Ce mémoire étudie la rétention de trois métaux lourds (Pb, Cu, Zn) dans un sol principalement composé d'argile illitique. Celui-ci a été initialement saturé avec du calcium et du magnésium. Le mécanisme de rétention des métaux lourds a été expérimenté en laboratoire en utilisant la méthode d'équilibre de lots et des tests de précipitations. L'analyse a par la suite été complétée analytiquement en utilisant le modèle d'équilibre d'espèces géochimiques MINTEQA2. La rétention des métaux lourds a été examinée à la fois dans un environnement non-compétitif (métal simple) et compétitif (multi-métaux). Comme bien d'autres chercheurs ont déjà démontré, une adsorption sélective d'ordre Pb>Cu>Zn a été établie lors de cette étude. En comparant la quantité de métaux lourds retenus et la quantité de calcium et de magnésium relâchés, une rétention par échange d'ions a été observée. Dans la majorité des cas l'échange d'ions était le mécanisme de rétention dominant et ce même à une valeur de pH neutre. L'effet d'une solution de métaux lourds avec son pH initial sur la rétention des métaux lourds a aussi été exploré. Une comparaison a été faite entre les tests de lots d'équilibres concus avec des solutions métalliques ajustées initialement à un pH de 3 et les tests effectués avec des solutions métalliques non-ajustées, donc avec un pH initial supérieur. Dans plusieurs cas, il a été trouvé qu'une plus grande rétention se produisait lorsque le pH initial des solutions métalliques étaient de 3 comparativement à des valeurs initiales plus élevées. Pour les lots d'équilibres simples l'utilisation du modèle de spéciation, lorsque comparé aux résultats expérimentaux, s'est avéré adéquat. Dans les cas plus complexes de multi-métaux le modèle démontre moins de succès.

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TABLE OF CONTENTS

CHAPTER 1

INTRODUCT	(ION 1
1.1	The Sources
1.2	The Risk
1.3	The Hope
1.4	Problem Statement 4
1.5	Objectives and Tasks of the Study 6
1.6	Organization of this Thesis 7

CHAPTER 2

.

LITERATURE	REVIEW	9
2.1	The Nature of Clay Soils	9
2.2	Heavy Metal Properties	13
2.3	Heavy Metal Speciation in Natural Waters	15
	2.3.1 General	15
	2.3.2 Hydrolysis	16
2.4	Retention	19
2.5	Retention Selectivity	23
	2.5.1 pH and Hydrolysis	24
	2.5.2 Ionization Potential	24
	2.5.3 Ion Radius	26
	2.5.4 Hard Soft Acid Base Theory	26
2.6	Modelling	28
	2.6.1 Geochemical Speciation Modelling	28
	2.6.2 Adsorption Modelling	29
	2.6.3 MINTEQA2	33

CHAPTER 3

.

÷

MATERIALS	AND METHODS 3	6
3.1	Soil Preparation	6
3.2	Identification of Soil Properties	6
3.3	Stock Solution Preparation	9
3.4	Batch Equilibrium Tests 4	0
3.5	Estimation of Heavy Metal Precipitation (Blanks) 4	1
3.6	Geochemical Modelling 4	3

TABLE OF CONTENTS CONTINUED

CHAPTER 4

RESULTS AN	D DISCUSSION
4.1	General
4.2	Soil Characterization Results 49
4.3	Metal Precipitation Test Results
4.4	Single Metal Batch Equilibrium Tests
	4.4.1 Experimental Retention 59
	4.4.2 Modelled Retention and Speciation
	4.4.3 Mass Balance
	4.4.4 lsotherms
4.5	Two Metal Pb and Cu Batch Equilibrium Tests
	4.5.1 Experimental Retention 79
	4.5.2 Modelling Retention and Speciation
	4.5.3 Mass Balance
	4.5.4 lsotherms
4.6	Two Metal Pb and Zn Batch Equilibrium Tests 92
	4.6.1 Experimental Retention
	4.6.2 Modelling Retention and Speciation
	4.6.3 Mass Balance 97
	4.6.4 lsotherms 100
4.7	Two Metal Cu and Zn Batch Equilibrium Tests 101
	4.7.1 Experimental Retention
	4.7.2 Modelling Retention 102
	4.7.3 Mass Balance 106
	4.7.4 lsotherms 108
4.8	Three Metal Batch Equilibrium Tests
	4.8.1 Experimental Retention 110
	4.8.2 Modelling Retention 111
	4.8.3 Mass Balance 117
	4.8.4 lsotherms 120
4.9	Discussion Summary 122
	-

CHAPTER 5

CONCLUSIC	DNS	130
5.1	Concluding Remarks	130
5.2	Future Research Recommendations	133

TABLE OF CONTENTS CONTINUED

CHAPTER 6 REFERENCES 135 APPENDIX A 145 A.1 Units of Concentration 145 A.2 How to Read the MINTEQA2 Geochemical Speciation 147 Tables 147 A.3 Explanation of Isotherm Graphs - Experimental 148 A.4 Explanation of Isotherm Graphs - Modelled 149

APPENDIX B

Tabulated Experimental and Modelling Results		150
--	--	-----

APPENDIX C

Isotherm Graphs	 165
isomenni Oraphs	 100

APPENDIX D

:

Initial and Final pH	I Graphs	176
----------------------	----------	-----



LIST OF TABLES

Table 2.1 - Heavy Metal Speciation (%) as a function of pH (Harter,	
1983)	19
Table 2.2 - Summary of Selectivity Orders	23
Table 3.1 - Batch Equilibrium Tests Performed	40
Table 3.2 - Precipitation Tests Conducted	43
Table 4.1 - Soil Properties and Composition	49
Table 4.2 - Precipitation pH of Metal Solutions	52
Table 4.3- Initial and Final pH Ranges for Single Metal Batch	
Equilibrium Tests	62
Table 4.4 - Langmuir K values Calculated from Experimental Data	64
Table 4.5a MINTEOA2 Model Batch Equilibrium Tests for Pb Initial	•••
Unadiusted pH	68
Table 4 5b - MINTEOA2 Model Batch Equilibrium Tests for Ph with	00
Initial Adjusted nH 3	69
Table 4.6a - MINTEOA2 Model Batch Equilibrium Tests for Cu	05
Linadiusted Initial nH	70
Table 4.6h - MINTEOA2 Model Batch Equilibrium Tests for Cu Initial	/0
Adjusted nH 3	71
Table 4.7a - MINTEOA2 Model Batch Equilibrium Tests for 7n	71
Linadiusted Initial nH	72
Table 4 7b - MINITEGA2 Model Batch Equilibrium Tests for 7p Initial	12
Adjusted nH 3	72
Table 4.8 - Initial and Final pH Panges for Ph \pm Cu Batch Equilibrium	12
Table 4.0 - Initial and Final pri Kanges for FD + Cu batch Equilibrium	81
Table 4.9 Langmuir K values Calculated from Experimental Data	01
Table 4.9 - Langman K Values Calculated noin Experimental Data	05
for Ph and Cu Linediusted Initial Solution and	02
Table 4 10h MINITEOAD Model Patch Fauilibrium Tasta Speciation	00
Table 4.100 - MINTEQAZ Model balch Equilibrium resis specialion	07
Tor PD and Cu Adjusted Initial Solution pri 3	07
Table 4.11 - Initial and Final pri Kanges for PD + Zn Batch	00
Equilibrium lests	93
Table 4.12 - Langmuir K values Calculate d from Experimental Data	94
Table 4.13a - MINTEQA2 Model Batch Equilibrium Tests (unadjusted	~~
pH) Speciation for Pb and Zn	96
Table 4.13b - MIN I EQA2 Model Batch Equilibrium Tests (Initial pH 3)	
Speciation for Pb and Zn	97
Table 4.14 - Initial and Final pH Ranges for Cu + Zn Batch	
Equilibrium Tests	102
Table 4.15 - Langmuir K values Calculated from Experimental Data	103
Table 4.16a - MINTEQA2 Model Batch Equilibrium Tests (Unadjusted	
Initial pH) Speciation for Cu and Zn	105

LIST OF TABLES CONTINUED

Table 4.16b - MINTEQA2 Model Batch Equilibrium Tests (initial pH 3)	
Speciation for Cu and Zn	106
Table 4.17 - Initial and Final pH Ranges for Pb, Cu and Zn Batch	
Equilibrium Tests	111
Table 4.18 - Langmuir K values Calculated from	
Experimental Data (Pb, Cu and Zn)	113
Table 4.19a - MINTEQA2 Model Batch Equilibrium Tests (unadjusted	
initial pH) Speciation for Pb, Cu and Zn	116
Table 4.19b - MINTEQA2 Model Batch Equilibrium Tests (initial	
adjusted pH 3) Speciation for Pb, Cu and Zn	117
Table 4.20 - Summary of Precipitation pH of Metal Solutions	123
Table 4.21 - Summary of Metal Retention and Ca+Mg Released	125
Table 4.22 - Summary of Selectivity	126

viii

LIST OF FIGURES

Figure 4.1 - pH effect on the precipitation of Pb at varying initial concentrations.	53
Figure 4.2 - pH effect on the precipitation of Cu at varying initial concentrations.	53
Figure 4.3 - pH effect on the precipitation of Zn at varying initial concentrations.	53
Figure 4.4 - pH effect on the precipitation of Pb and Cu at equal initial concentrations.	54
Figure 4.5 - pH effect on the precipitation of Pb and Zn at equal ini concentrations.	tial 55
Figure 4.6 - pH effect on the precipitation of Cu and Zn at equal initial concentrations.	56
Figures 4.7 - pH effect on the precipitation of Pb, Cu and Zn at equal initial concentrations.	57
Figure 4.8a - Pb Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH	
solutions Figure 4.8b - Pb Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3	64
solutions Figure 4.9a - Cu Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH	65
solutions Figure 4.9b - Cu Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3	65
solutions Figure 4.10a - Zn Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH	66
solutions. Figure 4.10b - Zn Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3	66
solutions	67
Pb batch equilibrium test - Ca + Mg Released, Pb Retained versus Initial Applied Metal Concentration	74
Figure 4.11b - Mass Balance Graph for adjusted initial pH 3 solutions, Pb batch equilibrium tests - Ca + Mg Released, Pb Retained	75
Figure 4.12a - Mass Balance Graph for unadjusted initial pH solutions,	, ,
versus Initial Applied Metal Concentration.	75

LIST OF FIGURES CONTINUED

Figure 4.12b - Mass Balance Graph for adjusted initial pH 3 solutions,
Cu batch equilibrium test - Ca + Mg Released, Cu Retained
versus Initial Applied Metal Concentration
Figure 4.13a - Mass Balance Graph for initial unadjusted pH solutions,
Zn batch equilibrium test - Ca + Mg Released, Zn Retained
versus Initial Applied Metal Concentration
Figure 4.13b - Mass Balance Graph for initial adjusted pH 3 solutions,
Zn batch equilibrium test - Ca + Mg Released, Zn Retained
versus Initial Applied Metal Concentration.
Figure 4.14a - Pb and Cu Retention, experimental and modelled, in
the double metal batch equilibrium tests with unadjusted initial
pH solutions
Figure 4 14h - Pb and Cu Retention, experimental and modelled in
the double metal batch equilibrium tests with adjusted initial
nH 3 solutions 84
Figure 4.15a Mass Balance Graph for upadjusted initial pH colutions
Phand Cu batch aquilibrium torts Ca 1 Ma Polosod Phan
PD and Cu Datch equilibrium tests - Ca + Mg Released, PD +
Culketained versus initial Metal Concentration
Figure 4.150 - Mass Balance Graph for adjusted initial pri 3 solutions,
Pb and Cu batch equilibrium tests - Ca + Mg Keleased, Pb +
Cu Retained versus Initial Metal Concentration
Figure 4.16a - Pb and Zn Retention, experimental and modelled, in the
double metal batch equilibrium tests with unadjusted initial pH
solutions
Figure 4.16b - Pb and Zn Retention, experimental and modelled, in
the double metal batch equilibrium tests with adjusted initial
pH 3 solutions 95
Figure 4.17a - Mass Balance Graph for unadjusted initial pH solutions,
Pb and Zn batch equilibrium tests - Ca + Mg Released, Pb +
Zn Retained versus Initial Total Metal Concentration
Figure 4.17b Mass Balance Graph for initial adjusted pH 3 solutions,
Pb and Zn batch equilibrium tests - Ca + Mg Released. Pb +
Zn Retained versus Initial Total Metal Concentration
Figure 4.18a - Cu and Zn Retention, experimental and modelled, in
the double metal batch equilibrium tests with unadjusted initial
nH solutions
Figure 4 18b - Cu and Zn Retention experimental and modelled in
the double metal batch equilibrium tests with adjusted initial
nH 3 colutions 104
Figure 4 192 - Mass Balance Graph for unadjusted initial all colutions
r_1 solutions balance Graph for unadjusted initial prior bouldons, Cu and Zn batch aquilibrium tests - Ca $\pm Ma$ Released Cu i
The Pote in and yorgan Initial Motal Concentration 107

٠

LIST OF FIGURES CONTINUED

Figure 4.19b - Mass Balance Graph for initial adjusted pH 3 Cu and	
Zn batch equilibrium tests - Ca + Nig Released, Cu + Zn	
Retained versus Initial Metal Concentration.	108
Figure 4.20a - Experimental Pb, Cu and Zn Retention in the triple	
metal batch equilibrium tests unadjusted initial pH solutions	114
Figure 4.20b - Modelled Pb, Cu, and Zn Retention in the triple metal	
batch equilibrium tests unadjusted initial pH solutions	114
Figure 4.21a - Experimental Pb, Cu, and Zn Retention in the triple	
metal batch equilibrium tests adjusted initial pH3 solutions	115
Figure 4.21b - Modelled Pb, Cu, and Zn Retention in the triple metal	
batch equilibrium tests adjusted initial pH3 solutions.	116
Figure 4.22a - Mass Balance Graph for unadjusted initial pH, Pb, Cu	
and Zn batch equilibrium tests - Ca + Mg Released, Pb + Cu	
+ Zn Retained versus Initial Metal Concentration.	119
Figure 4.22b - Mass Balance Graph for initial adjusted pH 3 Pb, Cu	
and Zn batch equilibrium tests - Ca + Mg Released, Pb + Cu	
+ Zn Retained versus Initial Metal Concentration	120
Figures C.23a,b - Pb batch equilibrium test (unadjusted initial pH)	
isotherm a) based on experimental results b) based on	
modelling results	165
Figures C.24a,b - Pb batch equilibrium test (adjusted initial pH 3)	
isotherm a) based on experimental results b) based on	
modelling results	165
Figures C.25a,b - Cu batch equilibrium test (unadjusted initial pH)	
isotherm a) based on experimental results b) based on	
modelling results	166
Figures C.26a,b - Cu batch equilibrium test (adjusted initial pH 3)	
isotherm a) based on experimental results b) based on	
modelling results.	166
Figures C.27a,b - Zn batch equilibrium test (unadjusted initial pH)	
isotherm a) based on experimental results b) based on	
modelling results.	167
Figures C.28a,b - Zn batch equilibrium test (adjusted initial pH 3)	
isotherm a) based on experimental results b) based on	
modelling results.	167
Figures C.29a,b - Pb and Cu batch equilibrium test (unadjusted initial	
pH) Pb isotherm a) based on experimental results b) based on	
modelling results.	168
Figures C.30a, b - Pb and Cu batch equilibrium test (adjusted initial pH	
3) Pb isotherm a) based on experimental results b) based on	
modelling results.	168



-

LIST OF FIGURES CONTINUED

Figures C.31a,b - Pb and Cu batch equilibrium test (unadjusted initial pH) Cu isotherm a) based on experimental results b) based on	
modelling results.	169
Figures C.32a,b - Pb and Cu batch equilibrium test (adjusted initial pH	
3) Cu isotherm a) based on experimental results b) based on	
modelling results.	169
Figures C.33a, b - Pb and Zn batch equilibrium test (initial unadjusted	
pH) Pb isotherm a) based on experimental results b) based	
on modelling results.	170
Figures C.34a,b - Pb and Zn batch equilibrium test (initial adjusted	
pH 3) Pb isotherm a) based on experimental results b) based	
on modelling results.	170
Figures C.35a,b - Pb and Zn batch equilibrium test Zn isotherm based	
on a) experimental results initial unadjusted pH tests b)	
experimental results initial pH 3	171
Figures C.36a,b - Cu and Zn batch equilibrium test (unadjusted initial	
pH) Cu isotherm a) based on experimental results b) based on	
modelling results.	171
Figures C.37a,b - Cu and Zn batch equilibrium test (adjusted initial pH	
3) Cu isotherm a) based on experimental results b) based on	
modelling results.	172
Figures C.38a,b - Cu and Zn batch equilibrium test Zn isotherms based	
on a)experimental results unadjusted pH b) experimental results	
initial pH 3 tests.	172
Figures C.39a,b - Pb, Cu and Zn batch equilibrium tests (unadjusted	
initial pH) Pb isotherm a) based on experimental results b)	
based on modelling results	173
Figures C.40a,b - Pb, Cu and Zn batch equilibrium tests (adjusted	
initial pH 3) Pb isotherm a) based on experimental results b)	
based on modelling results	173
Figures C.41a,b - Pb, Cu and Zn batch equilibrium tests (unadjusted	
initial pH) Cu isotherms a) based on experimental results b)	
based on modelling results	174
Figures C.42a,b - Pb, Cu and Zn batch equilibrium tests (adjusted	
initial pH 3) Cu isotherms a) based on experimental results b)	
based on modelling results	174
Figures C.43a,b - Pb, Cu and Zn batch equilibrium tests Zn isotherms	
based on experimental results a) unadjusted pH b) adjusted	
initial pH 3	175
Figures D.44a,b - Initial and Final supernatant pH of Pb batch	
equilibrium tests a) unadjusted initial pH b) adjusted to initial	
pH 3	176

LIST OF FIGURES CONTINUED

Figures D.45a,b - Initial and Final supernatant pH of Cu batch equilibrium tests a) unadjusted initial pH b) adjusted to initial	
рН 3	176
Figures D.46a,b - Initial and Final supernatant pH of Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial	
рН 3	177
Figures D.47a,b - Initial and Final supernatant pH of Pb + Cu batch equilibrium tests a) unadjusted initial pH b) adjusted to initial	
рН 3	177
Figures D.48a,b - Initial and Final supernatant pH of Pb + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial	
рН 3	178
Figures D.49a,b - Initial and Final supernatant pH of Cu + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial	
рН 3	178
Figures D.50a,b - Initial and Final supernatant pH of Pb, Cu + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to	
initial pH 3	179

xiii

CHAPTER 1

INTRODUCTION

1.1 The Sources

Industrial pollutants, landfill leachates, and sewage sludges are just a few of the many sources of heavy metal contaminants polluting our natural surroundings. In order to protect our environment and prepare for the future, the fate of these contaminants must be addressed. The first step towards accomplishing this goal is to recognise the sources of heavy metal contaminants, many of which were outlined by Moore and Ramamoorthy (1984) and Yong et al. (1992) in their studies on heavy metals in aqueous environments. Once the sources are identified the possible fates of heavy metals can be examined.

The mining and smelting industries are principal sources of heavy metal contaminants. The by-products from metal smelting, sludge and blast furnace fine dust, contain both Zn and Pb. Base, precious, and uranium mines contain mineralized metals in the ore and waste rock which are combinations of many metals (Pb, Cu, Ni, Zn, and Ag) and sulphur (Yong et al., 1992). These sulphide minerals oxidize easily in the presence of oxygen and water producing sulphuric acid which increases the mobility of heavy metals in an environmental problem known as acid mine drainage. Lead (Pb) mining, typically performed as a co-product of Zn production or as a by-product of polymetallic ores, produces waste slag and slurries from SO₂ scrubbing containing high concentrations of Cd, Cu, Pb, and Zn.

Copper (Cu) smelting and refining produces waste containing Cu concentrations as high as 380,000 mg/l. Discharges from mine tailings (Allard et al., 1991) and flyash are the source of approximately 75% of solid Cu waste. Electrostatic precipitator (ESP) dust is reported to contain Cu concentrations from 240,000 to 280,000 mg/l and Pb and Zn concentrations in the ESP dust and sludge can exceed 10,000 mg/l (Yong et al., 1992).

Other industries also release pollutants and produce wastes containing heavy metals. Metal plating and finishing industries release metals in their waste streams. Petroleum refining wastes can contain trace metals used as corrosion inhibiters. Paint and Allied industries produce paints and coatings which use a number of metal compounds as pigments (Yong et al., 1992). The post consumer waste aspect of the paint and allied industry is also a potential source of heavy metals at landfill sites.

Copper (Cu) is also emitted directly to the environment as an agricultural poison and algicide during water purification in the compound named blue vitriol. Zinc (Zn) is emitted from natural sources such as windblown dusts, forest fires, volcanic particles and vegetation, accounting for approximately 43.5 million kilograms per year.

Municipal Solid Waste contains heavy metals which are leached by infiltrating precipitation and carried in the leachate (Freeze and Cherry, 1979) at concentrations as high as 100ppm. Sewage Sludge, mining wastes, and some industrial wastes (e.g. electroplating, pulp and paper, and chemical industries) can contain metals concentrations ranging from 100 to 10,000 ppm (Yong and DiPerno, 1991). Sewage Sludges contain high concentrations of heavy metals and are often applied to agricultural lands as a method of treatment and disposal.

1.2 The Risk

When one speaks of risk it is usually in terms of risk to human health. All these contaminants, released to the environment or disposed of in landfills, can enter natural environments used as drinking water sources, recreational areas, and wildlife habitats and ultimately put our own health at risk. Once contaminants enter the natural system the number of pathways that they can travel are numerous and varied, for example, contaminants can migrate to the groundwater table and contaminate drinking water sources, remain in the shallow soil surface and possibly be absorbed by plantlife, or be retained by the soil. Regardless of the pathway, ultimately, contaminants can reach a human receptor through skin contact, consumption, or inhalation. At this point in the discussion, the issue of toxicity comes into play. What is considered a toxic level? What concentration can safely be consumed? This opens up a whole new debate which cannot be addressed in this thesis except to say it is known and accepted that heavy metals are toxic to human health but what levels represent toxic levels are uncertain.

1.3 The Hope

The only buffer nature offers to protect our environment from heavy metal contamination is soil and its' many fractions; organic and inorganic, living and non living. Soil can attenuate, to a limited extent, certain contaminants by mechanisms such as adsorption, complexation, precipitation and filtration. Biological activity in the soil can transform or degrade organic contaminants to more or less toxic forms. The means of contaminant retention are not always discussed in research since all mechanisms result in retardation of migrating contaminants. However, researchers have come to realize that these mechanisms may be reversible should a change in the soil environment occur. Thus, in order to determine the fate of heavy metal contaminants in the subsurface, the interactions between soil and heavy metals must be defined and the limits of soil as an attenuating medium must be quantified. In this text, the word retention is used to describe all mechanisms of removal from the aqueous phase - the partitioning of solutes between the free moving liquid (porewater) and solid (precipitated and adsorbed) phases. The term adsorption is reserved for mechanisms of removal involving interactions of the solutes with soil fractions and particle surfaces.

The present research was undertaken to determine the mechanisms of heavy metal retention in clay soils and to study the competition involved in heavy metal retention when more than one heavy metal is present. Competitive retention of heavy metals was examined both experimentally and analytically with the use of an equilibrium speciation model. The results of this thesis will improve our understanding of heavy metal-soil interaction and contribute to engineering fields such as landfill design, site remediation technology, and pollutant fate modelling.

1.4 Problem Statement

Heavy metals are considered toxic to human health and detrimental to the natural environment (Yong, et al., 1992; Henry and Heinke, 1989; Moore and Ramamoorthy, 1984) however, the concentration at which various heavy metals are considered toxic is debatable and will not be discussed in this research.

Concentrations of individual heavy metals vary from 0-100 ppm in municipal solid waste leachate to 100 - 10,000 ppm in sewage sludge, mining wastes, and some industrial wastes (Yong et al., 1992, Yong and DiPerno, 1991). A pollutant containing heavy metals often contains more than one heavy metal as in the case of Cu smelting which produces waste containing Cu, Pb and Zn.



The mechanisms and processes involved in heavy metal retention include precipitation as a solid phase (oxide, hydroxides, carbonates), ion exchange adsorption, and complexation reactions (Harter, 1979; Yanful, 1988a; Farrah and Pickering, 1977a, 1978; Maguire et al. 1981; Yong et al., 1990). Heavy metals begin to precipitate at a neutral pH resulting in 100% retention in basic environments. The research linking pH and heavy metal retention in soils is well documented and consistently shows increased retention with increased pH (see eg. Allard et al., 1991; Farrah and Pickering, 1977; Frost and Griffin ,1977; Harter, 1983; Maguire et al., 1981; Phadungchewit, 1990). The mechanisms of retention are not always defined by the researchers, however, most recognize the importance of precipitation citing that as pH increases heavy metal solubility decreases (Allard et al., 1991; Jeffery and Uren, 1983; Harter, 1983).

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Experimentally, many researchers have been unable or unwilling to differentiate between the mechanism of heavy metal retention in soils, specifically, heavy metal precipitation and adsorption by soil particles. Perhaps differentiation was not considered of importance since both mechanisms resulted in retention, the ultimate goal. However, a changing soil environment can modify contaminant retention characteristics. For example, should the soil pH environment change, dissolution of precipitates could occur, or, if contaminant pore water concentrations vary, one contaminant may be displaced by another. With this in mind, retention mechanisms have become a critical factor in determining the stability of the soil-contaminant systems. Farrah and Pickering (1978) identified four possible mechanisms that may mobilize heavy metals in soils 1) changing acidity 2) changing the system ionic strength 3) changing the oxidation reduction potential and 4) formation of complexes. These findings by Farrah and Pickering (1978) stress the importance of identifying and understanding the mechanism of retention in an aqueous soil environment, be it surface water sediments, soil-groundwater, or landfill clay liner.

It has now been established that heavy metals are pollutants, some sources have been identified, and the mechanisms of heavy metal retention have been briefly introduced. However, as described above, rarely is one heavy metal found in isolation. In fact, as Section 1.1 detailed, many heavy metals are found in the presence of other contaminants including other heavy metals (Moore and Ramamoorthy, 1984). Heavy metals are predominantly positively charged species in their ionic (e.g. Pb²⁺) or complexed (e.g. PbOH⁺) forms. Whereas, clay soil surfaces are negatively charged due to a phenomena called isomorphic substitution which is described further in Section 2.1. The heavy metal cations can be adsorbed by the negatively charge clay soil surface in the interest of electro-neutrality. However, all the cations must compete for the limited adsorption sites on the surface of the soil particle in what is referred to as competitive adsorption. To study competitive adsorption it was necessary to differentiate between soil retention and adsorption. In this research differentiation is accomplished by examining ion exchange adsorption and heavy metal precipitation in the absence of soil. Presented in the following thesis is a study of competitive adsorption and retention of three heavy metals (Lead (Pb), Copper (Cu), Zinc (Zn)) by a clay soil in single, double, and triple metal solutions.

1.5 Objectives and Tasks of the Study

The objectives of this research were to study the selective retention of heavy metals on a clay soils in situations where competition exists between different heavy metal species in solution, and where the pH environment varies.

To obtain these objectives heavy metal retention and exchangeable cation displacement were studied in the laboratory in competitive (multimetal) and non competitive (single metal) batch equilibrium tests. Heavy metal precipitation in the absence of soil was also examined in single and multi-metal solutions across a wide pH range. The laboratory experiments were then modelled using an equilibrium speciation computer model.

1.6 Organization of this Thesis

This thesis is arranged in five chapters and four appendices as described below:

- Chapter 1: presents the environmental problem and the scope, objectives, and organization of the study.
- Chapter 2: introduces the general nature of clay soils and heavy metals and reviews pertinent previous research to the present study.
- Chapter 3: describes the experimental methods and materials, and the computer speciation modelling employed in the study.
- Chapter 4: presents and discusses the results of the laboratory and geochemical speciation modelling studies on the retention mechanisms (adsorption and precipitation) of heavy metals in clay soil and the competitive adsorption of heavy metals.
- Chapter 5: contains the concluding remarks and suggestions for further research.
- Appendix A: discusses topics that may help the reader to understand the text (ie: concentration units and descriptions of graphs and tables)



- Appendix B: presents a summary of the batch equilibrium tests experimental and modelling results.
- Appendix C: presents the isotherm graphs illustrating the experimental and modelling results.
- Appendix D: presents graphs depicting the initial and final pHs of the batch equilibrium tests.

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CHAPTER 2

LITERATURE REVIEW

2.1 The Nature of Clay Soils

Soil inherently safeguards our natural waters by retarding contaminant migration. In artificial environments such as landfill clay liners, clay is used to inhibit leachate migration by acting as it does in nature to protect groundwater and surface water. In surface water, soil sediments can adsorb contaminants, buffer pH, aid in the precipitation of contaminants, and host biological activity which may transform or degrade contaminants. Soil can retard contaminant migration into the groundwater by acting as a membrane, a physical filter, a precipitation surface, a pH buffer, a host to biological activity, and an adsorbent as detailed below.

Membrane - Compact fine grained soils behave as a low permeability boundary by lowering advective groundwater flow velocities to millimetres per year.

Physical Filter - Soil also behaves like a filter by physically retaining contaminants larger than the pore diameters.

Precipitation Surface - Contaminants may precipitate on the surface of soil particles as a thin films or layers, facilitated by the soils' clay particles and carbonates.

pH Buffer - Clay minerals and carbonates in the soil buffer the pH of the soil porewater which helps to minimize the effect of acid precipitation on contaminant mobilization (Phadungchewit, 1990).

Biological Host - Soil hosts a wide range of micro and macro biology which can transform and degrade contaminants.

Adsorbent - More important, clay and other soil fractions can act as adsorbing medium by retaining contaminants through, electrostatic attractions, complexation or exchange reactions. Soil adsorption is further described below.

The non living soil fractions are composed of organic and inorganic (crystalline and amorphous) portions. Primary and secondary minerals constitute the inorganic fractions with primary minerals comprising a major portion of the sand and silt size particles and a minor part of the clay size fraction. The clay size fraction is composed predominantly of layer silicates which are generally described as clay minerals. The inorganic soil fractions are composed of unaltered organics such as plant roots, transformed organics such as amorphous humic substances, and decayed materials like polysaccharides (Yong et al.1992).

Mixed in and perhaps coating the soil particles are carbonates and amorphous materials. These components along with the layer lattice clay mineral particles and the organic fraction make up the most active components of the soil system.

Primary minerals, the most common of which is quartz, retain water and contaminants through capillary action which is derived from relatively weak Van der Waals attractive forces, but, clay soils which are secondary

minerals have charged surfaces originating from a positive charge deficit in the laver lattice. The positive charge deficit results from isomorphic substitution of atoms in the layer lattice for atoms of smaller valence (ie. Al for Si in illite). The charged surface allows clay soils to retain water and contaminants in an effort to obtain charge neutrality. The other active components (amorphous materials, carbonates and organic) contribute a great deal to the overall retention through exchange, complexation, and bonding reactions, as has been shown by sequential extraction studies (Phadungchewit, 1990, Tessier et al., 1979). Amorphous materials (metal oxides and hydroxides) can adsorb either positively or negatively charged ions depending on the soil pH environment or possibly co-precipitate ions in solution. Stumm et al. (1976) discussed the importance of the hydrous oxide surfaces in cation adsorption and the influence of their pH dependent surface charge. Soil organics can retain metals through complexation, adsorption and chelation reactions (Yong et al. 1992). Sequential extraction procedures define contaminant retention by clay soils in terms of the five following operational clay fractions; exchangeable, carbonate, hydroxide/oxide, organic, and residual (Yong and Phadungchewit, 1993).

Tessier et al. (1979) used sequential extraction to examine the partitioning of metals to different soil fractions. Tessier et al. (1979) found that Pb in sediments collected from two 'rivers in Canada was associated predominantly with the residual and oxide soil fractions with smaller amounts associated with the organic and carbonate fractions. The residual fraction represents the primary and secondary minerals in the sediment or soil, therefore, metals associated with residual fractions are locked in the crystalline structure and will generally not be released to the environment. The highest concentration of Cu extracted was from the residual fraction, with decreasing amounts extracted from organic, oxide, and carbonate fractions. Zinc (Zn) was found primarily in the residual fraction, with significant concentrations also

associated with the oxide fraction and relatively small amounts were associated with the carbonates and organic fractions. It is interesting to note that only very small amounts of all three metals were extracted from the exchangeable soil fraction.

Phadungchewit (1990) conducted similar research with clay soils using sequential extraction to determine heavy metal concentrations associated with different soil fractions. Phadungchewit (1990) studied an iilite clay soil and found Pb, Cu and Zn associated predominantly with exchangeable, carbonate, and hydroxide fractions with the later two phases increasing their retention as equilibrium pH values increased.

Sealbond

The soil used in the research presented in this thesis is composed primarily of illite clay, a member of the mica group. Illite is described as having a 2:1 structure, indicating an alumina sheet between two silica sheets which constitutes one layer. The layers are bonded together by potassium ions which fit into the hexagonal holes of the silica sheet. The charged surfaces originating from isomorphic substitution in the illite clay layer lattice, attracts cations in the nature of charge neutrality. Heavy metals are predominantly positively charged species in both their non-complexed and speciated forms. These positively charged species are retained by the negatively charged clay surface. This reaction, being a surface reaction, is called adsorption. The reader must be reminded that there are other soil fractions which contribute significantly to adsorption especially amorphous and organic fractions. There are three basic approaches to modelling adsorption, namely: electrostatic models, adsorption isotherm models and mass action reaction models.

Adsorption Models

Models termed electrostatic, complexation, or double layer models

have been developed to described the electrostatic attraction of ions to the clay particle surface. These models, namely the Gouy Chapman model (Gouy, 1910, 1917; Chapman, 1913), the Stern Model (Stern, 1924), the Graham Model (Graham, 1947), the DLVO model (Derjaquin and Landau, 1941; Verwey and Overbeek, 1948) and the Ion Hydration Model (Allammawi, 1988) will not be discussed in any detail except to introduce them to the reader.

Isotherm models describe adsorption on clay surfaces as a functional equilibrium distribution of adsorbate (contaminant) with concentration of adsorbent (soil) in a solution at constant temperature. The two most common isotherm models are Langmuir Model (Langmuir, 1916a, 1916b, 1918) and Freundlich Model (Freundlich, 1926). The Langmuir model was developed from theoretical bases however, the Freundlich model is an empirical model based on laboratory research. These models will be discussed further in Section 2.6 on equilibrium adsorption modelling.

The final approach to adsorption analysis, which will be discussed further in Section 2.6, is called ion exchange which is governed by the law of mass action.

2.2 Heavy Metal Properties

Now that the nature of clay soils and sealbond have been briefly described the second half of the dilemma is the contaminants, which in this research, are the heavy metals Pb, Cu, and Zn. In general, heavy metals can easily lose electrons to form positive ions, usually conduct electricity, have high densities, and are toxic. The theory of hard and soft acid base (HSAB) is used to describe many heavy metal chemical phenomena (Pearson, 1968).

Lead

Lead (Pb) is a member of the group IV elements of the periodic classification and unlike other members of this group, Pb is more electropositive in nature making it truly metallic compared to C and Si. Lead (Pb), unlike C and Si, does not bind to another identical atom, shows a decrease in covalency, and has stable +2 and +4 oxidation states. Lead (Pb) is classified as an intermediate acceptor, between hard and soft acid, according to the hard soft acid base theory (HSAB) which is further discussed in Section 2.5.4.

Copper

Copper (Cu) belongs to the third transition metal series, exhibiting a wide variation in properties such as high conductivity, and spectral and magnetic capabilities. Copper (Cu) complexes in oxidation states +1, +2, and +3, although +2 is the most common. Copper (Cu) is found widely in nature in the free state as well as in complexes with sulphides, arsenides, chlorides, and carbonates. Copper (Cu) is classified as an intermediate between hard and soft acids in its chemical interactions with donors, hard acids. Hard acids prefers O donors forming essentially electrovalent bonds and soft acceptors prefer S and Se donor atoms forming covalent bonds.

Zinc

Zinc (Zn) is a member of the group IIb triad of the periodic classification of elements. It resembles transition metals in its ability to form complexes particularly with ammonia, amines, halide ions, and cyanide. Zinc (Zn) in its interaction with ligands is between a hard and soft acceptor. Zinc (Zn) forms complexes with both hard (oxygen donors) bases and soft (sulphur donors) bases which is reflected in the occurrence of Zn as both carbonate and sulphide ores.

2.3 Heavy Metal Speciation in Natural Waters

2.3.1 General

The basic nature of clay soil fractions and the sources and properties of the heavy metal contaminants have been described but the interactions which may occur between the two has not been discussed. The interactions that may form between the heavy metals and clay soil fractions depend on the species form that contaminants take in the porewater. One approach to understanding and predicting the retention is to examine contaminant speciation in the porewater, and model surface reactions to predict retention based on the soil fractions present.

Tessier et al. (1979) and Phadungchewit (1990) used sequential extraction to examine the retention of metals on the clay fractions which can be used to determine the retained metal speciation. Yong and Phadungchewit (1990) described that the heavy metal retention, as determined by sequential extraction, depends on the soil solution pH, soil fractions and speciation of heavy metals.

Laboratory analyses of equilibrium concentrations in the supernatant from a batch equilibrium test, or analysis of trace metal concentrations in groundwater samples determines the total concentration of each metal, with no information regarding speciation. However, speciation information enables contaminant interactions with soil fractions to be predicted.

A characteristic of most metals in water is the tendency to form hydrolysed species and complexes with inorganic ions (ie. NO_3^- , F, Cl⁻, $SO_4^{2^-}$, $CO_3^{2^-}$, and HCO_3^-). Freeze and Cherry (1979) used Zn as an example, some of the hydrolysed and inorganic species that must be considered for Zn would include ZnOH⁺, Zn(OH)₂, Zn(OH)₄²⁻, ZnCl⁻, ZnSO₄, and ZnCO₃.



Solubility

The solubility of the metals is an important consideration in the analysis of heavy metal attenuation. In this research the metals were used in their highly soluble nitrate forms. At the concentrations studied in the research, complete dissolution under the initial conditions can be assumed given the following solubilities at 25°C;

$Pb(NO_3)_2$	37.6 g/cc or 13 M/I
Cu(NO ₃) ₂ 2 1/2 H ₂ O	137.8 g/cc or 592 M/
$Zn(NO_3)_2 6 H_2O$	184.3 g/cc or 619 M/

The presence of soil organic fractions affects the solubility of heavy metals. Heavy metals are often chelated with soil organic compounds and these compounds formed by chelation may be more soluble than inorganic precipitates. The distribution of the various hydroxyl species is also important in predicting the degree of solubility of different heavy metal ions.

2.3.2 Hydrolysis

Hydrolysis Reactions

The total concentration of a trace metal, M_{τ} , that in its unhydrolysed or uncomplexed form exists as M^{n+} is;

$$M_T = (M^{n+}) + (MOH^{(n-1)+}) + (M(OH)_2^{(n-2)+}) + \dots$$

If the total concentration M_{τ} (total metal concentration regardless of speciation) is known then the concentration of each species can be calculated using mass action equations with equilibrium constants derived from thermodynamic data (Leckie and James, 1974).

Benefield et al. (1982) offers an excellent discussion on metal ion

hydrolysis and its effect on solubility. Benefield et al. (1982) describes that metal ions exist in aqueous solutions as hydrated ions. Complex forming reactions between the hydrated metal ion (Me) and hydroxyl ions (OH-) occur forming hydroxocomplexes as shown below:

 $\begin{array}{rl} {\sf Me}^{2+}{}_{(aq)} \ + \ {\sf OH}^{\text{-}}_{(aq)} \ - \ {\sf MeOH}^{\text{-}}_{(aq)} \\ {\sf Me}^{2+}{}_{(aq)} \ + \ 2{\sf OH}^{\text{-}}_{(aq)} \ - \ {\sf Me}({\sf OH})_{2(aq)} \\ {\sf Me}^{2+}{}_{(aq)} \ + \ 3{\sf OH}^{\text{-}}_{(aq)} \ - \ {\sf Me}({\sf OH})^{+}{}_{3(aq)} \end{array}$

Benefield et al. (1982) explains that hydrated metal cations are weak acids and the formation of metal hydroxocomplexes may be considered as an ionization of these cation acids.

 $\begin{array}{l} {\sf Me^{2+}}_{(aq)} \,+\, {\sf H_20} \,-\, {\sf MeOH^{\text{-}}_{(aq)}} \,+\, {\sf H^+} \\ {\sf Me^{2+}}_{(aq)} \,+\, 2{\sf H_20} \,-\, {\sf Me(OH)}_{2(aq)} \,+\, 2{\sf H^+} \\ {\sf Me^{2+}}_{(aq)} \,+\, 3{\sf H_20} \,-\, {\sf Me(OH)^+}_{3(aq)} \,+\, 3{\sf H^+} \end{array}$

The reactions shown above occur when a salt containing metal ions dissolves in water and produces H⁺ ions resulting in an acidic solution. These reactions also significantly increase the solubility of heavy metal salts.

Hydroxyl Species Precipitation

The metals of interest in this research are Pb, Cu, and Zn, and the hydroxide precipitation reactions and solubility product constants (K_{sp}) are given below. As the reader can note these reactions are highly pH dependent. The K_{sp} show an order in terms of decreasing solubility of Me(OH)₂ species of Pb > Zn > Cu.

Reaction	K _{sp} (25℃)	
$Pb(OH)_{2(s)} = Pb^{2+} + 2OH^{-}$	4.5 x 10 ⁻¹⁵	
$Cu(OH)_{2(s)} = Cu^{2+} + 2OH^{-}$	1.6 x 10 ⁻¹⁹	
$Zn(OH)_{2(s)}^{-1} = Zn^{2+} + 2OH^{-1}$	4.5 x 10 ⁻¹⁷	



These solubilities represent precipitation from the liquid phase to form a unique solid phase of metal hydroxide. However, since precipitation depends on the pH of the soil and the soil pore water, clay particle surfaces may facilitate precipitation by increasing local pH and ion concentrations near the particle surface, perhaps, allowing precipitation below the saturation point. Sposito (1984) described that precipitation of mixed precipitates can be as inhomogeneous solids restricted to a thin outer layer, and thereby, difficult to distinguish from adsorption.

Speciation and pH

Many researchers have found that soil solution pH plays a key role in heavy metal retention due to the formation of hydroxyl species. Clays promote the precipitation of metal hydroxides by increasing pore water pH (Farrah and Pickering, 1976 a,b and c; Phadungchewit, 1990). Jeffery and Uren (1983) studied the effect of soil solution pH on Cu and Zn species. The researchers concluded that the two metals respond differently to changes in the soil pH environment. Zinc (Zn) solubility varies widely with soil pH and metal concentration, but Cu shows far less variance in solubility. Most Zn in solution was found to exist as free metal ions or liable species (can dissociate), whereas Cu seems to exist as species moderately liable (dissociate in the presence of a chelating agent) or as species that cannot dissociate. This is also supported by research conducted by Harter (1983) which shows the persistence of Zn^{2+} species beyond pH7 but not Cu²⁺. The results of Harter's research is summarized in Table 2.1.

Hahne and Kroontje (1973) discussed metal hydrolysis in their research on Pb and Zn. Heavy metals belong to a group of oxyphilic and sulphophilic elements distinguishing themselves from earth and alkaline elements by undergoing hydrolysis at lower pH values and by displaying multiple hydrolysis. Below pH 7, Zn²⁺ is present, whereas Pb can be found in both the



divalent Pb^{2+} and monovalent $Pb(OH)^+$ species. Between pH 7 and 10, Hahne and Kroontje (1973) found that $Zn(OH)_2$ was the dominant species form for Zn which is contrary to what was found by Harter (1983) (Table 2.1). Hahne and Kroontje (1973) calculated the concentrations of different Pb species and found $Pb(OH)^+$ was dominant between pH 7 and 10. Under more alkaline conditions Zn was speciated as $Zn(OH)^-_3$ and $Zn(OH)^{2-}_4$ and $Pb(OH)_4^{2-}$, $Pb(OH)_3^-$ and small quantities $Pb(OH)_2$ were the species forms of Pb. If $Zn(OH)_2$ is present between pH 7 and 11 as discussed by Hahne and Kroontje (1973) precipitation will occur only when concentrations exceed the intrinsic solubilities. The same can be said for Cu and Zn although the research did not examine Cu and Zn. The formation of hydroxide species may promote mobilization of these metals since they reduce the charge on the metal and increase the overall sclubility.

Table 2.1 - Heavy Metal Speciation (%) as a function of pH (Harter, 1983).						
рН	4	5	6	7	8	
Pb ²⁺	100	100	98	83	33	
РЬОН⁺	-	-	2	17	66	
Pb(OH) ₂		-	-		1	
Cu ²⁺	100	100	96	33	1	
CuOH⁺	-	-	2	7	1	
Cu(OH) ₂	-	-	2	56	92	
Zn ²⁺	100	100	98	83	31	
Zn(OH)+	-	-	2	17	64	
Zn(OH) ₂	-		-	-	5	

2.4 Retention and pH

The mechanisms and processes involved in heavy metal retention include precipitation, adsorption, and complexation. Farrah and Pickering
(1976) examined the retention of Zn by clay illite soils. The uptake of Zn²⁺ by clay increased significantly with pH. The pH effect was considered to be due to decreased competition from H⁺ ions for active sites and exposure of new sites on the clay mineral surface. The research also indicated that the effect of pH and ligands on the uptake of Zn by illite resembles that of kaolinite more than montmorillonite. Since adsorption on kaolinite is due mainly to the hydroxyl groups at broken edges, Farrah and Pickering (1976) concluded that illitic steric factors must minimize the contribution of classic ion exchange retention.

The research found that pH plays a key role because clays promote the precipitation of metal hydroxide (Farrah and Pickering, 1976; Phadungchewit, 1990). That the amount of Zn hydroxide adsorbed can be minimized by reducing the pH to below 6. Farrah and Pickering (1976) further concluded that both Zn ions and hydroxyl ions are retained by the clay surface, with interactions yielding a chemisorbed species. Farrah and Pickering (1976) concluded that the process controlling Zn adsorption on illite appears to be the attachment of hydroxyl species to particular sites on the particle edge.

Similarly, in two papers by Farrah and Pickering published in 1976 they examined the uptake of Cu by clays, specifically illite, montmorillonite and kaolinite. They found that the adsorption of Cu by montmorillonite can be interpreted by the ion exchange model but for illite and kaolinite, the controlling process appears to be the formation of polymeric hydroxy species attached to particular sites on the clay surface. They based their conclusions on a logarithmic plot of metal ion concentration adsorbed versus hydroxyl concentration since the formation of these hydroxy bridges is highly pH dependent.

Farrah and Pickering (1977) went on to study the adsorption of Pb and

Cd. They found that the retention of the heavy metals as a function of pH increased to a threshold pH where upon total retention occurred. The increase was thought by Farrah and Pickering (1977) to be due to decreased competition from protons for adsorption sites. The conclusions were similar to that of Cu adsorption. They found the role of hydroxy species to be critical and multiple. The addition of base leads to the formation of slightly soluble hydroxy metal complexes. Adsorption of hydroxyl ions is also considered to be responsible for the increased adsorption of metals either through hydroxyl bridges or through proton extraction from functional groups.

In a paper published in 1979, Farrah and Pickering proposed that the increased adsorption which is experienced with increased pH is due to decreased competition from protons. Their research also confirmed that the presence of clay lowered the pH required for precipitation of sparingly soluble metal hydroxy species. The authors concluded that simple ion exchange is not the most appropriate model for interpreting clay adsorption behaviour. The authors found that allowance must be made for the variable capacity introduced by dissociation reactions and base adsorption, both processes are very pH dependent.

Frost and Griffin (1977) studied the affect of pH on the adsorption of Cu, Zn and Cd from a landfill leachate. The authors conclude that at low pH, adsorption dominated the removal of heavy metals from solution but at high pH the formation of hydroxy species and precipitation were the dominant factors.

Harter (1983) concluded that the retention of heavy metals, specifically Pb, Cu, Zn and Ni, by soils is strongly influenced by the soil pH. Harter (1983) postulated that the degree of hydrolysis of metal species and precipitation to solid phase at high pH are the retention mechanisms. For all



four metals studied, rapid increase in metal retention did not occur until the pH was at or greater than 7.0.

Maguire et al, (1981) found that the amount of Cu and Zn retained increased with pH prior to precipitation of hydroxyl species and the researchers discerned a difference in the pH-dependent capacity of the soil.

The research conducted by Phadungchewit (1990) is perhaps the most important research as a precursor to the research presented in this thesis. Phadungchewit and Yong (1993) concluded that the amount of metals retained in the soil depends on the soil solution pH, which is directly affected by the buffering capacity of the soil. The higher the buffering capacity of the soil the more resistant the soil is to pH change upon the addition of acid from sources such as acid rain. As the pH decreases the dominant retention mechanisms change from precipitation to cation exchange. They found that illite and montmorillonite have higher initial pH and buffer capacities than kaolinite, and accordingly have higher metal retention capabilities. They explained that the presence of carbonates in the soil enhances the buffering capacity.

Besides examining overall metal retention, Phadungchewit and Yong (1993) also examined the competitive retention of heavy metals and found a selectivity order of Pb>Cu>Zn>Cd for illite clays. This same selectivity order was found for montmorillonite and a natural clay soil at pH values above 4 or 5, but when the pH was lowered a selectivity order of Pb>Cd>Zn>Cu was seen for kaolinite and montmorillonite. While the research conducted by Phadungchewit (1993) discusses both adsorption and retention it was not possible to distinguish between the two experimentally.

2.5 Retention Selectivity

Selectivity or affinity refers to one heavy metal being preferred over another for adsorption by a soil.

Metal selectivity orders have long been established by many researchers and some of these orders are summarized below in Table 2.2. Many theories exist as to why selectivity occurs, most based on the metal properties. These theories are briefly presented in the following text.

Table 2.2 - Summary of Selectivity Orders			
Biddappa, C.C. et al. 1981.	Pb>Cu>Zn>Cd>Ni Select Soils of Japan		
Elliot,H.A. et. al. (1986)	Pb>Cu>Zn>Cd	Mineral soils with no organic matter	
	Pb>Cu>Cd>Zn	Mineral Soils with with organic matter	
Harter, R.D. (1983)	Pb>Cu>Zn>Ni		
Farrah and Pickering, (1977)	Cu>Pb>Cd>Zn Pb>Cu>Zn>Cd Pb>Cu>Cd,Zn	Kaolin Illite Montmorillonite	
Allard, B., et. al. (1991)	Cu>Zn>Cd	Illite	
Benjamin, M.M., and Leckie,J.O.,(1981)	Pb <cu<hg<zn<co< td=""><td>Amorphous Iron Oxyhydroxide</td></cu<hg<zn<co<>	Amorphous Iron Oxyhydroxide	
Puls and Bohn (1988)	Cd – Zn > Ni Cd>Zn>Ni	Montmorillonite Kaolinite	
Yong and Phadungchewit and (1990)	Pb>Cu>>Zn-Cd $Pb>Cu>Zn>Cd$ $Pb>Cd>Zn>Cu$ $Pb>Cu>Zn>Cd$ $Pb>Cu>Zn>Cd$ $Pb>Cd>Zn>Cd$	Illite Montmorillonite pH <u>></u> 3 Montmorillonite pH <u><</u> 3 Natural Clay Natural Clay High pH Kaolinite	

Bowden et al. (1977) describes unequal adsorption as some ionic

species forming a closer association with the surface than other species due to factors such as ion size, charge and electron configuration of both the surface and the ion. Some of the factors affecting unequal adsorption, as described by Bowden et. al. (1977), are also used to explain selectivity.

2.5.1 pH and Hydrolysis

James et al. (1975) postulated that mono-hydroxy cations (MOH) may be preferentially retained. At the pH of precipitation, the concentration of such species in solution was very small compared to M^{2+} , therefore, James et al. (1975) believed that the affinity order must be MOH⁺ >> M^{2+} . Alternatively, one can suggest that retained metal ions hydrolyse more readily, with deprotonation of coordinated water molecules being followed by hydroxy bridging and polymer formation. While James et al. (1975) is referring to a sort of selectivity, the selectivity is within one element between species rather than two different elements. According to James (1975) theory, one could postulate that the metal existing at highest concentrations in hydrolysed form at the equilibrium pH is preferentially adsorbed. If this was true, according to information presented in Section 2.3.2, a selectivity order of Cu > Pb > Zn would be established.

Allard et al. (1991) studied Cu, Zn and Cd concentrations migrating from a deposit of mine tailings within an illitic clay formation and ran parallel laboratory batch equilibrium experiments. The study concluded that the lower pH range has a limited quantitative impact on mobility of Cu, Zn and Cd but as the pH exceeds 5, they are almost completely immobilized in the order of Cu > Zn > Cd. Allard et al, (1991) concluded that retardation mechanisms are related to the degree of hydrolysis which leads to the topics of pK values and ionization potentials.

2.5.2 Ionization Potential

Elliot et al. (1986) explained that at high pH, metals hydrolyse resulting is soluble metal complexes which may precipitate onto the soil (Section 2.5.1). This precipitation can be experimentally indistinguishable from adsorption. The adsorption affinity of hydrolysable metals in soil may be related to the pK of the first hydrolysis product of the metal (Forbes et al., 1974) where K is the equilibrium constant for the reaction below and n-1.

$$M^{2+}(aq) + nH_20 = M(OH)_n^{2+n} + nH^+$$

The ranking in terms of increasing pK values (below) follows the same selectivity order found by many researchers (Farrah and Pickering, 1977; Harter, 1983; Elliot, 1986; Biddappa, 1981; Phadungchewit, 1990);

Metal (pK of first hydrolysis product) Pb(6.2)>Cu>(8.0)>Zn(9.0)>Cd(10.1)

At higher pH values Phadungchewit (1990) found that this order of selectivity no longer holds for illite and montmorillonite, likely because the hydrolysis reaction described by the pK value is very pH dependent.

Organic Matter and pK Values

Elliot et al. (1986) examined the effect of organic matter on the selectivity of heavy metal adsorption and found that the selective adsorption of Zn and Cd was affected. In the absence of organic matter, selectivity under acidic conditions followed the order Pb>Cu>Zn>Cd. As pointed out by Elliot et al. (1986) this order follows the increasing pK of the first hydrolysis product. When organic matter was not removed from the soil Cd became preferred over Zn so the selectivity order became Pb>Cu>Cd>Zn. Extraction of the soil organic matter resulted in an overall decrease in adsorption of all metals and the corresponding CEC was lowered. Elliot et al. (1986) also noticed that the overall adsorption of Cu and Cd decreased by a sizable amount when the soil organic matter was removed.

2.5.3 Ion Radius

For ion exchange material the strength at which cations of equal charge are held is generally proportional to the unhydrated radii, thus, the predicted order of selectivity of the heavy metal cations based on unhydrated radius (Bohn, 1979) is as follows;

Pb^{2+} (.120nm)> Cd^{2+} (.097nm)> Zn^{2+} (.074nm)> Cu^{2+} (.072nm)

Elliot et al. (1986) also found a correlation exists between ionic size and selectivity for a system of divalent metals at equal concentration applied to a soil.

2.5.4 Hard Soft Acid Base Theory

The theory of hard and soft acid base is used to help understand heavy metal chemical phenomena such as solubility, solution equilibrium, gas phase equilibrium, hydrogen bonding, charge transfer complexes, and metal atom and metal surface behaviour (Pearson, 1968). Heavy metals easily lose electrons to form cations which are Lewis acids while most anions are Lewis bases. Hard acids prefer to react or complex with hard Lewis bases and soft acids prefer to complex with soft bases. Some characteristics of lewis acids and bases, hard and soft, are listed below:

Hard Acid	Small in size High Positive charge High electronegativity Low Polarizability No unshared pairs of ele in the valence shell	Soft Acid	Large in size Lowelectronegativity High Polarizability Unshared pairs of electrons in valence shell
Hard Bases	High electronegativity Low polarizability Hard to Oxidize	Soft Bases	Lowelectronegativity High Polarizability Easy to Oxidizes

Hard and soft are relative terms such that borderline species exist that can act relatively hard or soft. Selectivity based on Misono softness parameter (Hard Soft Acid Base Theory) was explored by Puls and Bohn (1988). Puls and Bohn (1988) found that clay minerals seem to be soft bases relative to water which is a very hard base. The HSAB principle predicts that softer cations will replace harder cations, such as the replacement of oxygen by the hydroxide ion in the siloxane ditrigonal cavity which is a harder lewis base.

Sullivan (1977) found it is possible to use HSAB theory for describing ion exchange selectivity reactions in soil systems, if an estimate of softness can be obtained. Misono et al (1967) assumes softness (Y) is the consequence of a metal ion forming a dative pi-bond, and is calculated as a function of ionization potential, charge on metal ion, and ionic radius.

$$Y = \frac{10 \text{ l}_{r}}{\text{l}_{z} + \sqrt{z}}$$

r.

Where I_z is the ionization energy for a cation of valence z and radius

Metal Ion	Pb ²⁺ , Cu ²⁺ , Zn ²⁺
Softness	3.58, 2.89, 2.34

These softness numbers classify $Pb^{2+} > Cu^{2+} > Zn^{2+}$ which would support the selectivity order found by most researchers (Phadungchewit and Yong, 1990; Elliot et al., 1986; Biddappa et al., 1981; Benjamin and Leckie, 1981; Farrah and Pickering, 1977). Sullivan (1977) maintains that the theory describes a wide range of chemical phenomena in a qualitative manner and is helpful as a predicative tool but is not infallible. As can be seen the HSAB theory is composed of individual properties (pK, charge, ionization potential, radius) also used to explain selectivity. Sullivan (1977) stated that the oxidation state of the cation is the dominant factor controlling selectivity. Increased selectivity with increased oxidation state and valence is included in the calculation of Misono Softness Parameter. Sullivan (1977) found in general the higher the softness the more stable the species. Selectivity studies have found that borderline acids (transition metals) are preferred over hard acids (Na¹⁺, Mg²⁺, Ca²⁺, etc...). Sullivan (1977) classifies soil exchange material as a soft base and according to the HSAB theory, harder cations will usually be replaced by softer cations. Research performed by Sullivan (1977) found that this only occurs within the same oxidation state. Most selectivity research is conducted within the same oxidation state since increased attraction with increased oxidation states is easily described by electrostatic forces.

2.6 Modelling

Modelling is used to predict the fate of contaminants in the natural environment. Geochemical equilibrium speciation modelling and contaminant transport modelling are two basic types of modelling used today. The present challenge facing researchers is in bringing these two models together; incorporating equilibrium speciation modelling into transport modelling (Mangold and Tsang, 1991). The model used in this research was a geochemical equilibrium speciation model.

2.6.1 Geochemical Speciation Modelling

Mangold and Tsang (1991) offer an excellent discussion on transport and speciation modelling and reviewed several models. They outlined the theoretical basis of modelling and discussed the many limitations. Mansgold and Tsang (1991) explain that speciation modelling uses thermodynamic databases to find the equilibrium species formed with minimum energy expenditure (Gibbs Energy). Allison, et al. (1990) describe that there are two basic approaches to solving multicomponent geochemical speciation problems: 1) minimization of the systems free energy under mass balance constraints - similar method to that described by Tangs and Mangold (1991) or 2) simultaneous solution of non-linear mass action expressions and linear mass balance. Most models can incorporate dissolution and precipitation reactions as well as complexation reactions. Some models can also describe adsorption although more information is required from the user since thermodynamic data on adsorption is specific to the soil and contaminant.

Most equilibrium speciation models assume instantaneous reactions and do not account for kinetics, which is a problem when considering some redox reactions and other reactions that are relatively slow.

2.6.2 Adsorption Modelling

When modelling surface reactions an operational model must be used to describe the adsorption. Both electrostatic and non-electrostatic models are available, electrostatic models being diffusion double layer models and non electrostatic models typically being isotherm and mass action models. Electrostatic models, such as Gouy Chapman, Stern, Constant Capacitance, Triple Layer Model and the Ion Hydration Model, were not used and therefore will not be discussed in detail.

Adsorption Isotherm models such as Linear, Langmuir and Freundlich models describe the equilibrium distributions of adsorption with the concentration of adsorbate in solution at constant temperature. There are other adsorption isotherm models less frequently used such as BET and Gibbs models.

The linear model is the simplest adsorption isotherm model. It describes a constant partitioning of the solute between the liquid phase and the adsorbing surface. Generally, linearity is found to be unrealistic although it is often the adsorption model used in contaminant transport modelling. $q_e = K_p C_e$

K_p = partitioning coefficient

- qe the amount of solute adsorbed per unit weight of adsorbent.
- C_e equilibrium concentration of liquid phase.

The Langmuir model (Langmuir, 1916a, 1916b, 1918) assumes a constant energy of adsorption which is independent of surface coverage. The adsorption occurs at localized sites with no interaction between adsorbate particles and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate.

$$q_e = Q_o bC_e$$

1+bCe

- Q_o the solid phase concentration corresponding to complete coverage of available sites or the limiting adsorption capacity.
- b the adsorption coefficient.

The Freundlich model (Freundlich, 1926) is based on experimental data and takes the form of;

$q_e = K_f C_e^{1/n}$

Where, K_f and n are constants. K_f is an indicator of adsorption capacity and 1/n is an indicator of the energy of the reaction.

Benjamin, M.M. and Leckie, J.O., (1981) discussed adsorption isotherm modelling of heavy metals in their research on multiple site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. They described the Langmuir adsorption isotherm as treating surface sites analogous to dissolved complexing ligrands, further, it is derived by combining an adsorption equilibrium constant with a mass balance on the total number of adsorption sites. However, the Freundlich adsorption isotherm is derived by assuming that the free energy of adsorption decreases logarithmical as adsorption density increases.

The Ion Exchange model is a mass action model which describes the exchange of an ion in solution for an ion adsorbed on the solid soil surface. The ion exchange model assumes the surface site is originally occupied by an exchangeable ion that is released into solution during the exchange process, as shown by the following expression:

clay- $M_1 + M_2 = clay-M_2 + M_1$ $M_1 = initially adsorbed ion$ $M_2 = ion adsorbed by displacing M_1$

Under this model the concentration of released ions (M_1) could be used to determine the amount of ion exchange adsorption occurring in the overall retention.

Bladel et al. (1993) studied ion exchange adsorption in soil suspensions and explained that the K_c selectivity coefficient, when applying the mass action theory, is as follows:

 $K_{c} = \frac{(M_{2})\{M_{1}\}TM_{1}}{(M_{1})\{M_{2}\}TM_{2}}$

Where; (), $\{ \}$ and τ represent the equivalent fractions of total exchange capacity occupied by the ions specified, the equivalent fractions and the activity coefficients of the ions in the equilibrium solution, respectively.

Sposito (1985) examined several surface chemical models available and found that good quantitative description can be obtained by curve fitting techniques, but that the adsorption models are not sensitive to the detailed structure of the interfacial region. Sposito (198) believes researchers have found excellent fits to data regardless of the adsorption models and thereby the underlying molecular hypothesis.

Adsorption Reaction Stoichiometry

To model adsorption equilibria accurately, it is necessary to characterize the stoichiometry of the adsorption reaction. Benjamin and Leckie (1981) characterize reactions between surface oxide groups as shown below:

$2SOH + Me^{2+} = S_2O_2Me + 2H^+$	(Stoichiometry 2:1 - 1:2)
SOH + Me^{2+} + H_2O = SOMeOH + $2H^+$	(Stoichiometry 1:1-1:2)

Where SOH represents the surface hydroxyl group and Me represents the metal.

Sposito (1984) described the adsorption of metal cations to form an inner sphere surface complex with a surface hydroxyl group, typical of the constant capacitance model, using the following chemical reactions.

Inner Sphere SOH(s) + $Me^{2+}(aq) = SOMe^{1+}(s) + H^{+}(aq)$ (Stoichiometry 1:1 = 1:1) 2SOH(s) + $Me^{2+}(aq) = (SO)_2Me^{1+}(s) + 2H^{+}(aq)$ (Stoichiometry 2:1 = 1:2)

Sposito (1984) also described the adsorption of a metal cation to form an outer sphere surface complex with a surface hydroxyl group, typical of the triple layer model, using the following chemical reactions. **Outer Sphere**

SOH(s) + $Me^{2+}(aq) = SOMe^{1+}(s) + H^{+}(aq)$ (Stoichiometry 1:1 = 1:1) SOH(s) + $Me^{2+}(aq) + H_2O = SOMeOH(s) + 2H^{+}(aq)$ (Stoichiometry 1:1 = 1:2)

One or two protons are displaced for each divalent cation adsorbed indicating that adsorption to a surface hydroxyl group would have the affect of lowering pH as it displaces H⁺.

If the soil is saturated with a cation then an ion exchange reaction may occur and the adsorbing cation will displace the adsorbed cation according to the law of mass action as shown below and discussed in Section 2.6.2 as ion exchange adsorption.

clay surface- $M_1 + M_2$ = clay surface- $M_2 + M_1$ (Stoichiometry 1:1 = 1:1)

2.6.3 MINTEQA2

The MINTEQA2/PRODEFA2 Geochemical Assessment Model for Environmental Systems, Version 3.0 is a geochemical equilibrium speciation model first developed by Battelle Pacific Northwest Laboratories and used by the U.S. Environmental Protection Agency (USEPA). MINTEQA2 uses a thermodynamic database, developed by the U.S. Geological Jurvey, to model the reactions. The data base is restricted to 25°C and 1 atmosphere conditions (Standard Pressure and Temperature - SPT). The interactive input program PRODEFA2 develops an input file to be executed by MINTEQA2 through the executable program Minrun.

MINTEQA2 works with activities (thermodynamic equivalent of concentration, refer to Appendix A) rather than concentrations because it calculates equilibrium in terms of thermodynamics. The cycle of calculations followed by MINTEQA2 is called the equilibrium constant method in that it

simultaneously solves the linear mass action expressions and linear mass balance relationships.

Program Algorithm

Aqueous Phase Equilibrium

1) First, the program takes all of the components in the system and guesses at their activities (typical components being Pb, Cu, Zn, NO_3).

2) Then species activities are calculated based on the mass action equations in the database and/or provided by the user.

3) From the activities of the species the program calculates the concentration of the individual components which derive the species (M_T) .

4) The concentrations of the components are then compared to the equilibrium concentration entered by the user.

5) If the concentrations of components do not match concentrations entered by the user, within a limited tolerance level, the program performs a new guess at the activities and returns to the first step of the calculation cycle.

Once equilibrium within the aqueous phase is established it must

check for over saturation and under saturation of the species present.

Overall Equilibrium

1) Species which are over saturated in the aqueous phase are allowed to precipitate and enter the solid phase starting at the species with the highest saturation index. Any species that are under saturated and have a solid phase are allowed to dissolve in the same respect.

2) This step of dissolution and precipitation has now changed the concentrations of species in the aqueous phase and the program returns to the first step to reach equilibrium in the aqueous phase.

The whole cycle continues until overall equilibrium is reach within all phases and convergence is reached within a limited tolerance.



Any surfaces available for adsorption are treated simply as another aqueous phase ligand with which components can react. Adsorption is simply modelled as an aqueous phase reaction, and is part of the aqueous phase equilibrium calculations.



CHAPTER 3

MATERIALS AND METHODS

3.1 Soil Preparation

The soil used in this research is a soil obtained from pulverized shale, consisting of sand, silt, and clay portions. The soil is commercially identified as Sealbond obtained from the Canada Brick Company. To ensure uniformity and avoid the presences of multiple cation forms the soil was saturated with calcium (Ca) and magnesium (Mg). While it is common to saturate a clay soil with one cation few researchers perform a saturation with two cations. Natural clay soils are saturated with several cation species (Ca, Mg, Na, K), thus, a saturation with two cations offers a more interesting and natural situation.

The soil was washed repeatedly (6 times) in an equal proportioned mixture of 1 N CaCl₂-6H₂O and 1 N MgCl₂-6H₂O solution. The suspension was prepared at a 4% soil to solution concentration by mass. In an effort to wash out the excess chloride the soil was then washed with a 20:80 ethanol:water mixture. After each ethanol:water wash the soil supernatant was tested for excess chloride (Cl) by means of a simple silver nitrate test. After four washes the silver nitrate test did not detect excess Cl⁻ and a titration confirmed a non-detectable level of Cl⁻ in the supernatant. The clay soil was then air dried in a desiccator for a period of 2 weeks and once dry, ground to a fine texture.

3.2 Identification of Soil Properties

Laboratory analyses performed on the treated soil to identify the soil properties are listed below:

Mineralogical Analysis Soil pH Soluble Cations Cation Exchange Capacity Exchangeable Cations Surface Area Organic Content Carbonate Content Amorphous Material Determination

For determination of mineral composition, four x-ray diffraction slides were prepared using four different soil treatments as described by Starkey et al. (1984) and Mitchell (1975). The slides were then analyzed using a Siemens D-500 x-ray diffractometer.

The soil used for the following prepared slides was first fractionated and passed through a number 200 sieve (division between silt and clay size particles).

- Untreated sample	No Treatment
- Acid Treated Sample	Sample heated in concentrated HCL acid for 30 minutes and washed with distilled water 3 times.
- Heat treated Sample	Prepared slide was heated in 550°C furnace for 40 minutes.
- Magnesium Saturated Sample	Sample was washed twice with $MgCl_2$ solution and twice with $Magnesium$ Acetate and once more with $MgCl_2$ and concluded with three washes with ethanol and water.

37

Soil solution pH was measured in a 1:10 soil: distilled water solution ratio with a Beckman Φ^{TM} 12/pH/ISE meter.

To determine the amount of soluble cations, a sample of the soil was washed in distilled water for a period of 24 hours and measured for Calcium (Ca), Magnesium (Mg), Sodium (Na) and Potassium (K). The soluble cations were determined at both an unadjusted initial pH and an adjusted initial pH of 3.

The cation exchange capacity (CEC) was determined using three methods, 2 non-pH dependent and 1 pH dependent. The first method employed at pH 7 uses silver-thiourea as the saturating agent, this method was conducted as described by Chabbra et al. (1975). The second method used armonium acetate as the saturating agent. Both of these methods were also used to obtain the proportions of extractable cations found on the clay surface. To determine the exchangeable cation proportions first the soluble cation concentrations must be subtracted from the extractable cation concentration. The pH dependent method for the determination of CEC is an earlier derivation of a procedure developed by Hendershot (1993) but employs ammonium chloride as the saturating agent instead of barium chloride. Both CEC and AEC can be measured as a function of pH making this method particularly useful for pH variable charge clay soils such as kaolinite. In fact, this method is useful for measuring the pH dependent charge of all variable charge surfaces such as amorphous metal oxides.

The presence of amorphous materials was determined using the method described by Segalen (1968). The three types of amorphous materials examined were silicon dioxide (SiO₂), iron oxide (Fe₂O₃), and aluminum oxide (Al₂O₃).



The surface area was measured using ethylene glycol-monoethyl ether (EGME), according to the procedure described by Eltantaway and Arnold (1973).

The titration method described by Jackson (1956) was used to determine the organic content of the soil.

Soluble carbonate, bicarbonate and chloride content was determined using the titration method described by Hesse (1971).

3.3 Stock Solution Preparation

Stock heavy metal solutions were prepared from the following nitrate forms of each heavy metal studied; $Pb(NO_3)_2$, $Cu_2(NO_3)_2$ -2.5H₂O, and $Zn(NO_3)_2$ -6H₂O. The stock Pb, Cu and Zn solutions were prepared at a concentration of 300 meq/L of metal (0.3 Normality or 0.15 Molarity). For example, to prepare a 300 meq/L stock solution of Pb (given the molecular weight of Pb is 207.2), 49.68 g of Pb(NO₃)₂ (Molecular Weight 331.20) was added to 1 litre of distilled water. For descriptions of concentrations units please refer to Appendix A.

 $0.15M \text{ of Pb/L} = 31.08 \text{ g of Pb/L} = 49.68 \text{ g of Pb(NO}_3)_2/L$

Dilutions and pH adjustments

Other concentrations were prepared by accurately measuring the appropriate amount of stock solution with a pipette or volumetric flask and diluting it to a predetermined volume with distilled water (ie. to make a 75 meq/L solution from 300 meq/L, 250 millilitres (mls) of stock solution is diluted to 1 L). If the solution then requires a pH adjustment the pH was lowered using Nitric Acid (HNO₃) or raised using Sodium Hydroxide (NaOH).



3.4 Batch Equilibrium Tests

The three heavy metals studied (Pb, Cu, Zn) in this research were mixed with the prepared sealbond clay soil in a suspension test also known as a batch equilibrium test. Metal concentrations ranged from 6 to 300 meq/100g of soil. The heavy metals were used in their nitrate forms; $Pb(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$. The following table (Table 3.1) shows the various combinations of heavy metals applied.

Table 3.1 - Batch Equilibrium Tests Performed			
Type of Test	Metals Applied	Conc. Range of each metal (meq/100g)	
One Heavy Metal	Pb Cu Zn	2-300 meq/100g 8-300 meq/100g 6-300 meq/100g	
Two Heavy Metal (Equal meq/100g)	Pb:Cu Cu:Zn Pb:Zn	10 - 100 meq/100g 10 - 100 meq/100g 10 - 100 meq/100g	
Three Heavy Metal (Equal meq/100g)	Pb:Cu:Zn	10 - 100 meq/100g	

Two sets of batch equilibrium tests were conducted for each scenario. One set of heavy metal solutions were applied with an initial pH measurement but no pH adjustment, and the other set of solutions were applied at an adjusted initial pH of approximately 3. Upon completion of the batch equilibrium test and supernatant separation, the pH of the supernatant was measured.

In order to easily compare the results of this research to previous research conducted by Phadungchewit (1990) a similar batch equilibrium procedure was required. The solutions were applied to each sample using a 1:10 ratio, 3 grams of dry soil to 30 millilitres (mls) of solution. The soil



suspension was equilibrated by shaking in a horizontal shaker at room temperature for a period of 24 hours. The samples were then centrifuged at approximately 5,000 rpm for 10 minutes. This method is similar to the method recommended by Griffin et al. (1986) to the ASTM as a standard method.

In the final supernatant the equilibrium concentration of the heavy metals and concentration of Ca and Mg released were measured using a GBC902 double beam atomic adsorption spectrophotometer. The amount of heavy metal retained in the soil was calculated as the difference in the heavy metals applied and remaining in solution with respect to a 100g of soil.

 $C_{R} (meq/100g) = (C_{o} - C_{E}) * V_{c} * 100$ M_{s}

 C_o = Initial Concentration (meq/L) C_E = Equilibrium Concentration (meq/L) C_R = Retained Concentration (meq/100g) V_s = Volume of Solution (L) (typically 0.03L) M_s = Mass of Soil (g) (typically 3g)

The concentration of Ca and Mg in the supernatant minus the soluble Ca and Mg is presumed to be the concentration displaced from the soil surface by ion exchange adsorption of the applied heavy metals as shown by the reaction below.

Surface-(Ca or Mg) + Metal = Surface-Metal + (Ca or Mg)

3.5 Estimation of Heavy Metal Precipitation (Blanks)

During a batch equilibrium test heavy metals are removed from solution by precipitation and adsorption mechanisms, therefore, the two processes must be considered in analysing any set of batch equilibrium test



results. However, distinction between the two processes is not always easy. Precipitation can occur on the surface of the soil particle, and in the pore water as the formation of a new solid phase. Adsorption characterises accumulation at the soil water interface do to interactions with the soil particle surface, while precipitation is concerned with the formation of a separate new solid phase. However, as described by Sposito (1984) precipitation of mixed precipitates can form inhomogeneous solids restricted to a thin outer layer, and thereby, difficult to distinguish from adsorbed phases.

Precipitation test were conducted using the three heavy metals in solution at varying concentrations and pHs. The precipitation was performed in the absence of soil to ensure the only mechanism of removal from solution was precipitation. Single metal solutions (Pb, Cu, Zn), double metal solutions (Pb+Cu, Pb+Zn, Cu+Zn) and triple metal solutions (Pb + Cu + Zn) were prepared at 6 different total metal concentrations ranging from 6 to 300 meq/L of equal individual metal concentration.

From the stock solutions of 300 meq/L (Pb, Cu or Zn) lower concentrations were prepared by measuring an appropriate amount of stock solution and diluting it with distilled water. For each concentration and combination of metals 5-50 ml solutions were prepared and the pH of each solution was adjusted. The adjusted pHs were approximately 3, 4, 5, 6, and 7. Nitric Acid (HNO₃) was used to decrease pH and Sodium Hydroxide (NaOH) was used to increase pH. The solutions were left to equilibrate overnight and then the pH was measured again and re-adjusted, if necessary. The following table (Table 3.2) details the precipitation tests conducted.

Table 3.2 - Precipitation Tests Conducted			
Test Type (Number of Metals)	Metals Applied (Equal Proportions)	pH Range	Range of Initial Metal Concentrations Individual / Total (meq/L)
One Heavy Metal	Pb Cu Zn	3 - 7	2.5 - 300 / 2.5 - 300 10 - 300 / 10 - 300 10 - 300 / 10 - 300
Two Heavy Metals (Equal meq/100g)	Pb:Cu Pb:Zn Cu:Zn	3 - 7	10 - 100 / 20 - 200 10 - 100 / 20 - 200 10 - 100 / 20 - 200
Three Heavy Metals (Equal meq/100g)	Pb:Cu:Zn	3 - 7	10 - 100 / 30 - 300

3.6 Geochemical Modelling

The MINTEQA2/PRODEFA2 Geochemical Assessment Model for Environmental Systems, Version 3.0, was used to model the experimental results. The program is a geochemical equilibrium speciation model first developed by Battelle Pacific Northwest Laboratories and later refined and used by the U.S. Environmental Protection Agency. MINTEQA2 uses the thermodynamic database developed by the of the U.S. Geological Survey. The data base is restricted to 25°C and 1 atm (SPT). The interactive input program PRODEFA2 helps the user develop an input file. The program algorithm was summarized in Section 2.6.3. The general approach used by MINTEQA2 for solving multicomponent chemical equilibrium problems is called the equilibrium constant method. It simultaneously solves nonlinear mass action expressions and linear mass balance relationships.

MINTEQA2 offers seven adsorption models including distribution coefficient K_d, isotherm models (Langmuir and Freundlich), mass action model (ion exchange), and surface complexation and electrostatic models (triple



layer, constant capacitance and diffusion double layer). After experimenting with all the models the Langmuir Isotherm model was chosen to model adsorption in the laboratory experiments for two reasons. First, the Langmuir model was chosen because it allowed the user to examine competition by limiting the concentration of surface adsorption sites. Second, in the calculation of K_L it was possible to consider 0 equilibrium concentration of metals in the final supernatant. All the electrostatic complexation models required data that could not be measured in the laboratory or calculated with the information available and therefore, could not be used. Neither the Freundlich nor the Ion Exchange Models, according to the MINTEQA2 calculation methods, allows the user to consider 0 equilibrium concentrations in the calculation of K - both models result in a division by 0 and, therefore, an error. Furthermore, the Ion Exchange Model limits the specification of initial surface cations to 1 whereas the soil in this research was saturated with two cations (Ca and Mg). The Freundlich model can examine competition, but only by varying the stoichiometric parameter of each adsorbing metal ion, since the Freundlich model assumes unlimited adsorption sites on the soil particle surface.

For each set of batch equilibrium results, when it was possible, an equilibrium constant K_L for partitioning was determined and used in the model.

$$\frac{[M]}{[SOHM]} = \frac{1}{K_L[SOH]_T} + \frac{[M]}{[SOH]_T}$$

Where; M is the equilibrium concentration of the metal. SOHM is the retained concentration of metal. SOH_{τ} is the concentration of adsorption sites.

. .

The author recognizes that there are many assumptions involved in using the Langmuir Isotherm model. The Langmuir model assumes a constant energy of adsorption which is independent of surface coverage and assumes that the adsorption occurs at localized sites with no interaction between adsorbate particles. The model also assumes maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. However in reality, multi-layer adsorption likely does occur and particles do interact with each other especially as solute concentrations increase. Ion exchange stoichiometry may also oversimplify the system since one to one ion exchange is assumed when in fact more complicated stoichiometric reactions may occur. Researchers have indicated that ion exchange does not accurately describe adsorption on clay soils (Farrah and Pickering, 1979).

Also required to model the adsorption is the stoichiometry of the adsorption reaction. Since only one K value could be calculated from the laboratory research only one adsorption reaction could be provided for each metal, if an isotherm fit was obtained. Since the soil was originally saturated with Ca and Mg, the maximum concentration of Ca + Mg released during each set of batch equilibrium tests was used to obtain a concentration of surface sites, based on ion exchange stoichiometry as shown below.

Surface-Ca + Pb^{2+} = Surface-Pb + Ca²⁺

Using the quantity of Ca + Mg released is also an assumption that may oversimplify the system. By assuming the maximum Ca+Mg released represents the concentration of surface sites all other adsorption reactions which do not involve the release of a Ca or Mg ions are eliminated. Also, ion exchange does not account for multiple species forms. However, according to the research presented in Section 2.3.2 ion exchange may not be an unreasonable assumption at pH levels below 6 where the Pb²⁺, Cu²⁺, and Zn²⁺ ions are dominant.

The PRODEFA2 program is used to develop an input file to be run by MINTEQA2. The PRODEFA2 program is divided into four editing levels in which information is entered. A great deal more information could have been entered then was, but as recommended in the program guide, the problem was kept as simple as possible. A typical sequence of information entered in the running of this program is presented below.

Editing Level 1

The units of concentration are set, in this case to meq/L. Over saturated solids were permitted to precipitate. The pH was set to the equilibrium pH of the final supernatant.

Editing Level 2

Aqueous components (ions; Pb^{2+} , Cu^{2+} , Zn^{2+} and counter ions; NO_3) were specified and total initial concentrations were entered.

An adsorption model was specified, in this case the Langmuir model, and adsorption site concentrations was specified using the total concentration of Ca and Mg released.

The surface adsorbed species were named and the adsorption reaction stoichiometry was given.

ie. Surface-(Ca+Mg) + Pb^{2+} = Surface- Pb^{2+} + (Ca + Mg)

The K_L for partitioning (determined from experimental data) was given.

Editing Level 3

This level acts like a line editor, allowing the user to review all the

· • • •

information entered and make any required changes or corrections.

Editing Level 4

Editing level 4 deals with utility functions. The user can make MINTEQA2 perform a series of multiple runs in which one parameter iterates or changes each time. This allows the user to perform sensitivity analysis on different parameters used in the program (ie. pH, pE, or initial concentration of a component). In editing level 4 the user can also write files importable to a spreadsheet program.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General

The results of all experiments described in the previous chapter are presented in this chapter as follows;

Section 4.2 presents the results of the soil characterization experiments.

Section 4.3 examines the metal precipitation tests results.

Sections 4.4 to 4.8 presents the experimental and modelling results of the batch equilibrium tests.

Section 4.9 offers an overall summary and general discussion of the results.

For each set of batch equilibrium tests, graphs illustrating retention and mass balance are required to present the experimental results, and isotherm graphs are used to interpret the results. Throughout the graphically presented results in Appendix C, a small * is used to indicate hypothetical estimated adsorption concentrations which have been calculated using the total retention and heavy metal solution precipitation results.

The results of the modelling are presented in graphs illustrating percent retained and isotherms in the same manner as the experimental data. Graphs depicting mass balance are not provided from the modelling since mass balance is intrinsic to the modelling results. The modelling results presenting



percent retained versus initial concentration are often plotted on the same graph as the experimental data for easy comparison. Isotherm plots are also presented for the results of the modelling, where possible, side by side with the experimental isotherms for easy comparison (Appendix C).

The geochemical modelling results provide quantitative analysis of equilibrium species. As was explained in Section 2.3.1, the experimental equilibrium concentration of cations, measured using atomic absorption spectrophotometry, does not provide information on speciation. Whereas, the modelling results give detailed speciation information which is of particular interest. Therefore, in each section (Sections 4.4...4.8), tables listing the modelling speciation are presented with discussion.

4.2 Soil Characterization Results

Physical and chemical properties of the soil experimentally determined are presented in Table 4.1. below:

<u>Table 4.1 - Se</u>	<u>oil Properties and</u>	Composition

Soil pH (1:10 soil:water)		8.7	
Cation Exchange Capacity			
Silver Thiourea Method		40 mea/100g	
pH Dependent Method		38 meg/100g	
(no pH dependency evident)		1 0	
Ammonium Acetate Method		35 meq/100g	
Exchangeable Cations			
Silver Thiourea Method	Ca	87%	
	Mg	13%	
Ammonium Acetate	Ca	85%	
	Mg	15%	



Table 4.1 - Soil Properties and Composition Cont'd

Soluble Cations	Ca (pH3) Mg (pH3)	0.3(meq/100g) 1.1(meq/100g) 0.7(meq/100g) 1.7(meq/100g)
Surface Area		55 m²/g
Organic Content		0.9 %
Amorphous Material	SiO ₂ Fe ₂ O ₃ Al ₂ O ₃ Total	12 mg/g 27 mg/g 1 mg/g 40 mg/g
Soluble Carbonates		0%
Clay (<2 microns) (Phadungchewit, 1990)		40%
Mineral Composition (in decreasing abundance)		Illite Chlorite Quartz Feldspar Calcite

The results of the soil properties and composition analysis are slightly different than those found by Phadungchewit (1990). Although the same soil was used in her research, she did not subject it to any pretreatment. It is believed that in this study the pretreatment of the Sealbond resulted in a loss of some of the amorphous, organic, and carbonate phases, and perhaps, some very fine clay fractions, affecting the measured amorphous, organic, and carbonate quantities, and the Specific Surface Area.

Chi, et. al. (1977) examined the Ca and Mg exchange for sodium on

three different illite soils. The exchange isotherms were examined and the relative strength of Ca and Mg adsorption was assessed. They found that the exchange followed a Gapon-type equation regardless of whether Ca or Mg was the dominant cation. No evidence was found that Ca ions were being held stronger at exchange sites than Mg.

In the preparation of the illite soil for experimental use, Ca and Mg was applied to the soil at equal concentrations in an effort to saturate the exchange sites with Ca and Mg (Section 3.1). The results of exchangeable cation determination revealed that approximately 85% of the exchange sites are occupied by Ca and 15% by Mg. Obviously, the soil selectively preferred Ca for adsorption over Mg.

4.3 Metal Precipitation Test Results

For each combination of metals tested in the batch equilibrium experiments, parallel sets of precipitation tests were conducted to determine the concentration of metals in solution at various pH levels, in the absence of soil. The following Table 4.2 summarises the pH range at which precipitation starts, and Figures 4.1 to 4.7 depict the precipitation results of each test. The pH at which precipitation begins was evaluated as the point where the curve (Figures 4.1 - 4.7) starts to break - the pH at which concentrations starts to drop drastically below the initial concentration. During the precipitation tests the formation of precipitates was witnessed. Often as precipitation began the solutions became turbid and actual particulates or flocs could be seen.

Table 4.2 - Precipitation pH of Metal Solutions		
Precipitation Test Type	Metal(s) in Solution	Approximate pH at which Precipitation commences
Single Metal Tests	РЬ	> 100meq/l - pH4 < 100meq/l - pH5
	Cu	pH4 (Higher initial concentrations lower final concentration)
	Zn	pH6
Double Metal Tests	Pb Cu	pH5 pH5 (Cu precipitates more)
	Zn Pb	pH5 pH5 (Pb precipitates more than Zn)
	Cu Zn	рН4 рН5
Triple Metal Test	Pb Cu Zn	рН4 рН4 рН4

Single metal precipitation begins at the lowest pH for Cu followed by Pb and Zn (Figures 4.1 to 4.3). Copper (Cu) acts differently than Pb and Zn by precipitating out to lower concentrations with increased initial concentration, in what can be described as a "sweep floc" effect.



Figure 4.1 - pH effect on the precipitation of Pb at varying initial concentrations.



Figure 4.2 - pH effect on the precipitation of Cu at varying initial concentrations.



Figure 4.3 pH effect on the precipitation of Zn at varying initial concentrations.

.7

As can be seen from the two metal precipitation results one metal may facilitate the precipitation of the others (Figures 4.4 - 4.6). In the case of Cu and Zn (Figure 4.6), Zn acts in the same manner as increased Cu concentration did in the single species Cu test by causing more precipitation of Cu at a lower pH, therefore, in the overall precipitation initial metal concentration is an important factor. This effect is not as predominant when Pb and Cu is precipitated together (Figure 4.4), in fact Cu precipitation is inhibited when in the presence of Pb although Pb precipitation appears to be facilitated by the presence of Cu. Compared to the individual metal precipitation results - the curves describing the double metal Pb and Cu precipitation would fall somewhere in between the two sets of single metal curves describing Pb and Cu precipitation alone.



Figure 4.4 - pH effect on the precipitation of Pb and Cu at equal initial concentrations.

54

In the case of Pb and Zn, precipitation (Figure 4.5) is more or less the same as it was in a single species solution, however, the Pb precipitation is slightly facilitated by the presence of Zn. It is also interesting to note that when all three metals are together in solution each will precipitate out at a lower pH than when they are in solution as a single species.



Figure 4.5 - pH effect on the precipitation of Pb and Zn at equal initial concentrations.


Figure 4.6 - pH effect on the precipitation of Cu and Zn at equal initial concentrations.

In a triple metal solution (Figure 4.7) at total concentration 300 meq/l (100 meq/l of each species) Cu precipitation is basically the same as the 300 meq/l single species Cu precipitation curve, therefore, Cu precipitation seems to be affected by the total metal concentration of the solution and is not metal specific. However, Pb and Zn precipitation in the triple metal tests is greater than the equivalent single metal test in terms of total concentration, therefore, the presence of other metals seems to facilitate the precipitation of Pb and Zn.





In summary the precipitation study indicates, Cu precipitation is not metal specific, increased precipitation occurs with increased total metal concentration in what appears to be similar to a sweep floc effect. In other words an initial concentration of 300 meq/l of Cu will precipitate out in the same manner (in terms of % of initial concentration) as a 100 meq/l Cu concentration with equal concentrations of Pb and Zn. However, Pb and Zn are facilitated by the presence of other metals, especially Cu, and precipitation will be greater in a 3 metal solution of equal total metal concentration as in the single metal solution.

The observed results of the precipitation tests can probably be

correlated to the difference in the activities of the solutions (Appendix A) which are a function of the ionic strength and valence of charged species. Activity is the thermodynamic equivalent of concentration and accounts for the interaction between ions in solution as concentrations increase. In a nonideal solution the activity coefficient is below 1 and the value of the activity coefficient approaches unity as the solution approaches infinite dilution. The ionic strength for different mixtures of heavy metals at the same total metal concentration will vary due to the different species present. For example, at a set pH, one metal is present in its ionic form of valence 2+ (i.e. Pb²⁺), but another metal may be present as a hydroxide (i.e. ZnOH⁺), at equal concentrations the metal speciated at a higher valence will have a lower activity. Generally, in non ideal solutions the activity (effective concentration thermodynamically) will be lower than the chemical concentration and the higher the valence of the species the lower the activity.

Copper (Cu) does have the lowest K_{sp} and therefore should precipitate at the lowest pH, which is what was found in the single metal tests. Copper (Cu) is also present at high concentrations as a neutral species (Cu(OH)₂) at low pHs, before either Pb or Zn (Section 2.3.2) form their respective neutral species, making Cu closer to an ideal solution and the activity closer to the chemical concentration. However, Pb and Zn may have more charged species in solution, especially at low and neutral pHs, and therefore, will have activities less than their chemical concentrations making them act thermodynamically as though they were at a lower concentrations than Cu.

The precipitation research was done with heavy metal solutions at varying pHs in the absence of soil. If soil had been present it would of been impossible to differentiate between adsorption and precipitation removal from solution. Since the precipitation was examined without clay the applicability to precipitation in the presence of clay is questionable. A clay surface can facilitate precipitation by concentrating ions at it surface, influencing local pHs, and acting as a nuclease for growth of precipitates. This is suggested in a statement by Farrah and Pickering (1979) which proposes that the presence of clay likely lowers the pH of hydroxide species precipitation. In a batch equilibrium test both adsorption and precipitation are occurring simultaneously - one affecting the other.

The results of the precipitation research are used to estimate a hypothetical adsorption from the retention data. For each batch equilibrium test performed, the equilibrium supernatant pH was used to estimate the maximum possible precipitation from solutions based on the precipitation tests experimental results. The speculated adsorption was assumed to be the retention minus the calculated precipitation. The author realizes this is an oversimplification of the problem since both adsorption and precipitation processes are occurring simultaneously one affecting the other. Therefore, the hypothesized adsorption based on precipitation data, is presented for discussion purposes only and should not be seen as an absolute value.

4.4 Single Metal Batch Equilibrium Tests

4.4.1 Experimental Retention

For each metal, two sets of metal solutions were applied to the pretreated sealbond soil, one at an adjusted pH of 3, and the other without any pH adjustment. For a detailed description of the batch equilibrium test experimental procedure refer to Section 3.5. Comparisons will be made throughout this thesis between the adjusted and unadjusted pH batch equilibrium tests, however, the reader should realize that the solution tests involving adjusted initial pH 3 solutions represent a well controlled situation in terms of pH, but, the tests performed with unadjusted initial pH solutions were not controlled. In the unadjusted initial pH tests, the pH of the heavy metal solutions were measured and were found to vary up to 2 or 3 units

because the heavy metal solution pHs decreased as heavy metal concentrations increased (Section 2.3.2). However, the pH of the unadjusted initial pH metal solutions were always greater than the pH 3 of the adjusted pH solutions, allowing a comparison between the two sets of tests on a very general level. For a graphic presentation of initial and final pH of the metal solutions refer to (Appendix D, Figures D.44, D.45, D.46).

The retention curves demonstrate the percent of the initial applied concentration retained. As shown on Figures 4.8a,b, close to 100 % retention was obtained for Pb up to an initial applied metal concentration of 75 meq/100g. Similarly, for Cu (Figures 4.9a,b) up to an initial applied metal concentration of 100meq/100g close to 100% retention has been obtained. Beyond these concentrations, the retentions decrease with increased initial metal concentrations. For Zn (Figures 4.10a,b), 100 % retentions were not obtained at any concentration, however, the highest retentions were obtained at the lowest initial Zn concentrations with retention decreasing as concentrations increased.

In the single metal solution tests, based on the total quantity of metal retained, it appears that Cu was the most readily retained, followed by Pb and Zn (Figures 4.8 - 4.10). However, based on the calculated K_L (Langmuir Equilibrium Constants, Table 4.4) values for the isotherms (Appendix C, Figures 4.23 - 4.28) Pb had the highest retention. It is important to note that the only competition that exists in the single metal batch equilibrium tests is between different species of the same metal (ie. Pb²⁺, PbOH⁻, Pb(OH)₂). The single metal batch equilibrium tests were not a competitive adsorption scenario between metals, each metal was mixed individually and separately with a measured soil sample, allowing a comparison between three sets of single metal batch equilibrium test results.

Lead (Pb) and Cu retention increased when the initial pH of the solution was lowered to 3. This is contrary to the general understanding of the effect of pH on retention (Farrah and Pickering, 1976, 1977, 1979; Harter, 1983; Phadungchewit, 1990). Researchers have traditionally found that retention increases as pH increases, owing to heavy metal precipitation mechanisms. Contrary to Pb and Cu, Zn retention decreased for the tests involving adjusted initial pH 3 solutions. The distinction that must be made here is that researchers usually quote the equilibrium supernatant pH (the supernatant pH at the end of the batch equilibrium test) when they discuss the effect of pH on retention. The increased retention noted in this study occur when a lower initial adjusted pH of the heavy metal solution was added to the soil. The final equilibrium pHs of the supernatant in both the unadjusted and adjusted pH cases were actually quite similar (Table 4.3 and Figures D.44, D.45, D.46 in Appendix D), because of the high buffering capacity of the sealbond soil, allowing the soil to resist change in pH upon the addition of acids (Phadungchewit, 1990).

Perhaps lower initial pH limits early precipitation of metals increasing the concentration gradient driving force for adsorption reactions. According to Sposito (1984) adsorption releases H⁺ ions, if the adsorption reactions reflect the Stoichiometry presented by Sposito (1984), discussed in Section 4.6.2. The final pH of the Zn batch equilibrium tests were higher than the other metals (Table 4.3) perhaps indicating less adsorption may be occurring (Sposito, 1984). By lowering the initial pH of the metal solutions the heavy metal are driven to their ionic form (Me²⁺) as shown by the following equilibrium expressions describing the formation of hydroxocomplexes.

$$Me^{2+}{}_{(aq)} + H_20 - MeOH^{-}_{(aq)} + H^+$$

 $Me^{2+}{}_{(aq)} + 2H_20 - Me(OH)_{2(aq)} + 2H^+$
 $Me^{2+}{}_{(aq)} + 3H_20 - Me(OH)^+{}_{3(aq)} + 3H^+$



The ionic species (Me²⁺) has a higher affinity for the clay particle surface, based on electrostatic attraction, perhaps explaining the increased adsorption with decreased initial solution pH.

	Table 4.3-Initial and Final pH Ranges							
	for Single Me	letal Batch Equilibrium Tests						
		<u>Unadjusted</u>	Adjusted					
Pb	Initial Supernatant pH	4.1-6.6	3					
	Final Supernatant pH	4.3-7.6	4.6-7.5					
Cu	Initial Supernatant pH	3.9-4.9	3					
	Final Supernatant pH	4.4-7	4.5-7.1					
Zn	Initial Supernatant pH	5.5-6.8	3					
	Final Supernatant pH	5.4-7.5	5.6-6.8					

Another interesting difference between the metals is the pH of the initial unadjusted metal solutions. Copper (Cu) solutions have the lowest initial pH followed by Pb and than Zn. Benefield et al. (1982) explained that when a salt containing metal ions dissolves in water, hydrogen ions are produced resulting in an acidic solution (Section 2.3.2). This is also reflected in the initial pH of the three solutions. The reaction with water to form $Cu(OH)_2$ produces two H⁺ ions when the reaction for CuOH⁻ only produces one H⁺ ion, possibly the lower initial pH in the Cu solution is an indicator of the speciation, specifically, that there may be more Cu present as Cu(OH)₂ than in the other solutions. A comparison of the speciation of Pb, Cu and Zn was also performed by Harter (1983) and shows the predominance of Cu(OH)₂ at neutral pHs over Zn(OH)₂ and Pb(OH)₂.

The K_{sp} of Cu(OH)₂ is the lowest of the three metals (1.6 x 10⁻¹⁹) followed by Zn than Pb indicating Cu(OH)₂ will precipitate the easiest over all the other metals (Section 2.3.2). Once the solubility of this species is



exceeded precipitation will commence indicating Cu is the most likely to be removed from solution due to precipitation mechanisms followed by Zn and Pb (Section 2.3.2).

4.4.2 Modelled Retention and Speciation

The single metal batch equilibrium tests were modelled using the MINTEQA2/PRODEFA2 Speciation model. The retention and speciation are discussed and detailed in this section. The experimental and modelling retentions are graphical presented on Figures 4.8a to 4.10b and the speciation results given by the geochemical model are summarized in Tables 4.5a to 4.7b. For a detailed description of the model, and a typical outline of the information provided for the modelling, please refer to Section 3.5. The Langmuir isotherm adsorption model was chosen as described in Section 3.5. The K_L (Langmuir partitioning coefficients, Table 4.4), obtained from the experimental results, were used to describe the adsorption reaction with excellent r^2 (least squares) fits. The maximum concentration of Ca and Mg released from exchange sites, during the batch equilibrium tests, was employed to define a concentration of adsorption sites.

The retention results of the modelling are presented on the same graph as the experimental results for easy comparison (Figures 4.8a,b; 4.9a,b; and 4.10a,b). The MINTEQA2 modelled single metal retention of Pb and Cu at concentrations below 100 meq/100g but as concentrations increased and retention decreased experimentally, the model started to underestimate retention for Zn in both sets of tests (Figures 4.10a,b), and Pb and Cu for the tests conducted using the initial adjusted pH3 solutions (Figures 4.8a, 4.9a).

Table 4.4 Langmuir K values Calculated from Experimental Data - Single Metal Tests						
Batch Equilibrium Tests Modelled	K _L (Langmuir) for Retained Conc.	Comments				
Lead (no pH adjustment)	Log K _L = 4.07 r ² = 0.99					
Lead (pH 3 adjustment)	Log K _L = 3.93 r ² = 0.99	Last point dropped to obtain a better fit.				
Copper (no pH adjustment)	$Log K_1 - 3.2$ r ² - 0.98	Last point dropped to obtain a better fit.				
Copper (pH 3 adjustment)	Log K _t - 3.49 r ² - 0.96					
Zinc (no pH adjustment	$Log K_{L} = 2.00$ r ² = 0.97					
Zinc (pH 3 adjustment)	$Log K_{L} = 1.99$ r ² = 0.98	First point dropped to obtain a better fit.				



Figure 4.8a - Pb Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH solutions.



Figure 4.8b - Pb Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3 solutions.



Figure 4.9a - Cu Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH solutions.



Figure 4.9b - Cu Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3 solutions.



Figure 4.10a - Zn Retention, experimental and modelled, in the single metal batch equilibrium tests with unadjusted initial pH solutions.





Figure 4.10b - Zn Retention, experimental and modelled, in the single metal batch equilibrium tests with adjusted initial pH 3 solutions.

Information that the model offers that cannot be obtained experimentally is of particular interest. The model separates adsorption on surface sites from precipitation and offers a complete outline of speciation of components at equilibrium. The following tables (Tables 4.5 - 4.7) summarizes the mass balance and speciation results of the MINTEQA2 geochemical speciation model for the single metal batch equilibrium tests. For a detailed description of the speciation tables and how to read them please refer to Appendix A under the heading "How to Read the Speciation Tables"

Lead

At initial metal concentrations equal to and below 100 meq/100g the modelling predicted that Pb exists almost completely as adsorbed and precipitated species (Tables 4.5a,b). Above 75 meq/100g the amount of

retention starts to decrease as the adsorption limits are exceeded and the precipitation ceases. The model predicted that the dissolved Pb in solution would be in the Pb^{2+} and $PbNO_3^+$ forms.

The means of retention are specified by the model (precipitation and adsorption) in the mass balance output (Tables 4.5-4.7. For Pb (unadjusted initial solution pH), the model predicts increasing removal by precipitation with increasing concentration up to an initial solution concentration of 75 meq/100g (Figure 4.8a and Table 4.5a). For the adjusted initial solution pH 3 tests, the model predicts consistently large amounts of precipitation up to a concentration of 75meq/100g (Figure 4.8b and Table 4.5b). The batch equilibrium tests modelled beyond these concentrations indicated retention by adsorption.

Table 4.5a MINTEQA2 Model Batch Equilibrium Tests for Pb Initial Unadjusted pH										
Initial Dissolved or Surface Components	Equili- brium	Percent of Aqueous and Adsorbed Components (Dissolved or on Soil Surface) Bound in Equilibrium Species								
	Species	Initial I	Initial Pb Concentration in Applied Solution (meq/100g)							
		300	200	100	75	50	10	5		
Surface (Sur)	Surface	1.0	1.5	11.5	79.1	83.3	93.9	96.0		
	Sur-Pb	99.0	98.5	88.5	20.9	16.7	6.1	4		
Pb ²⁺	Sur-Pb	32.9	50.2	92.5	99	99.3	99.7	99.7		
	Pb ²⁺	21.3	19.3	3.6	-	-	-	-		
	PbNO3+	45.7	30.5	3.8	-		-	-		
NO3-	NO3	88.6	92.4	99.0	100	100	100	100		
	PbNO ₃	11.4	7.6	-	-	-	-	-		
Components	Solids	Percent of Initial Pb Precipitated from Solution As								
Pb ²⁺	Pb(OH)2	0	0	0	70.4	63.8	32.1	11.2		

68

Table 4.5b MINTEQA2 Model Batch Equilibrium Tests for Pb, Initial Adjusted pH 3									
Initial Dissolved or Surface Components	Equili- brium	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species							
	Species	Initial	Initial Pb Concentration in Applied Solution (meq/100g)						
		300	200	100	75	50	25	10	
Surface (Sur)	Surface	1.3	2.1	14.4	95.8	98.4	99.6	99.9	
	Sur-Pb	98.7	97.9	85.6	4.2	1.6			
Pb ²⁺	Sur-Pb	33.7	51.4	92.1	98.9	99.2	99.4	99.5	
	Pb ²⁺	21.0	18.8	3.8	-	-	-	-	
	PbNO3+	45.2	29.8	4.1			-	-	
NO3.	NO3	88.7	92.6	99.0	100	100	100	100	
	PbNO ₃ +	11.3	7.4	1.0		-		-	
Components	Solids	Percen	Percent of Initial Pb Precipitated from Solution As						
Pb ²⁺	Pb(OH) ₂	0	0	0	93.8	96.6	98.2	98.7	

Copper

For Cu, the model indicated almost complete retention by precipitation, up to an initial solution concentration of 100 meq/100g, for tests performed on the unadjusted initial pH solutions (Figure 4.9a and Tables 4.6a). For the tests using the initial adjusted pH 3 solutions, retention by precipitation was high, up to an initial metal concentration of 75 meq/100g, with decreasing retention by precipitation with increasing initial metal concentration beyond 75 meq/100g (Figure 4.9b and Table 4.6b). The precipitated species were Tenorite and Cu₂(OH)₃-NO₃. At concentrations greater than 100 meq/100g the non - adsorbed species in solution exists in the Cu²⁺ form.

<u>,</u>*

Each batch equilibrium test was modelled using the experimental equilibrium pH of the final supernatant. As the initial heavy metal concentrations increased, the final equilibrium supernatant pH decreased. The initial pH decrease with concentration increase explains why the lower initial heavy metal concentration tests modelled have a higher precipitation than the higher initial heavy metal concentration tests. This is the same reason that the hypothesized adsorption, based on experimental retention and precipitation results, are low.

<u>Table 4.6a</u> MINTEQA2 Model Batch Equilibrium Tests for Cu Unadjusted Initial pH										
Initial Dissolved or Surface	Equili- brium	Percent (Dissol Bound	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species							
Components	Species	Initial (Initial Cu Concentration in Applied Solution (meq/100g)							
[300	200	100	75	50	15.7	7.9		
Surface	Surface	4.3	2.1	93.9	98.8	99.3	99.9	100		
(Sur)	Sur-Cu	95.7	97.9	6.1	1.2	-	<u> </u>	-		
Cu ²⁺	Sur-Cu	46.4	51.4	96.4	96.7	97.0	96.1	94.5		
	Cu ²⁺	53.5	18.8	3.6	3.1	2.7	2.0	1.7		
l	Cu(OH) ₂	-	<u> </u>	<u> </u>	<u> </u>	<u> </u>	1.8	3.6		
NO3.	NO3	100	92.6	100	100	100	100	100		
Components	Solids	Percen	Percent of Initial Cu Precipitated from Solution As							
Cu ²⁺	Tenorite	0	0	93.6	98.4	98.4	99.4	99.4		

Table 4.6b MINTEQA2 Model Batch Equilibrium Tests for Cu Initial Adjusted pH 3										
Initial Dissolved or Surface	Equili- brium	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species								
Components	Species	Initial	Initial Cu Concentration (meq/100g)							
		300	200	100	75	50	25	10		
Surface	Surface	2.7	4.0	73.6	98.3	98.8	99.6	99.9		
(Sur)	Sur-Cu	97.3	96.0	26.4	1.7	1.2	<u> </u>	-		
Cu²+	Sur-Cu	52.6	63.8	97.7	98.3	98.5	98.4	96.7		
	Cu ²⁺	47.4	36.1	2.3	1.6	1.4	1.1	2.3		
NO;	NO3	100	100	100	100	100	100	100		
Components	Solids	Percen	Percent of Initial Cu Precipitated from Solution As							
Cu ²⁺	Cu ₂ (OH) ₃ - NO ₃	38.9	24.3	72.3	97.7	97.4	98.4	99.2		

Zinc

Zinc (Zn) exists, according to the modelling, as either adsorbed surface species or in it's ionic form, Zn²⁺. Precipitated Zn species were not predicted - all retention was through adsorption mechanisms (Figures 4.10a,b and Tables 7a,b). However, Zn retention was consistently underestimated by the model.

Perhaps Zn should not be modelled using an ion exchange reaction which seems to underestimate retention (Figure 4.10a,4.10b). Farrah and Pickering (1976) explained that Zn is adsorbed less by illite because, illite adsorbs the hydroxide species of Zn which are less common at neutral pHs than in Pb or Cu solutions, and obviously do not follow the ion exchange model. This point is not substantiated by the speciation modelling results presented in Tables 4.7a,b, which do not show the presence of ZnOH⁻ in the equilibrium supernatant.

Table 4.7a MINTEQA2 Model Batch Equilibrium Tests for Zn Unadjusted Initial pH										
Initial Dissolved or Surface Components	Equili- brium Species	Percent (Dissolv Bound	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species							
		Initial Z	Initial Zn Concentration (meq/100g)							
		299	150	99.7	74.8	49.9	30	15		
Surface	Surface	23.5	39.5	50	57	66.5	76.4	86.7		
(Sur)	Sur-Zn	76.5	60.5	50	43	33.5	23.6	13.3		
Zn ²⁺	Sur-Zn	18.1	28.7	36.7	42.2	49.6	57.1	64.6		
	Zn ²⁺	81.9	71.3	63.3	57.8	50.4	42.8	35.1		
NO3.	NO ₃ -	100	100	100	100	100	100	100		

Table 4.7b MINTEQA2 Model Batch Equilibrium Tests for Zn Initial Adjusted pH3									
Initial Dissolved or	Equili- brium	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species							
Components	Species	Initial Zn Concentration (meq/100g)							
L		300	100	75	50	25	10		
Surface	Surface	22.7	47.5	54.0	63.1	76.7	88.9		
(Sur)	Sur-Zn	77.3	52.5	46.0	36.9	23.3	11.1		
Zn ²⁺	Sur-Zn	13.1	27.6	32.3	39.1	49.5	59.0		
	Zn ²⁺	86.9	72.4	67.7	60.9	50.4	40.8		
NO,	NO ₃ .	100	100	100	100	100	100		

4.4.3 Mass Balance

Besides giving heavy metal retention data (Section 4.4.2), the soil-heavy metal solution batch equilibrium tests also provided concentrations of displaced exchangeable cations. As was described in Section 3.1, the soil was initially saturated with Ca and Mg, therefore, according to the ion exchange theory, each time a heavy metal cation is adsorbed it must displace an



exchangeable Ca or Mg. As the concentration of initial applied heavy metal solution increased, the Ca + Mg displaced tends to plateau. The maximum displaced Ca + Mg is obtained. The maximum Ca + Mg released in each set of batch equilibrium results was used to determine the concentration of surface sites, based on cation exchange reactions.

The figures presented in this section are referred to as the mass balance graphs (Figures 4.11a,b for Pb, Figures 4.12a,b for Cu and Figures 4.13a,b for Zn). Each figure shows the total concentration of heavy metals retained and the Ca+Mg released (minus the soluble Ca and Mg), versus the initial metal concentration applied. In an ideal ion exchange situation the Ca+Mg released curve would overlap the metal retained curve, showing a one to one exchange of cations.

The mass balance plots for Pb and Cu (Figure 4.11, 4.12) demonstrate that the total concentration of metals retained is similar to the Ca + Mgreleased up to an initial metal concentration of approximately 100 meg/100g. Beyond 100 meg/100g initial metal concentration, in the unadjusted initial solution pH tests (Figure 4.11a), the Ca and Mg released from the soil exceeds the Pb retained. Conversely, for Cu (both adjusted and unadjusted initial solution pHs) and Pb applied at an adjusted pH of 3, the retention (Figures 4.11b, 4.12a,b) exceeds Ca and Mg released. As stated above, the Ca and Mg released is assumed to be the result of ion exchange reactions at the soil particle surface. In the case of Pb (unadjusted initial solution pHs), one could then postulate that the Ca + Mg released over represent the retention above 100 meg/100g, however, for both sets of Cu tests and the Pb tests performed at adjusted initial solution pH 3, the retention continues to increase even when the ion exchange of Ca and Mg has ceased. This further retention beyond the maximum Ca and Mg released, may be due to precipitation mechanisms or other retention reactions not involving ion exchange.

73

Copper (Cu) does form a neutral species at a lower pH than either Zn or Pb (Harter, 1983), furthermore, the neutral species $(Cu(OH)_2)$ has a solubility product smaller than the equivalent species for Pb $(Pb(OH)_2)$ and Zn $(Zn(OH)_2)$ (Section 2.3.3). The precipitation of Cu at lower pH than Pb and Zn is also demonstrated by the precipitation tests presented in Section 4.3.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.1-B.4). The Ca + Mg released values were consistently higher than the hypothetical adsorption for both cases of single metal Cu and Pb tests. Overall, the retention values were closer to the Ca + Mg values than the hypothetical estimated adsorption indicating the hypothesis regarding precipitation, used to calculated the estimated adsorption values, does not hold in these cases (single metal Pb and Cu retention).



Figure 4.11a - Mass Balance Graph for unadjusted initial pH solutions, Pb batch equilibrium test - Ca + Mg Released, Pb Retained versus Initial Applied Metal Concentration.





Figure 4.11b - Mass Balance Graph for adjusted initial pH 3 solutions, Pb batch equilibrium tests - Ca + Mg Released, Pb Retained versus Initial Applied Metal Concentration.



Figure 4.12a - Mass Balance Graph for unadjusted initial pH solutions, Cu batch equilibrium tests - Ca + Mg Released, Cu Retained versus Initial Applied Metal Concentration.

75





Figure 4.12b - Mass Balance Graph for adjusted initial pH 3 solutions, Cu batch equilibrium test - Ca + Mg Released, Cu Retained versus Initial Applied Metal Concentration.

The Zn concentrations retained in the unadjusted initial solution pH tests, followed the Ca + Mg released up to an initial concentration of 150 meq/100g (Figures 4.13a,b). Beyond 150meq/100g initial metal concentration, the Ca + Mg released did not increase but the Zn retention continued to increase. For the adjusted initial solution pH 3 tests, performed at initial concentrations above 25 meq/100g, the Ca + Mg released is less than the Zn retained, perhaps, indicating that Zn is retained by mechanisms other than ion exchange as described in Section 4.4.2. There was also less retention of Zn in the initial adjusted solution pH 3 batch tests, than in the initial unadjusted solution pH test (which is the opposite of Cu and Pb). This may be due to increased competition from H⁺ ions (Farrah and Pickering, 1979; Phadungchewit, 1990, 1993).



Figure 4.13a - Mass Balance Graph for initial unadjusted pH solutions, Zn batch equilibrium test - Ca + Mg Released, Zn Retained versus Initial Applied Metal Concentration.



Figure 4.13b - Mass Balance Graph for initial adjusted pH 3 solutions, Zn batch equilibrium test - Ca + Mg Released, Zn Retained versus Initial Applied Metal Concentration.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.5-B.6). Since very little precipitation was estimated the hypothetical adsorption was almost exactly the same as the experimental retention and both measured retention and hypothetical adsorption exceed the Ca + Mg released values.

Overall, in terms of Ca and Mg quantities released, the retention of Pb results in the largest displacement of Ca and Mg followed by the retention of Cu than Zn. Lead (Pb) and Cu released approximately the same amount for both their adjusted and unadjusted batch equilibrium tests. However, Zn exhibited approximately 25% less displacement of Ca and Mg for the pH 3 adjusted batch equilibrium tests than for the unadjusted pH tests.

4.4.4 Isotherms

The experimental and modelling isotherm plots are presented in Appendix C of this text (Figures C.23-C.28). The experimental and MINTEQA2 geochemical speciation isotherm plots for the same set of tests are presented side by side for easy comparison. The graphs presented in Section 4.4.1 to 4.4.3 (Retention and Mass Balance graphs) have all been in terms of the initial applied heavy metal concentrations. However, in an isotherm plot the abscissa is the final supernatant equilibrium heavy metal concentration.

Three curves can be found on each isotherm graph; precipitation, adsorption and retention. The experimental precipitation and adsorption graphs are interpretive and involve numerous assumptions and speculation. These curves are present for discussion purposes only and are not to be taken as absolutes. For more information regarding the construction of the isotherm graphs, please refer to Appendix A under the subheading "Explanation of Isotherm Graphs".

Both adsorption and precipitation reactions are assumed to be occurring simultaneously, therefore, the full solute concentration is not available for precipitation, as occurred in the precipitation tests. Also, the soil surface facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface, and offering a location for a precipitate nuclease to form. It is postulated that the actual experimental adsorption lies somewhere between the lines representing retention and estimated adsorption and is likely best represented by the Ca and Mg released, rather than by estimates from precipitation, however, this hypothesized adsorption is presented for discussion purposes on the isotherm graphs and in Appendix B.

While these plots are not extensively discussed in this research they show the reader the obvious isotherm shape of some metal retentions and the lack of isotherm shape, or weaker isotherm shape of other metal retentions (Appendix C, Figures C.23-C.28). For example, the single metal Pb and Cu isotherms show a shape typical of high affinity adsorption (Yong et al., 1992; Sposito, 1984), while the Zn isotherms are typical of a lower affinity adsorption. The maximum concentration of metals retained is limited by the concentration of surface sites entered into the model. The maximum concentration of Ca and Mg released for each set of tests was used as the concentration of surface sites for modelling purposes. Therefore, if the experimental retention was higher than the Ca+Mg released, then the modelling isotherms often underestimate the total retention.

4.5 Two Metal Pb and Cu Batch Equilibrium Tests

4.5.1 Experimental Retention

Two sets of batch equilibrium tests were conducted with equal concentrations of Pb and Cu in solution, one set of tests was conducted with unadjusted initial pH solutions, and the other set of tests was conducted with adjusted initial pH 3 solutions. Both sets of batch equilibrium tests revealed a definite preferred retention of Pb over Cu (Figures 4.14a,b).

The Pb and Cu batch equilibrium tests performed, using the unadjusted initial pH solutions, exhibited a high retention of Pb, but lesser retention of Cu (Figure 4.14a). At total initial metal concentrations below 50 meq/100g (25 meq/100g of each metal), both Cu and Pb are completely retained, but as total metal concentrations increase Cu retention quickly drops to retentions below 20% at high total metal concentrations. Conversely, Pb retention remains strong with 85% or more of the initial applied Pb remaining retained.

The batch equilibrium tests performed with the initial adjusted pH 3 solutions demonstrated high retention of both Pb and Cu, with Pb retention remaining higher than Cu retention (Figure 4.14b). At low initial concentrations, Pb is 100% retained, dropping to approximately 90% retention at higher initial total metal concentrations. The Cu retention is also 100% at low initial total metal concentrations, falling to approximately 80% at high initial total metal concentrations.

The author postulates that perhaps the lower pH allows more adsorption because the Cu remains in it's Cu²⁺ state and, therefore, is highly attracted to the clay surface. The lower initial pH may limit early precipitation of metals increasing the concentration gradient driving force for adsorption reactions, as was discussed in Section 4.4.1. However, in the unadjusted initial pH solution tests, neutral species may form and precipitation, accounting for removal from solution. This is particularly interesting considering that the final pH of the supernatant is not that different in the adjusted and unadjusted cases (Table 4.8) because of the high buffering capacity of the soil (Phadungchewit, 1990). A graphical presentation of the initial and final pHs of the supernatant are also present in Appendix D, Figures D.47a,b.

	Table 4.0 million and Tinar prinkinges							
<u>for Pb + Cu</u>	<u>Batch Equilibrium Te</u>	<u>ests</u>						
	Unadjusted	Adjusted						
Initial Supernatant pH	5-4.5	3						
Final Supernatant pH	5-7	4.6-7						

Table 4.8 Initial and Final pH Ranges

4.5.2 Modelling Retention and Speciation

As in the single metal batch equilibrium tests the double metal batch equilibrium tests were modelled using the MINTEQA2/PRODEFA2 Geochemical speciation model. The experimental and modelling retentions are graphically presented on Figures 4.14a,b and the speciation results given by the geochemical model are summarized in Tables 4.10a,b. For a detailed description of the model, and a typical outline of the information provided for the modelling, please refer to Section 3.5. The Langmuir isotherm adsorption model was chosen to describe the heavy metal adsorption, as described in Section 3.5. In most cases, the K_Ls (Langmuir partitioning coefficients, Table 4.9) obtained from the experimental results were used to describe the adsorption reactions with excellent r^2 fits. However, for the retention of Cu in the unadjusted pH case it was not possible to obtain a K_L as described in Section 4.5.1. The maximum concentration of Ca and Mg released from exchange sites, during the batch equilibrium tests, was employed to define a concentration of adsorption sites. For the batch equilibrium tests modelled with the unadjusted initial pH solutions, the model underestimated Pb retention and overestimated Cu retention, however, Cu retention was modelled using only precipitation since an adsorption reaction could not be provided based on the experimental data (Figure 4.14a). For the pH3 adjusted batch equilibrium tests the model under estimated both Pb and Cu retention (Figures 4.14b).

The results of the batch equilibrium tests modelled using the unadjusted pH solutions indicated almost complete retention of Cu by precipitation below total metal concentrations of 100 meq/100g, decreasing to 40% removal by precipitation at a total metal concentration of 200 meq/100g. The model predicted approximately 80% to 90% of the Pb precipitates at total concentrations up to 50 meq/100g. Beyond 50 meq/100g initial metal concentration, most of the Pb is adsorbed or remains in the aqueous phase.

The batch equilibrium tests modelled using solutions initially adjusted to pH 3, predicted almost complete precipitation of Cu and 50% precipitation of Pb at and below 50 meq/100g total initial metal concentration. Copper (Cu) and Pb are both retained as surface species, but, found in solution at increasing concentrations as initial metal concentrations increase (Tables 4.10a,b).

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<u>Table 4.9 Langmuir K values</u> <u>Calculated from Experimental Data (Pb + Cu)</u>					
Batch Equilibrium Tests K _t for Retained Concentrat					
Lead	Log K _L = 3.88				
(no pH adjustment)	r ² = 0.99				
Copper (no pH adjustment)	No Fit				
Lead	Log K _L = 3.9				
(pH 3 adjustment)	r ² = 0.99				
Copper	Log K _L = 3.38				
(pH 3 adjustment)	r ² = 0.95				



Figure 4.14a - Pb and Cu Retention, experimental and modelled, in the double metal batch equilibrium tests with unadjusted initial pH solutions.

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Figure 4.14b - Pb and Cu Retention, experimental and modelled, in the double metal batch equilibrium tests with adjusted initial pH 3 solutions.

Information that the model offers that cannot be obtained experimentally is of particular interest. The model separates adsorption on surface sites from precipitation and offers a complete outline of speciation at equilibrium. The following tables (Tables 4.10a,b) summarize the mass balance output and speciation results of the model for the double metal Pb and Cu retention tests. For information regarding the format of the speciation tables please refer to Appendix A under the subheading "How to Read the Speciation Tables".

Lead Speciation

Large amounts of Pb precipitation, as Pb(OH)₂, was predicted by the model up to an initial total metal concentration of 50meq/100g (Table 4.10a). The remaining Pb (not precipitated) is almost completely adsorbed (Sur-Pb) up to a total metal concentration of approximately 100 meq/100g, beyond this concentrations adsorption starts to decrease. In the both sets of batch equilibrium tests, the model predicts dissolved Pb in solution as Pb²⁺ and PbNO₃⁺ with both species increasing in concentration with increased initial metal concentration as adsorption limits are exceeded and precipitation decreases.

Copper Speciation

Large amounts of Cu precipitation as Tenorite, and some precipitation as $Cu_2(OH)_3NO_3$, was predicted by the model up to an initial total metal concentration of 50meq/100g (Table 4.10b). The remaining Cu (not precipitated), in the initial pH3 adjusted solution tests, was partially adsorbed with adsorption decreasing as initial metal concentrations increased. The batch equilibrium tests performed using an unadjusted initial solution pH could not be modelled for adsorption as described above (Table 4.9). In both sets of batch equilibrium tests the model predicts Cu in solution as Cu^{2+} increasing in concentration with increased initial metal concentration as adsorption limits are exceeded and precipitation decreases. The test performed using the unadjusted initial solution pH also predicted a small quantity of CuOH⁺ and Cu(OH)₂ in solution.

Table 4.10a MINTEQA2 Model Batch Equilibrium Tests Speciation								
	for Pb and Cu Unadjusted Initial Solution pH							
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species						
Components		Initial Pi	o + Cu Co	oncentratio	on (meq/1	00g)		
		200	150	100	50	20		
Surface	Surface	8.0	17.3	40.1	94.9	98.7		
(Sur)	Sur-Pb	92.0	82.7	59.9	5.1	1.3		
Pb²+	Pb ²⁺	10.9	5.6	2.3	-	-		
	Sur-Pb	71.9	87.1	95.5	98.7	99.2		
	PbNO3+	17.2	7.3	2.2	-	•		
Cu²+	Cu(OH) ₂	-	-	-	15.1	47		
	Cu ²⁺	99.8	99.8	99.6	82.6	49.9		
	CuOH⁺	-		[2.0	2.9		
	NO3.	97.8	99.1	99.7	100	100		
NO ₃ .	PbNO3	2.2	-		-			
Components	Solids	Percent	of Initial N	Aetals Pred	cipitated A	s		
Cu ²⁺	Cu ₂ (OH) ₃ NO ₃	40.3	40.2	63.31	-	-		
	Tenorite	-	-	-	100	100		
Pb ²⁺	Pb(OH)2		-	-	83.4	89.2		

Table 4.10b MINTEQA2 Model Batch Equilibrium Tests Speciation								
for Pb and Cu Adjusted Initial Solution pH 3								
Initial Dissolved or	Equilibrium Species	Percent of Compon Bound in	of Aqueou ents (Disso 1 Equilibri	s and Ads olved or S um Specie	orbed oil Surface s	*)		
Surface Components		Initial Pb + Cu Concentration (meg/100)						
		200	150	100	50	20		
Surface	Surface	2.2	3.2	8.9	87.2	94.5		
(Sur)	Sur-Cu	45.2	44.2	41.4	1.0	-		
	Sur-Pb	52.6	52.5	49.7	11.8	5.1		
Pb ²⁺	Pb ²⁺	22.0	18.2	8.0	-	-		
	Sur-Pb	43.4	58.4	83.7	98.7	99.2		
	PbNO3+	34.5	23.4	8.2	-	-		
Cu ²⁺	Cu ²⁺	62.6	50.7	24.1	2.4	1.8		
·	Sur-Cu	37.3	49.2	75.8	97.3	97.7		
NO3	NO ₃ -	95.7	97.1	99.0	100	100		
	PbNO ₃	4.3	2.9	1.0	•	-		
Components	Solids	Percent	of Initial N	Aetal Prec	ipitated As			
Cu ²⁺	Cu ₂ (OH) ₃ NO ₃	-	•	8.0	-	-		
	Tenorite	-		-	96.3	96.0		
Pb ²⁺	Pb(OH)2	РЬ(ОН), 59.4 56.3						

4.5.3 Mass Balance

Besides giving heavy metal retention data (Section 4.5.2), the soil-heavy metal solution batch equilibrium tests also provided concentrations of displaced exchangeable cations. As was described in Section 3.1, the soil was initial saturated with Ca and Mg, therefore, according to the ion exchange theory, each time a heavy metal cation is adsorbed it must displace an exchangeable Ca or Mg. As the concentration of initial applied heavy metal

solution increased, the Ca + Mg displaced tends to plateau. The maximum displaced Ca + Mg is obtained and used to define the concentration of surface sites, based on cation exchange reactions.

The figures presented in this section are referred to as the mass balance graphs (Figures 4.15a,b). Each figure shows the total concentration of heavy metals retained and the Ca+Mg released (minus the soluble Ca and Mg) versus the initial total metal concentration applied. In an ideal ion exchange situation the curve representing the Ca+Mg released would overlap the curve representing the total metal concentration retained, showing a one to one exchange of cations.

The mass balance plots (Figures 4.15a,b) for the batch equilibrium tests performed on the unadjusted initial pH solutions, exhibit a reasonable correspondence between Pb and Cu retained and Ca and Mg released up to an initial total metal concentration of approximately 150 meq/100g. At total metal concentrations above 75 meq/100g the Ca + Mg released is less than the total concentration of metals retained. Tests performed on the initial pH3 adjusted solutions exhibited increased retention without a corresponding increase in the Ca + Mg released, indicating that the increased retention was by some other mechanism other than ion exchange. The speciation modelling results indicated the presence of PbNO₃⁺ which, if present, may be reacting with the clay surface in a manner other than ion exchange. In terms of charge balance, one Ca²⁺ exchangeable cation, would make space for two PbNO₃⁺ to be adsorbed.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.7, B.8). The test performed using the

unadjusted initial pH solutions have an hypothetical estimated adsorption below the Ca + Mg released values up to an initial total solution concentration of 100 meq/100g. Above 100 meq/100g, the estimated adsorption and Ca+Mg values were quite similar, indicating that perhaps precipitation as it occurs in a solution without soil may be occurring for the tests performed at total concentrations equal to an above 100meq/100g at an unadjusted initial pH. For the tests performed using the adjusted initial pH 3 solutions, the hypothetical estimated adsorption did not match the Ca+Mg released any better than the total experimental retention.

The Ca and Mg released is very similar in both sets of batch equilibrium tests. If Ca and Mg release is used as an indicator of ion exchange adsorption, the results would indicate that similar amounts of ion exchange adsorption are occurring in both the adjusted and unadjusted pH cases.



Figure 4.15a - Mass Balance Graph for unadjusted initial pH solutions, Pb and Cu batch equilibrium tests - Ca + Mg Released, Pb + Cu Retained versus Initial Metal Concentration.





Figure 4.15b - Mass Balance Graph for adjusted initial pH 3 solutions, Pb and Cu batch equilibrium tests - Ca + Mg Released, Pb + Cu Retained versus Initial Metal Concentration.

4.5.4 Isotherms

The experimental and modelling isotherm plots are presented in Appendix C of this text, presented side by side for easy comparison (Figures C.29-C.32). The graphs presented in Section 4.5.1 to 4.5.3 (Retention and Mass Balance graphs) have all been plotted in terms of the initial applied heavy metal concentrations. However, in an isotherm plot the results are plotted in terms of the final supernatant equilibrium heavy metal concentrations. For a complete explanation of the isotherm graphs please refer to Appendix A, Sections A.3 and A.4, under the subheading "Explanation of Isotherm Graphs".

While these plots are not extensively discussed in this research they show the reader the obvious isotherm shape of some metal retentions and the lack of isotherm shape, or weaker isotherm shape, of other metal retentions. For example, the Pb isotherm, generated from the Pb and Cu batch equilibrium test results show a definite high affinity adsorption shape. However, the Cu isotherms reveal a weaker shape in the adjusted initial pH 3 solution tests and no isotherm shape in the unadjusted initial pH solutions tests. The maximum retained concentration presented on the modelled isotherms is limited by the concentration of surface sites entered into the model by the user. The concentration of Ca and Mg released was used as the concentration of surface sites. Since the experimental retention was higher than the Ca+Mg released, the modelling isotherms underestimated the total retention.

The Pb and Cu retention isotherms (Appendix C, Figures C.29, C.30, C.31, C.32) are well defined by the Langmuir model, except for Cu in the unadjusted initial pH solution tests, which could not be modelled because a K_L could not be obtained from the experimental data (Table 4.9). The r² factors (least squares) show excellent fits where isotherm modelling was accomplished. For retention and hypothetical estimated adsorption, the Pb isotherms demonstrate by their shape a high affinity type adsorption (Yong et al., 1992; Sposito, 1984). The Cu isotherm formed from the initial adjusted pH 3 solutions also shows a high affinity type adsorption, however, the adsorption from the unadjusted initial pH solutions did not exhibit an isotherm shape for Cu.

In most cases the experimental retention and hypothetical adsorption curves are quite similar in shape and often overlap. The adsorption and precipitation reactions are assumed to be occurring simultaneously, therefore, the full solute concentration is not available for precipitation as in the precipitation tests. Also the soil surface facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface. The author believes that the actual adsorption lies somewhere between the lines


representing retention and hypothetical adsorption and is likely best represented by the Ca and Mg released, rather than by estimates from precipitation, however, the estimated adsorption is presented for discussion purposes (Appendix B and Appendix C).

The modelling results consistently under estimate the overall retention, as can be seen by the maximum retained concentrations on the isotherms. The modelling results for retention and adsorption are similar and often overlap at high equilibrium metal concentrations, but at low concentrations they are quite different do to the large amounts of precipitation predicted by the model.

4.6 Two Metal Pb and Zn Batch Equilibrium Tests

4.6.1 Experimental Retention

Two sets of batch equilibrium tests were conducted with equal concentrations of Pb and Zn in solution, one set of tests without initial pH adjustment of solutions and one with initial adjustment to pH 3 of applied solutions. Both sets displayed a definite high affinity retention of Pb but small to zero retention of Zn in terms of initial metal concentration, (Figures 4.16a,b). Lead (Pb) is actually completely retained at total metal concentrations up to 150 meq/100g decreasing to approximately 90% retention at 200 meq/100g total metal concentration. At the lower total metal concentrations there was some retention of Zn but as the concentrations increased the retention dropped to zero. It was not possible to describe the Zn retention, in either case, using an isotherm model.

The experiments performed with pH 3 adjusted solutions and the unadjusted pH solutions result in approximately the same final pH (Table 4.11), due to the high buffering capacity of the illite clay soil (Phadungchewit, 1990). Of interest is the initial pH of the unadjusted batch equilibrium tests

which varies by only half a pH unit with concentration. A graphical representation of the initial and final pHs of the supernatant are also presented in Appendix D, Figures D.48a,b.

Table 4.11 Init	Table 4.11 Initial and Final pH Ranges					
<u>for Pb + Zn I</u>	<u>for Pb + Zn Batch Equilibrium Tests</u>					
	<u>Unadjusted</u>	Adjusted				
Initial Supernatant pH	4.5-4.7	3				
Final Supernatant pH	5.3-6.7	5.2-6.7				

4.6.2 Modelling Retention and Speciation

As in the case of Cu and Pb, the double metal Pb and Zn batch equilibrium tests were modelled using the MINTEQA2/PRODEFA2 Speciation model. For a detailed description of the model, and a typical outline of the information provided for the modelling, please refer to Section 3.5. The Langmuir isotherm adsorption model was chosen as described in Section 3.5. The K_Ls (Langmuir partitioning coefficients, Table 4.12) obtained from the experimental results were used to describe the adsorption reactions with excellent r² fits for Pb. However, for the retention of Zn in both cases it was not possible to obtain a K_L factor. The maximum concentration of Ca and Mg released from exchange sites, during the batch equilibrium tests, was employed to define a concentration of adsorption sites.

For both sets of batch equilibrium tests the model slightly underestimates Pb retention at higher concentrations (Figures 4.16a,b). Zinc retention could only be obtained by precipitation since adsorption reactions for Zn were not provided. Since the model did not predict any Zn

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precipitation, and adsorption could not be modelled, no Zn was retained in the modelling. Retention of Pb was predict as surface adsorption no precipitation was predicted by the model.

Table 4.12 Langmuir K values Calculated			
<u>nom_experimenta</u>	$\frac{11}{2} \frac{11}{2} \frac$		
Batch Equilibrium Tests	K (Langmuir) for Retained Concentration		
Lead (no pH adjustment)	$Log K_{L} = 5.73$ r ² = 0.98		
Zinc (no pH adjustment)	No Fit		
Lead (pH 3 adjustment)	$Log K_{L} = 5.47$ r ² = 0.99		
Zinc (pH 3 adjustment)	No Fit		



Figure 4.16a - Pb and Zn Retention, experimental and modelled, in the double metal batch equilibrium tests with unadjusted initial pH solutions.

94





The model separates adsorption on surface sites from precipitation and offers a complete outline of the speciation of all components at equilibrium. The following tables (Tables 4.13a,b) summarize the mass balance output of the model and the speciation results for the double metal Pb and Zn retention cases. For information regarding the format of the speciation tables please refer to Appendix A, Section A.2, under the subheading "How to Read the Speciation Tables".

The model predicts in both cases almost complete retention of Pb by adsorption, with only a minor amount of precipitation at one of the initial



adjusted pH 3 concentrations. In the both sets of batch equilibrium tests the model predicts Pb in solution as Pb^{2+} and $PbNO_3^+$, with both species increasing in concentration with increased initial metal concentration as adsorption limits are exceeded. In both sets of batch equilibrium tests Zn was not retained but found in solution as Zn^{2+} .

Table 4.13a MiNTEQA2 Model Batch Equilibrium Tests						
(unadjusted pH) Speciation for Pb and Zn						
Initial Dissolved or	itial ssolved Equilibrium Species Bound in Equilibrium Species					ecies
Components		Initial Pl	b + Zn Co	oncentratio	on (meq/1	00g)
		200	150	100	50	20
Surface	Surface	-	10.6	40.8	70.7	88.3
(Sur)	Sur-Pb	99.8	89.4	59.2	29.3	11.7
Pb2+	Pb ²⁺	6.7	-	-	-	-
	Sur-Pb	82.6	99.7	99.9	100	100
	PbNO3+	10.7	-	-	-	•
Zn ²⁺	Zn ₂₊	100	100	100	99.9	99.9
NO;	NO ₃ -	98.7	100	100	100	100
	PbNO ₃ -	1.3	-	-	-	

Table 4.13b MINTEQA2 Model Batch Equilibrium Tests								
L	(Initial pH 3) Speciation for Pb and Zn							
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Compone (Dissolved or Soil Surface) Bound in Equilibrium Species				nponents		
Components	 	Initial Pb	n (meq/10	10g)				
		200	150	100	50	20		
Surface	Surface	-	2.0	30.3	365.4	86.2		
(Sur)	Sur-Pb	99.8	98.0	69.7	34.6	13.8		
Pb ²⁺	Pb ²⁺	11.6	1.6	•	-	-		
	Sur-Pb	70	96.4	99.8	99.9	100		
	PbNO3.	18.3	2.0		-	-		
Zn ²⁺	Zn ₂₊	100	100	99.9	99.9	99.7		
NO3	NO ₃ ·	97.7	99.8	100	100	100		
	PbNO3	23.0	-	-		-		
Components	Solids	Percent of Initial Metal Precipitated As						
Pb ²⁺	Pb(OH) ₂	-	- 4.0					

4.6.3 Mass Balance

Besides giving heavy metal retention data (Section 4.6.2), the soil-heavy metal solution batch equilibrium tests also provided concentrations of displaced exchangeable cations. As was described in Section 3.1, the soil was initial saturated with Ca and Mg, therefore, according to the ion exchange theory, each time a heavy metal cation is adsorbed it must displace an exchangeable Ca or Mg. As the concentration of initial applied heavy metal solution increased, the Ca + Mg displaced tends to plateau. The maximum displaced Ca + Mg is obtained and used to define the concentration of surface sites, based on cation exchange reactions. The figures presented in this section are referred to as the mass balance graphs (Figures 4.17a,b). Each



figure shows the total concentration of heavy metals retained and the Ca+Mg released (minus the soluble Ca and Mg) versus the initial total metal concentration applied. In an ideal ion exchange situation the Ca+Mg released curve would overlap the metal retained curve, showing a one to one exchange of cations.

The mass balance plots for Pb and Zn, compiled from the batch equilibrium results performed with the initial unadjusted pH solutions, demonstrate that the total metal retained is similar to the Ca + Mg released up to a total metal concentration of approximately 150 meq/100g (Figure 4.17a). Beyond 150 meq/100g, Ca and Mg released is slightly less than the total metals retained. The tests performed using the initial adjusted pH 3 solutions, obtained Pb and Zn retentions greater than the Ca and Mg released (Figure 4.17b). This same decrease in Ca and Mg released was seen in the single metal Zn test and the two metal Pb and Cu tests at initial pH 3. This would indicate that a different mechanism of Zn retention, other than ion exchange, is occurring in the adjusted initial pH 3 batch equilibrium tests.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.9, B.10). The tests performed using the unadjusted initial pH solutions had hypothetical estimated adsorption values below the Ca + Mg released values. However, for the tests performed using the adjusted initial pH 3 solutions, the hypothetical estimated adsorption values values were closer to the Ca+Mg released values than the total experimental retention values.



Figure 4.17a - Mass Balance Graph for unadjusted initial pH solutions, Pb and Zn batch equilibrium tests - Ca + Mg Released, Pb + Zn Retained versus Initial Total Metal Concentration.



Figure 4.17b Mass Balance Graph for initial adjusted pH 3 solutions, Pb and Zn batch equilibrium tests - Ca + Mg Released, Pb + Zn Retained versus Initial Total Metal Concentration.



4.6.4 Isotherms

The experimental and modelling isotherm plots are presented in Appendix C of this text (Figures C.33-C.35). The experimental and geochemical isotherm plots for the same set of tests are presented side by side for easy comparison. The graphs presented in Section 4.6.1 to 4.6.3 (Retention and Mass Balance graphs) have all been in terms of the initial applied heavy metal concentration. However, in an isotherm plot the abscissa is the final supernatant equilibrium total heavy metal concentration. For a complete explanation of the isotherm graphs please refer to Appendix A sections A.3 and A.4 under the subheading "Explanation of Isotherm Graphs".

The experimental Pb retention isotherms (Appendix C, Figures C.33a, C.34a) are well defined by the Langmuir model, but Zn retention could not be modelled because a K_L could not be obtained from the experimental data (Table 4.12). The r² factors show excellent fits where isotherm modelling was accomplished. The isotherm plots for Pb appear very similar for both the adjusted initial pH 3 and unadjusted initial pH solution tests. The experimental Pb isotherms for, retention and hypothetical estimated adsorption, demonstrate by their shape a high affinity type adsorption (Yong et al., 1992; Sposito, 1984). The Zn isotherms (Figures C.35a,b) do not exhibit an isotherm shape.

The adsorption and precipitation reactions are assumed to be occurring simultaneously, therefore, the full solute concentration is not available for precipitation as in the precipitation tests. Also the soil surface facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface. The author believes that the actual adsorption lies somewhere between the lines representing retention and estimated adsorption and is likely best represented by the Ca and Mg released, rather than by estimates from precipitation, however, the estimated adsorption is presented for discussion purposes.

The modelling isotherms for Pb appear to describe the overall experimental retention quite well. The modelling results for retention and adsorption are similar and often overlap because the model predicted that Pb retention is due predominantly to adsorption and not precipitation.

4.7 Two Metal Cu and Zn Batch Equilibrium Tests

4.7.1 Experimental Retention

Two sets of batch equilibrium tests were conducted with equal concentrations of Cu and Zn in solution, one set of tests without initial pH adjustment of solutions and one with initial solutions adjustment to pH 3. Both batch equilibrium sets exhibited high retention of Cu but only minor retention of Zn (Figures 4.18a,b). All of the Cu was retained up to a total initial metal concentrations of 150 meq/100g with retentions remaining greater than 90% at total initial metal concentrations of 200 meq/100g. The relative retention of Zn decreased with increased initial total metal concentration. Also, Zn retention could not be described using the Langmuir isotherm model.

The pH adjusted experiments and the unadjusted experiments result in similar final pHs as seen in the other sets of batch equilibrium tests (Table 4.14). A graphical representation of initial and final pH can also be found in Appendix D, Figures D.49a,b.

Table 4.14 Initial and Final pH Ranges

for Cu + Zn Batch Equilibrium Tests

	<u>Unadjusted</u>	Adjusted
Initial Supernatant pH	4.3-4.9	3
Final Supernatant pH	5.2-6.8	5.3-6.7

4.7.2 Modelling Retention

As in the case of the other double metal batch equilibrium tests, the Cu and Zn batch equilibrium tests were modelled using the MINTEQA2/PRODEFA2 Speciation Model. The experimental and modelled retentions are graphically presented on Figures 4.18a,b, and the speciation results obtained from the geochemical model are summarized in Tables 4.16a,b. For a detailed description of the model, and a typical outline of the information provided for the modelling, please refer to Section 3.5. The K_L factors determined for the Langmuir isotherm adsorption model (Table 4.15) obtained from the experimental results were used to describe the adsorption reaction, and the maximum concentration of Ca and Mg released was employed to define a concentration of adsorption sites for which the Cu and Zn must compete. However, for the retention of Zn in both cases, it was not possible to obtain a K_L factor.

For both sets of batch equilibrium tests the model provides an excellent estimate of Cu retention (Figures 4.18a,b). Zinc (Zn) retention could only be obtained by precipitation (as described above), however, the model did not predict any Zn precipitation.

<u>Table 4.15 Langmuir K values Calculated</u> from Experimental Data (Cu. + Zn)			
Batch Equilibrium Tests K (Langmuir) for Retained			
Copper (no pH adjustment)	$Log K_{L} = 4.33$ r ² = 0.99		
Zinc (no pH adjustment)	No Fit		
Copper (pH 3 adjustment)	Log K _L = 4.94 r ² = 0.99		
Zinc (pH 3 adjustment)	No Fit		



Figure 4.18a - Cu and Zn Retention, experimental and modelled, in the double metal batch equilibrium tests with unadjusted initial pH solutions.



Figure 4.18b - Cu and Zn Retention, experimental and modelled, in the double metal batch equilibrium tests with adjusted initial pH 3 solutions.

For the tests performed using the unadjusted initial pH solutions, the model predicted that the retention of Cu, by mechanisms of precipitation, decreased with increased concentration from 80% to 11%, while adsorption of the aqueous phase Cu decreased from 100% to 89%. For the tests performed using the adjusted initial pH 3 solutions, the model predicted complete retention of Cu at all concentrations as a result of adsorption, with only a small percentage retained by precipitation. The minor amounts of Cu precipitation predicted, was as Tenorite and Cu₂(OH)₃NO₃, but no precipitation of Zn was predicted. The model determined that any Cu remaining in solution after precipitation and adsorption are complete, would be found in the Cu²⁺ form. Similarly, almost all Zn was predicted by the model to be in the Zn²⁺ form.

Table 4.16a MINTEQA2 Model Batch Equilibrium Tests (Unadjusted Initial pH) Speciation for Cu and Zn							
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species Initial Cu + Zn Concentration (meq/100g)					
Components							
200 150 100 50 20						20	
Surface	Surface	3.3	20.2	43.4	77.0	98.0	
(Sur)	Sur-Cu	96.7	79.0	56.6	23.0	2.0	
Cu ²⁺	Sur-Cu	88.6	98.1	99.2	99.6	99.7	
	Cu ²⁺	11.4	1.9	-	-	-	
Zn ²⁺	Zn ²⁺	100.0	100.0	100.0	99.9	99.5	
NO3.	NO3.	100.0	100.0	100.0	100.0	100.0	
Components	Solids	Percent of Initial Metal Precipitated As					
Cu ²⁺	Tenorite	-	11.0	5.6	23.2	83.1	
	Cu ₂ (OH) ₃ - NO ₃	11.1	-	-	-	-	

Table 4.16b MINTEQA2 Model Batch Equilibrium Tests (initial pH 3) Speciation for Cu and Zn						
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Component (Dissolved or Soil Surface) Bound in Equilibrium Species				
Surface Components		Initial C	u + Zn Co	oncentratio	on (meq/1	00g)
		200	150	100	50	20
Surface	Surface	1.3	15.4	43.8	72.1	88.9
(Sur)	Sur-Cu	98.7	84.6	56.2	27.9	11.1
Cu ²⁺	Sur-Cu	93.3	99.4	99.8	99.9	99.9
	Cu ²⁺	6.7	-		-	-
Zn ²⁺	Zn ²⁺	100.0	100.0	100.0	99.9	99.5
NO ₃ -	NO3 ⁻	100.0	100.0	100.0	100.0	100.0
Components	Solids	Percent of Initial Metal Precipitated As				
Cu ²⁺	Cu ₂ (OH) ₃ NO ₃	7.5		-	-	-

4.7.3 Mass Balance

Besides giving heavy metal retention data (Section 4.7.2), the soil-heavy metal solution batch equilibrium tests also provided concentrations of displaced exchangeable cations. As was described in Section 3.1, the soil was initial saturated with Ca and Mg, therefore, according to the ion exchange theory, each time a heavy metal cation is adsorbed it must displace an exchangeable Ca or Mg. The figures presented in this section are referred to as mass balance graphs (Figures 4.19a,b). Each figure has two curves, one depicting the total concentration of heavy metals retained, and the other depicting Ca + Mg released (minus the soluble Ca + Mg), versus the initial total metal concentrations applied. In an ideal ion exchange situation the Ca + Mg released curve would overlap the metal retained curve, showing a one to one exchange of cations.

The Ca + Mg released complies with the total metals retained up to a total initial metal concentration of 150 meq/100g in the unadjusted initial pH tests. In the initial adjusted pH 3 solution tests containing Cu and Zn, and all other initial pH 3 adjusted tests involving Zn, the Ca + Mg released is less than the total metal concentration retained indicating, as stated in the other discussion sections, another method of retention has occurred. The Ca + Mg levels displaced reach approximately the same level in both sets of data, however, the unadjusted initial pH tests show higher displacements of Ca + Mg at lower initial metal concentrations. Overall, based on the data from Ca + Mg displacement, significant levels of adsorption has occurred (Figures 4.19a,b) and precipitation is only a minor retention mechanisms. The modelling overestimates precipitation (Section 4.7.2) as does the precipitation test data when applied to the retention data (Appendix C).









Figure 4.19b - Mass Balance Graph for initial adjusted pH 3 Cu and Zn batch equilibrium tests - Ca + Mg Released, Cu + Zn Retained versus Initial Metal Concentration.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.11, B.12). Both sets of tests performed had hypothetical estimated adsorption values far below the Ca + Mg released values.

4.7.4 isotherms

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The experimental and modelling isotherm plots are presented in Appendix C of this text (Figures C.36-C.38). The experimental and geochemical modelling isotherm plots for the same set of tests are presented side by side for easy comparison. The graphs presented in Section 4.7.1 to 4.7.3 (Retention and Mass Balance graphs) have all been plotted in terms of the initial applied heavy metal concentration. However, in an isotherm plot the abscissa is the final supernatant equilibrium heavy metal concentration. For a complete explanation of the isotherm graphs please refer to Appendix A under the subheading "Explanation of Isotherm Graphs".

While these plots are not extensively discussed in this research they show the reader the obvious isotherm shape of some metal retentions and the lack of isotherm shape, or weaker isotherm shape, of other metal retentions. The Cu experimental retention isotherms (Appendix C, Figures C.36a,C.37a) are well defined by the Langmuir model. The r^2 factors show excellent fits where isotherm modelling was accomplished (Table 4.15). However, Zn retention could not be described by the Langmuir isotherm because a K_L could not be obtained from the experimental data (Table 4.15). The Cu isotherms for experimental retention (Appendix C, Figures C.36a, C.37a) demonstrate, by their shape, a high affinity type adsorption (Yong et al., 1992; Sposito, 1984), while Zn retention does not exhibit an isotherm shape (Appendix C, Figures C.38a,b).

Using the precipitation test results the adsorption was estimated based on the assumption that precipitation occurs at the equilibrium pH as it does in solution (in the absence of soil) as was discussed in Section 4.3. The resulting hypothetical precipitation is very high for all initial concentrations leaving very little Cu left over for adsorption (Figures C.36a,C.37a). Resulting in a strong precipitation curve and weak adsorption curve, however, the modelling isotherm shows the opposite results with adsorption making up for most of the retention and precipitation being a relatively weak contributor to retention (Figures C.36b, C.37b)

The adsorption and precipitation reactions are assumed to be occurring

simultaneously, therefore, the full solute concentration is not available for precipitation as in the precipitation tests. Also the soil facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface. The author believes that the actual adsorption lies somewhere between the lines representing retention and estimated adsorption and is likely best represented by the Ca + Mg released, rather than by estimates from precipitation, however, the estimated adsorption is presented for discussion purposes.

The modelling results consistently underestimate the overall retention, as can be seen by the maximum retained concentrations on the isotherms. The maximum retained concentration on the modelled isotherms is limited by the concentration of surface sites entered into the model. The concentration of Ca and Mg released was used as a concentration of surface sites. If the experimental retention was higher than the Ca+Mg released, then the modelling isotherms underestimate the total retention.

4.8 Three Metal Batch Equilibrium Tests

4.8.1 Experimental Retention

Two sets of batch equilibrium tests were conducted with equal concentrations of Pb, Cu and Zn in solution, one set of tests without initial pH adjustment of solutions and one with initial solutions adjustment to pH 3.

Both sets of batch equilibrium tests revealed a definite selectivity order of Pb>Cu>>>Zn (Section 4.8.2, Figures 4.20a,4.21a). This is the same selectivity order found by many researchers (see e.g., Farrah and Pickering, 1977; Harter, 1983; Elliot, 1986; Biddappa, 1981; Phadungchewit, 1990).

The batch equilibrium tests performed using the unadjusted initial pH

solutions resulted in a slightly higher retention of Cu than Pb at low initial metal concentrations (<75 meq/100g) and only minor retention of Zn. As overall metal concentration increased the retention of Pb exceeded the retention of Cu while Zn retention remained extremely weak (Figure 4.20a).

The retention tests performed using the initially adjusted pH 3 solutions presented an equally strong retention of Cu and Pb and weak retention of Zn, at low initial total metal concentrations (<75 meq/100g). However, as total metal concentrations increased, Cu retention dropping off but Pb retention remained strong while Zn retention remained extremely weak (Figure 4.21a).

Overall, the initially adjusted pH and unadjusted pH tests resulted in similar retentions of all three metals. Also, the pH adjusted experiments and the unadjusted experiments, resulted in similar final pH ranges as was seen in the other experimental results, due to the high buffering capacity of the soil (Table 4.17). The initial and final pH of the supernatant is presented graphically on Figures D.50a,b of Appendix D.

Table 4.17 Initial and Final pH_Ranges_for

Pb, Cu and Zn Batch Equilibrium Tests

	<u>Unadjusted</u>	Adjusted
Initial Supernatant pH	3.9-4.4	3
Final Supernatant pH	4.5-6.2	4.5-6.6

4.8.2 Modelling Retention

As in the case of the single and double metal batch equilibrium tests, the Pb, Cu and Zn triple metal batch equilibrium tests were modelled using the MINTEQA2/PRODEFA2 Speciation Model. The experimental and modelled retentions are graphical presented on Figures 4.20b and 4.21b, and the speciation results obtained from the geochemical model are summarized in Tables 4.16a,b. For a detailed description of the model, and a typical outline of the information provided for the modelling, please refer to Section 3.5. The K_L factors determined for the Langmuir isotherm adsorption model (Table 4.18) obtained from the experimental results were used to describe the adsorption reaction, and the maximum concentration of Ca + Mg released was employed to define a concentration of adsorption sites for which the Pb, Cu and Zn must compete. However, for the retention of Cu in the unadjusted initial pH solutions and for Zn in both cases, it was not possible to obtain a K_L factor. This is similar to the two metal tests where K_L could not be obtained for Zn in any of the cases, and for Cu in the Pb and Cu unadjusted initial pH case.

The modelling predicted, for both sets of batch equilibrium tests, similar amounts of Pb and Cu retention. When compared to the experimental retention results it can be concluded that the model underestimates Pb retention and overestimates Cu retention (Figures 4.20, 4.21). Zinc (Zn) retention could only be obtained by precipitation since adsorption reactions for Zn were not provided and the model did not predict any Zn precipitation.

The modelled retention of Pb in the triple metal unadjusted pH tests, at total initial metal concentrations below 50 meq/100g, was completely by precipitation, however, the retention mechanism changed to adsorption as concentrations increased (Table 4.19a). In the unadjusted pH test the model predicted almost complete retention of Cu by precipitation up to an initial total metal concentration of 150 meq/100g, decreasing to approximately 50% retention by precipitation beyond this concentration. Precipitation retention represents the entire retention of Cu since Cu adsorption could not be modelled.

112

For the modelling performed using the adjusted initial pH3 solutions, Pb retention was mostly by adsorption with only about 25% retention by precipitation predicted at the lowest concentrations (Table 4.19b). Modelling of the pH 3 adjusted tests predicted approximately 90% retention of Cu by precipitation, at initial concentrations below and equal to 75 meq/100g, with the other 10% retained by adsorption. In initial total concentrations above 75meq/100g retention of Cu was by adsorption mechanisms only, decreasing from 80% to 50% at total initial metal concentrations of 300 meq/100g.

In both cases Zn retention by precipitation was not predicted by the model and because an adsorption reaction K_L could not be supplied to the model from the experimental data, no retention by adsorption could be modelled.

<u>Table 4.18 Langmuir K values Calculated from</u> <u>Experimental Data (Pb, Cu and Zn)</u>				
Equilibrium Batch Tests	K (Langmuir) for Retained			
Lead (no pH adjustment)	$Log K_{L} = 2.54$ r ² = 0.72			
Lead (pH 3 adjustment)	Log K _L = 3.916 r ² =0.99			
Copper (no pH adjustment)	No Fit			
Copper (pH 3 adjustment)	$Log K_{L} = 3.54$ r ² = 0.99			
Zinc (no pH adjustment	No Fit			
Zinc (pH 3 adjustment)	No Fit			





Figure 4.20a - Experimental Pb, Cu and Zn Retention in the triple metal batch equilibrium tests unadjusted initial pH solutions.



Figure 4.20b - Modelled Pb, Cu, and Zn Retention in the triple metal batch equilibrium tests unadjusted initial pH solutions.



Figure 4.21a - Experimental Pb, Cu, and Zn Retention in the triple metal batch equilibrium tests adjusted initial pH3 solutions.



Figure 4.21b - Modelled Pb, Cu, and Zn Retention in the triple metal batch equilibrium tests adjusted initial pH3 solutions.



After precipitation and adsorption is complete the model predicts that Pb left in the aqueous phase will be in the forms Pb^{2+} and $PbNO_3^+$ and Cu remaining in solution will be in the Cu²⁺ form. Adsorption reactions could not be provided for Zn and the model did not predict any Zn precipitation, therefore, all the Zn will be as Zn²⁺ (Tables 4.19a,b).

<u>Tabl</u> (ui	Table 4.19a MINTEQA2 Model Batch Equilibrium Tests (unadjusted initial pH) Speciation for Pb, Cu and Zn						
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species					
Surface Components		Initial P (meq/10	b + Cu X0g)	+ Zn Cor	ncentratio	n	
		300	225	150	75	30	
Surface	Surface	54.3	60.3	68.3	98.4	99.6	
(Sur)	Sur-Pb	45.7	39.7	31.7	1.6	-	
Pb ²⁺	Pb ²⁺	18.1	18.8	18.0	12.7	10.5	
	Sur-Pb	41.8	49.1	59.7	76.7	84.6	
	PbNO3+	40.1	32.0	22.2	10.3	4.5	
Cu²+	Cu ²⁺	99.9	99.8	99.6	96.6	86.6	
	Cu(OH) ₂	-	-	-	2.2	11.2	
	CuOH+	-	-			1.8	
Zn ²⁺	Zn ²⁺	100.0	100.0	100.0	99.9	99.8	
NO3.	NO ₃ -	96.6	97.3	98.1	99.9	100	
L	PbNO3+	3.4	2.7	1.9	-	-	
Components	Solids	Percent	of Initial	Metal Pr	ecipitated	d As	
Pb ²⁺	Pb(OH)2	-	-	-	92.3	95.7	
Cu ²⁺	Tenorite			-	99.7	99.8	
	Cu ₂ (OH) ₃ NO ₃	49.5	23.2	78.8		-	



Table 4.19b MINTEQA2 Model Batch Equilibrium Tests (initial adjusted pH 3) Speciation for Pb, Cu and Zn							
Initial Dissolved or	Equilibrium Species	Percent of Aqueous and Adsorbed Components (Dissolved or Soil Surface) Bound in Equilibrium Species					
Surface Components		Initial P (meq/1(b + Cu ·)0g)	+ Zn Cor	centratio	n	
		300	225	150	75	30	
Surface	Surface	2.2	3.5	9.7	70.6	90.9	
(Sur)	Sur-Pb	44.5	46.8	45.3	26.2	8.1	
	Sur-Cu	53.3	49.7	45.0	3.2	-	
Pb ²⁺	Pb ²⁺	18.6	16.1	7.7	1.0	-	
	Sur-Pb	39.2	55.8	82.2	98.2	99.1	
<u></u>	PbNO3+	42.2	28.1	10.0	-	-	
Cu ²⁺	Cu ²⁺	53.0	40.7	18.3	2.4	1.4	
	Sur-Cu	47.0	59.3	81.6	97.5	98.4	
Zn ²⁺	Zn ²⁺	100.0	100.0	100.0	99.9	99.8	
NO3.	NO3	100	99.9	99.2	97.7	96.5	
	PbNO3+	-	-	-	2.3	3.5	
Components	Solids	Percent	of Initial	Metal Pr	ecipitated	d As	
Cu ²⁺	Tenorite	87.8 90.6					
Pb ²⁺	Pb(OH)2	-	2 24.7				

4.8.3 Mass Balance

Besides giving heavy metal retention data (Section 4.8.2), the soil-heavy metal solution batch equilibrium tests also provided concentrations of displaced exchangeable cations. As was described in Section 3.1, the soil was initial saturated with Ca and Mg, therefore, according to the ion exchange theory, each time a heavy metal cation is adsorbed it must displace an exchangeable Ca or Mg. The figures presented in this section are referred to as mass balance graphs (Figures 4.22a,b). Each figure has two curves, one

depicting the total concentration of heavy metals retained, and the other depicting Ca + Mg released (minus the soluble Ca and Mg), versus the initial total metal concentrations applied. In an ideal ion exchange situation the Ca + Mg released curve would overlap the metal retained curve, showing a one to one exchange of cations.

For the unadjusted initial pH solution tests the Ca and Mg released corresponds fairly closely to the total amount of metals retained, up to an initial total metal concentration of 225 meq/100g, indicating most metals where removed from solution by the mechanism of ion exchange. However, as the concentration increases the Ca and Mg released became slightly less than the total metals retained. In the adjusted initial pH 3 case the Ca and Mg released was much less than the total metal retained above total initial metal concentrations of 75 meq/100g. This was seen for all initial pH 3 batch equilibrium tests where Zn was involved, and the two metal tests involving Pb and Cu at initial adjusted solution pH 3.

The Ca + Mg released indicates that high levels of ion exchange adsorption are occurring (Figures 4.22a,b). The modelling results, discussed in Section 4.8.2, predicted retention mostly by precipitation at low initial metal concentrations, which is not what seems to occur experimentally according to the levels of Ca and Mg released.

In both sets of results, Ca and Mg released reaches approximately the same level, although in the unadjusted initial pH experiments the concentrations rise to a high level at lower initial metal concentrations than in the pH 3 adjusted experiments.

The hypothetical estimated adsorption (calculated as described in Section 4.3), based on the hypothesis that precipitation at equilibrium pH

occurs as it does in a solution without soil, was also compared to the Ca + Mg released (Appendix B, Tables B.13, B.14). Both sets of tests performed had hypothetical estimated adsorption values far below the Ca + Mg released values.



Figure 4.22a - Mass Balance Graph for unadjusted initial pH, Pb, Cu and Zn batch equilibrium tests - Ca + Mg Released, Pb + Cu + Zn Retained versus Initial Metal Concentration.



Figure 4.22b - Mass Balance Graph for initial adjusted pH 3 Pb, Cu and Zn batch equilibrium tests - Ca + Mg Released, Pb + Cu + Zn Retained versus Initial Metal Concentration.

4.8.4 Isotherms

The experimental and modeiling isotherm plots are presented in Appendix C of this text (Figures C.39, C.40, C.41, C.42, C.43). The experimental and geochemical modelling isotherm plots for the same set of tests are presented side by side for easy comparison. The graphs presented in Section 4.8.1 to 4.8.3 (Retention and Mass Balance graphs) have all been plotted in terms of the initial applied heavy metal concentration, however, in an isotherm plot the abscissa is the final supernatant equilibrium heavy metal concentration. For a complete explanation of the isotherm graphs please refer to Appendix A under the subheading "Explanation of Isotherm Graphs".

While these plots are not extensively discussed in this research they show the reader the obvious isotherm shape of some metal retentions and the lack of isotherm shape, or weaker isotherm shape, of other metal retentions. The experimental Pb retention isotherm from the initial pH 3 adjusted solutions (Figure C.40a in Appendix C) is the only high affinity isotherm in this set of tests. Low affinity adsorption isotherms are represented by the Pb (unadjusted initial pH solutions) and the Cu (adjusted initial pH 3 solutions) (Appendix C, Figures C.39a, C.42a). Other retentions measured, such as Cu from the unadjusted initial pH solutions and both Zn retentions, do not even result in an isotherm shape which can be described by the Langmuir model (Appendix C, Figures C.41a, C.43a,b).

Using the precipitation test results (Section 4.3) the adsorption was estimated based on the assumption that precipitation occurs at the equilibrium pH as it does in solution (in the absence of soil) as was discussed in Section 4.2. This hypothetical precipitation is then subtracted from the retention and a hypothetical adsorption is predicted. The resulting hypothetical precipitation is higher than the model predicts and the adsorption (especially at high initial total metal concentrations) is less than the model predicts. Also when this hypothetical calculated adsorption is compared to the Ca + Mg released it is much less (Appendix B). This lack of correspondence indicates that the hypothesis that precipitation occurs at equilibrium pHs as it would in a free solution does not hold.

The adsorption and precipitation reactions are assumed to be occurring simultaneously, therefore, the full solute concentration is not available for precipitation as in the precipitation tests. Also the soil facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface. The author believes that the actual adsorption lies somewhere between the lines representing retention and estimated adsorption and is likely best represented by the Ca and Mg released, rather than by estimates from precipitation, however, the estimated adsorption is presented for discussion purposes. The modelling results consistently under estimate the overall retention, as can be seen by the maximum retained concentrations on the isotherms. The maximum retained concentration on the modelled isotherms is limited by the concentration of surface sites entered into the model. The concentration of Ca and Mg released was used as a concentration of surface sites. If the experimental retention was higher than the Ca+Mg released, then the modelling isotherms underestimate the total retention as was seen in these cases.

4.9 Discussion Summary

This research examined the retention of heavy metals by clay soil in a competitive scenario. Generally, when heavy metals are discharged to the environment as pollutants - typically, industrial pollutants, landfill leachates, or sewage sludges - the pollutants contain several heavy metals in multiple species forms. It is well understood that clay soils have the ability to attenuate heavy metal transport through soils. However, the metals must compete for the adsorption sites on the soil solid surfaces and some metals are selectively favoured for adsorption over others. This research confirms the selective retention order of the heavy metals examined (see e.g., Farrah and Pickering, 1977; Harter, 1983; Elliot, 1986; Biddappa, 1981; Phadungchewit, 1990) and studies the retention mechanisms (precipitation and adsorption) involved.

The precipitation research was performed with heavy metal solutions at varying pHs in the absence of soil (Section 4.3). If soil had been present it would of been impossible to differentiate between adsorption and precipitation removal from solution. Since the precipitation was examined without clay, the applicability to precipitation in the presence of clay is uncertain. If adsorption and precipitation reactions are assumed to be occurring simultaneously, the full solute concentration is not available for precipitation as in the precipitation tests. Also the soil facilitates precipitation by increasing local pH and ion concentrations near the soil particle surface (Yong et al., 1992).

The precipitation study indicates Cu precipitation is not metal specific, increased precipitation occurs with increased total metal concentration in what appears to be similar to a sweep floc effect (Figures 4.4, 4.6, 4.7). In other words an initial concentration of 300 meq/l of Cu will precipitate out in the same manner (in terms of % of initial concentration) as a 100 meq/l Cu concentration with equal concentration of Pb and Zn. However, Pb and Zn are facilitated by the presence of other metals, especially Cu, and precipitation will be greater in a 3 metal solution of equal total metal concentration as a single metal solution (Figure 4.7). Table 4.20 summarizes the precipitation study as presented in Section 4.3. The reasons for this have not fully been examined, but is believed to be related to the speciation and individual activities of each metal.

Table 4.20 - Summary of Precipitation pH of Metal Solutions					
Precipitation Test Type	Metals in Solution	Approximate pH at which Precipitation begins			
Single Metal Tests	Lead Copper Zinc	4 - 5 4 (Sweep floc) 6			
Double Metal Tests	Lead:Copper Lead:Zinc Copper:Zinc	5 5 4 - 5			
Triple Metal Test	Lead:Copper:Zinc	4			

The highest overall retention in the single metal (non-competitive) retention tests was obtained by Cu followed by Pb than Zn, however, based on the K_L values Pb was retained more than Cu and Cu more than Zn. The K_L



values for the three metals were not generated from the same number of data points and initial metal concentrations which may of affected the results. If the Ca and Mg released is examined as an indicator of ion exchange adsorption Pb appears to be adsorbed the most readily followed by Cu and Zn.

The precipitation tests results were used to estimate a hypothetical adsorption by subtracting the possible precipitation which could occur during each batch equilibrium test from the total retention. Based on initial concentrations and equilibrium pH of the batch equilibrium supernatant a hypothetical precipitation was determined. Both the hypothetical adsorption and precipitation are presented on the experimental isotherm plots (Appendix C) and on the tables presented in Appendix B. When the Ca + Mg released (indicator of ion exchange adsorption) is compared to the hypothetical estimated adsorption it becomes obvious that the two values are quite different (Appendix B). It is postulated that the precipitation predicted, based on the equilibrium pH and precipitation tests, does not occur for several reasons linked to the kinetics of precipitation and adsorption reactions, the development of equilibrium pHs, and the local effect of the soil surface.

To compare overall retention between sets of tests the same initial total metal concentration must be compared so retentions and Ca + Mg released values at total metal concentrations of 200meq/100g where examined in Table 4.21 along with overall maximum retention and Ca + Mg released values. The maximum overall retention occurred in the single metal Cu tests performed with adjusted initial pH 3 solutions. The maximum overall Ca and Mg released occurred for Pb in the test involving the initial adjusted pH3 solutions. Except for the single metal Pb and Cu tests, which had slightly higher amounts, the Ca and Mg released was quite similar in most cases indicting similar amounts of ion exchange adsorption were occurring. The single metal Pb and Cu also obtained slightly higher retention of Cu and Pb

(unadjusted initial pH only) than the two metal Pb and Cu tests, indicating there may be some competitive factors inhibiting adsorption in the cases of Pb and Cu. A similar discussion was offered by Yong and Phadungchewit, (1993) on multi-metal versus single metal adsorption. However, when Zn was involved in the two metal tests (Cu+Zn, Pb+Zn) the retention reached levels similar to that of the single metal Zn tests. For the two metal tests involving Zn, adsorption is not inhibited do to competitive factors because Zn does not appear to compete with Pb or Cu.

Table 4.21 - Summary of Metal Retention and Ca+Mg Released							
Batch Equilibrium Tests Total Metals Retain (meq/100g)		Retained	Total Ca+Mg Released (meq/100g)				
Number of Metals and Metals Tested (initial adjusted pH)		Maximum	Initial Conc. 200 meq/100g	Maximum	Initial Conc. 200 meq/100g		
	Pb Pb (3)	140. 97	140 97	110 117	80 117		
Single Metal Tests	Cu Cu (3)	147 262	147 180	103 102	103 102		
	Zn Zn (3)	110 88	82 53	76 53	74 34		
Two Metal	Pb+Cu Pb+Cu (3)	105 169	105 169	80 85	80 85		
Tests	Pb+Zn Pb+Zn (3)	94 97	94 97	83 73	79 73		
	Cu+Zn Cu+Zn (3)	97 110	97 104	83 104	83 88		
Three Metal Tests	Pb+Cu+Zn Pb+Cu+Zn(3)	105 135	90' 97'	96 93	82 ¹ 77 ¹		

¹ - Estimated from Graphs



The two and three metal (competitive) retention tests confirmed a selectivity order of Pb>Cu>>>Zn. The results of each individual set of tests is summarized below (Table 4.22). The selectivity order determined is the same order found by many researchers for different soils. It is also the same order predicted by the Hard Soft Acid Base (HSAB) theory, Misono Softness Parameter and the pK value of the first hydrolysis product all of which were presented in Section 2.5. The selectivity found experimentally does not follow the order predicted by the theory based on ion radius (Section 2.5.2).

Table 4.22 - Summary of Selectivity				
Batch Equilibrium Tests	Selectivity Order (Retention)	Discussion		
Equal Pb and Cu	Pb>Cu	Some retention of Cu in unadjusted initial pH tests and with higher retention at adjusted initial pH 3 tests.		
Equal Pb and Zn	Pb>>>Zn	Minor amounts of Zn was retained		
Equal Cu and Zn	Cu>>>Zn	Minor amounts of Zn was retained		
Equal Pb, Cu and Zn	Pb>Cu>>>Zn	Copper adsorption decreases with increasing initial concentration and Pb concentration remains strong. Zinc (Zn) is not retained in any significant amount.		

The parallel sets of batch equilibrium tests performed examined the effect of initial pH on adsorption of heavy metals. Although researchers have generally found that increased equilibrium pH results in increased retention, the research presented in this thesis indicates that lower initial pH results in increased retention in many cases - Pb in the single metal tests, Pb and Cu in the two metal Pb + Cu tests, Cu in the Cu + Zn two metal tests, and Pb and Cu in the Pb, Cu and Zn three metal tests. It is hypothesized that this may be due to higher concentration of Me²⁺ species in the beginning of the tests, which will have a high affinity for the soil surface. As the pH increases, hydroxide species start forming which have a lower positive charge, therefore,



a lower affinity for the soil surface. Further increase in pH results in the formation of neutral hydroxide species Me(OH)₂ which may precipitate if the intrinsic solubilities are exceeded. As the concentration of Me²⁺ decreases the force driving ion exchange adsorption (concentration gradient) decreases. Interestingly, the final pH of the unadjusted and adjusted solutions did not vary a great deal due to the high buffering capacity of the soil used in this research (Phadungchewit, 1990).

It is likely that the equilibrium pH develops faster in the unadjusted initial pH tests and slower in the adjusted initial pH3 allowing more adsorption to occur. This is supported by geochemical speciation modelling, if one examines the Cu retention in the Zn and Cu two metal tests, the initial pH 3 tests had higher Cu retention by adsorption than the unadjusted pH test. However, one must remember that the K_L from the experimental results is used to model the batch equilibrium tests.

In most cases the pretreated clay soil used in this research retained heavy metals by ion exchange adsorption, which is evident from the mass balance curves which show similar amounts of Ca and Mg released to heavy metals retained (Figures 4.11, 4.12, 4.13a, 4.15a, 4.17a, 4.19a, 4.22a). Based on a comparison of the soil properties determined by Phadungchewit (1990) for untreated Sealbond and the properties of Sealbond determined for this research it seems that the pretreatment of the soil has partially "washed away" and decreased many of the other phases of the soil which traditionally would contribute to retention (ie. carbonate, amorphous and organic phases) leaving the exchangeable phase as the main contributor to adsorption.

In many of the pH 3 adjusted batch equilibrium tests performed, especially the ones involving Zn, lesser amounts of Ca and Mg were released than total heavy metals retained (Figures 4.13b, 4.15b, 4.17b, 4.19b, 4.22b).
Many of these sets of batch equilibrium tests are the same tests that obtained increased adsorption with decreased initial pH. It seems that at these adjusted pH 3 tests, particularly when Zn is involved, an adsorption or retention mechanism other than ion exchange is occurring. Farrah and Pickering (1976) found Zn is adsorbed on Illite as ZnOH⁻ which would not be adsorbed according to an ion exchange reaction -one Ca²⁺ released would make way for two ZnOH⁺ to be adsorbed in terms of electro-neutrality. Another explanation is that at lower initial pH Zn²⁺ may have difficulty competing with H⁺ ions. According to Sposito (1984) adsorption on to surface hydroxyl groups releases H⁺ ions (Section 2.6.2). The final pH of the Zn batch equilibrium tests was higher than the other metals indicating less adsorption may be occurring.

Yong and Phadungchewit (1993) concluded that as pH decreases, precipitation mechanisms become less dominant and cation exchange governs retention. This research demonstrates that even at unadjusted initial pHs with high resulting equilibrium pHs, ion exchange remains the largest retention mechanism for the three heavy metals examined.

The experimental result often indicate ion exchange adsorption as the major mechanism of retention when the speciation modelling indicates precipitation. This discrepancy is probably best explained by the kinetics of the reactions. The modelling was preformed using the equilibrium pH of the batch equilibrium supernatant which may not in fact develop immediately upon the commencement of the batch equilibrium test. In fact, adsorption may occur immediately, before pH levels have been buffered by the soil. In other words perhaps in terms of kinetics, ion exchange adsorption is faster than precipitation but since the equilibrium models assume instantaneous reactions it does not account for the kinetic variation between reactions.

The Langmuir isotherm treats surface sites analogous to dissolved complexing ligands, further, it is derived by combining an adsorption equilibrium constant with a mass balance on the total number of adsorption sites. Since an ion exchange type adsorption reaction was assumed, the Ca + Mg released was used as an estimate of the number of adsorption sites. The Langmuir isotherms assumes maximum adsorption occurs when a single layer of cations is adsorbed, perhaps this is also an oversimplification and the adsorption occurring is actually more complex and multi-layered. For example, the adsorbed heavy metals may be a nucleus for further growth.

The MINTEQA2 model was able to describe the retention of the single metal batch equilibrium experimental results, but in multi metal competitive scenarios when more than one metal was actually retained, the modelling does not describe the retention sufficiently. For example, for the two metal Pb and Cu batch equilibrium tests the modelling over predicted Cu adsorption and under predicted Pb adsorption when compared to the experimental results. The same difficulty occurred for the three metal Pb, Cu and Zn batch equilibrium modelling where Pb retention was under predicted and Cu retention was over predicted.

CHAPTER 5

CONCLUSIONS

5.1 Concluding Remarks

The objectives of this research were to study the selective retention of heavy metals on a clay soils in a competitive adsorption scenario and differentiate between soil retention and adsorption using the theories of ion exchange and by examining heavy metal precipitation studies.

To obtain these objectives heavy metal retention and exchangeable cation displacement were studied in the laboratory in competitive (multi metal) and non competitive (single metal) batch equilibrium tests. Heavy metal precipitation was also examined in single and multi metal solutions across a wide pH range. The laboratory experiments were then modelled using a equilibrium speciation computer model. The noteworthy observations and conclusions that can be drawn are summarized as follows:

1) Soil pretreatment saturated the exchangeable sites with Ca and Mg cations, resulting in a soil saturated with the two cations. However, the relative amounts of Ca and Mg adsorbed on the soil showed a definite preference for Ca over Mg by the soil. The repeated washes used to saturate the soil also resulted in a loss of some of the organic, amorphous, carbonate, and fine clay fractions.

2) The precipitation research indicated Cu precipitation is not metal specific, increased precipitation occurs with increased total metal concentration in what appears to be similar to a sweep floc effect. However, Pb and Zn precipitation is facilitated by the presence of other metals,

especially Cu, and precipitation will be greater in a 3 metal solution of equal total metal concentration than in a single metal solution. This occurrence requires further study to be fully understood, but is believed to related to the speciation of individual metals and the resulting activities.

3) The highest overall retention in the single metal (non-competitive) retention tests was obtained by Cu followed by Pb then Zn, however, based on the K_t values Pb was retained more than Cu and Cu more than Zn. The two and three metal (competitive) retention tests confirmed a selectivity order of Pb>Cu>>>Zn which is the same selectivity order predicted by the HSAB theory and the pK values of the first hydrolysis product.

4) The single metal Pb and Cu also obtained slightly higher retention of Cu and Pb (ur adjusted initial pH only) than the two metal Pb and Cu tests, indicating there may be some competitive factors inhibiting adsorption in the cases of Pb and Cu. However, when Zn was involved in the two metal tests (Cu+Zn, Pb+Zn) the retention reached levels similar to that of the single metal Zn tests, but levels less than the single Cu and Pb tests.

5) In most cases the pretreated clay soil used in this research retained heavy metals by ion exchange adsorption. This is evident from the mass balance curves which show similar amounts of Ca and Mg released to heavy metals retained.

6) If the Ca and Mg released is examined as an indicator of ion exchange adsorption in the single metal non competitive adsorption tests Pb appears to be adsorbed the most readily, followed by Cu and Zn. Except for the single metal Pb and Cu tests, which had slightly higher amounts, the Ca and Mg released was quite similar in most cases indicating similar amounts of ion exchange adsorption are occurring.



7) Although researchers have generally found that increased equilibrium pH results in increased retention, the research presented in this thesis indicates that lower initial pH results in increased retention in many cases such as Pb in the single metal tests, Pb and Cu in the two metal Pb + Cu tests, Cu in the Cu + Zn two metal tests, and Pb and Cu in the Pb, Cu and Zn three metal tests. It is postulated that this may be due to higher concentration of Me^{2+} species in the beginning of the tests which will have a high affinity for the soil surface.

8) Interestingly, the final pH of the unadjusted and adjusted solutions did not vary a great deal due to the high buffering capacity of the soil used in this research (Phadungchewit, 1990). It is likely that the equilibrium pH develops faster in the unadjusted initial pH tests and slower in the adjusted initial pH allowing more adsorption to occur as described in point 7.

9) Besides using Ca and Mg released as an estimate of ion exchange adsorption, a hypothetical estimated adsorption was also calculated from the total retention, based on the precipitation test results and the equilibrium pH of the batch equilibrium supernatant. However, when the results of Ca + Mg released (indicator of ion exchange adsorption) are compared to the estimated adsorption it becomes obvious that the two values do not match indicating that precipitation, as predicted by the precipitation tests, does not occur.

10) The experimental result often indicate ion exchange adsorption as the major mechanism of retention when the equilibrium speciation modelling indicates precipitation. This discrepancy is probably best explained by the kinetics of the reactions. The modelling was preformed using the equilibrium pH of the final supernatant which may not in fact develop immediately upon the commencement of the batch equilibrium test. Equilibrium speciation computer models assume instantaneous reactions and therefore, do not

account for kinetic variations between reactions.

11) The modelling seems to function quite well for simple scenarios involving the retention and adsorption of only one metal - in a fashion that can be described by an isotherm. When competitive adsorption is occurring and more than one metal is adsorbed the modelling becomes inaccurate, and perhaps requires refining and calibrating by the user to obtain satisfactory results.

5.2 Future Research Recommendations

To further improve our understanding of competitive adsorption and retention on clay soils more scenarios involving other heavy metals and clay soils should be examined.

While a selectivity order for heavy metal adsorption was established and supported by properties related to the heavy metals, further in depth study of heavy metal selectivity is required. While the pretreatment of the soil allowed for ion exchange mass balances it also resulted in the loss of some of the other active soil fractions. Future research could examine how these soil fractions contribute to competitive adsorption and/or competitive complexation, especially phases such as carbonates which are documented to increase heavy metal retention due to precipitation mechanisms.

For the soil preparation ethanol was used to wash out excess chloride ions. It was later suggested that ethanol may have affected the soil structure, this possibility should be investigated.

For this research the only competitive scenarios examined involved heavy metals at equal concentration ratios. It would be interesting to continue the examination of competitive adsorption be examining other concentration Oratios perhaps more representative of a typical industrial pollutant or landfill leachate.

Further analysis could be performed on the relative amount of each of the two exchangeable cations released during the adsorption reactions. Furthermore, the affect of the pre-saturated cation species could be examined. For example, if a saturation with just Ca had been attempted would similar amounts of ion exchange occur? For that matter, if a saturation with a monovalent cation (ie. Na) had occurred how would ion exchange adsorption be affected?

An interesting effect of initial pH on adsorption was noted in this research this could be further investigated by examining other initial pH's to determine if this effect continues and the possible mechanisms involved. Also, time dependent experiments could examine the possible affect of kinetics on pH developments and retention.

Further examination of the MINTEQA2 Equilibrium Speciation Model should be performed, particularly an extensive comparison of the seven adsorption models offered within MINTEQA2.

Comparison of the modelling and experimental result could continue until a calibration of the model is obtained such that the model could be used to predict laboratory results accurately.

CHAPTER 6

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APPENDIX A

A.1 Units of Concentration

All calculations, modelling and experimental displays of heavy metal concentrations are presented in concentration units of milliequivalents (meg) per Litre (L) or meg per 100 grams (g) of soil. The reader may not be familiar with the equivalent (eq) unit of measurement which describes a chemical weight in terms of combining capacity or reactive capacity. Starting with moles and molarity, a mole is a g-molecular weight (ie 331.20 g of Pb(NO₃)₂ is one mole since the molecular weight of $Pb(NO_3)_2$ is 331.2). A mole contains Avogadro's number of molecules. A 1 Molarity (M) solution is 1 gmolecular weight of solute per litre of solution $(331.2 \text{ g Pb}(NO_3)_2/L)$. An equivalent weight is a g-molecular weight divided by the combining capacity and, therefore, must be defined in terms of the specific reaction involving the substance. An equivalent weight is defined as the number of grams of substance that will provide Avogadro's number of reactions. In the case of a salts the reaction considered is dissolution. Since Pb(NO₃)₂ is a salt, the combining capacity is the total number of positive or negative charges, which is 2 in this case, and for each of the metal nitrates used in this research (Cu, Zn). Therefore, the equivalent weight is half of the molecular weight or 165.6 for Pb(NO₃)₂. Normality (N) is to equivalent weights what molarity is to moles, an expression in terms of litres of solution, such that 1N is 1 gequivalent weight of solute per litre of solution. It takes 1000 milliequivalents (meg) or 1 equivalent (eq) of solute per litre of solution to make a 1N solution. In this text the term meg is used most of the time instead of N because concentrations are often given in terms of g of soil and not litres of solution.



Activities

All of the above calculations assume an ideal solution which assumes that all ions act independent of any other ions in solution. However, this assumption is correct only for very dilute solutions. As the concentration of a solution increases the interaction between ions will increase and activities must be introduced. The activity of a solution is the effective concentration required to explain solutions thermodynamically - in other words - by examining activities it allows us to consider non ideal solutions as ideal. The activity of a solution is simply the concentration of the solution multiplied by an activity coefficient.

- $a = \gamma C$
- a activity (moles/l)
- γ activity coefficient
- C concentration (moles/l)

The activity coefficient, *y*, of a solute is a function of the ionic strength and valance of the species. It can be calculated using the Debye-Huckel limiting law for solutions of less than 0.005M ionic strength, the Debye-Huckel and Guntelberg relationships for solutions of ionic strengths less than 0.1M, and the Davies relationship for solutions of ionic strength less than 0.5M. The later is shown below since it is the relationship used to calculate activities in the geochemical speciation modelling.

Davies Equation for Activity Coefficient:

$$\log \gamma = -AZ^2 (\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I)$$

The ionic strength is a function of the concentration, C, and the valence, Z, of the species involved.

$$I = \frac{1}{2} \sum_{i=1}^{i=i} C_i Z_i^2$$

The ionic strength for different mixtures of heavy metals at the same total metal concentration will vary do to the different species present. For example, at a set pH if one metal is present in its ionic form of valence 2+ (Pb²⁺), but another metal is present as a hydroxide (ZnOH), the metal speciated at a higher valence will have a higher ionic strength and higher activity.

A.2 How to Read the MINTEQA2 Geochemical Speciation Tables

The speciation tables presented throughout chapter 4 (Tables 4.6, 4.7, 4.8, 4.9, 4.10, 4.13, 4.16, 4.19) present the speciation results of the MINTEQA2 geochemical modelling. The first column on the table list the initial components entered into the model. The second column lists the equilibrium species formed according to MINTEQA2. Along the top of the tables the initial total metal concentrations are tabulated. Below each total metal concentration are the percent of each initial component found in each equilibrium species. This is were the reader must be careful because the mass balance on the adsorbed and dissolved species is separate from the solid precipitates. The percentages of components in dissolved and adsorbed species are in term of total dissolved and adsorbed species and the percent of precipitated species are in terms of total initial component concentration.

For example in Table 4.5a, at initial total metal concentration of 50meq/100g, 99.3% of the dissolved fraction of component Pb²⁺ is bound in

Sur-Pb (Adsorbed Species) but only 16.70% of Sur (adsorbing surface) is occupied by Pb²⁺. However, 63.8 percent of the total initial Pb concentration is precipitated as Pb(OH)₂.

A.3 Explanation of Isotherm Graphs - Experimental

Three lines are presented on the experimental isotherms presented in Appendix C, each is determined as follows;

Retained - This line is the total heavy metal retention, determined by subtracting the initial applied heavy metal concentration from the final equilibrium heavy metal concentration.

Adsorbed^{*} - This curve on the graph shows the hypothesized adsorption. The ^{*} is used to denote a calculated number based on the hypothesis that precipitation of the initial applied metals at equilibrium pH has occurred as though they were in a solution without soil and that all of this precipitation occurs. It was determined by applying the equilibrium pH value of the batch equilibrium test supernatant, to the precipitation curves experimentally determined and discussed in Section 4.2. By interpolating to the equilibrium pH, along the initial metal concentration curve, an equilibrium concentration after precipitation can be determined. Once this values is obtained, it is subtracted from the overall retention (as presented in Sections 4.3 to 4.7) and the remaining concentration represents the postulated adsorption.

Precipitation[•] - This curve on the graph shows the estimated precipitation. A [•] is used to denote a calculated number based on the hypothesis that the precipitation of the initial applied metals at equilibrium pH has occurred as it would in solution without soil. Precipitation values are determined using the precipitation test presented in Section 4.2 and the

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equilibrium pH of the final supernatant. By interpolating to the equilibrium pH, along the initial metal concentration curve, the maximum possible amount of precipitation can be determined.

A.4 Explanation of Isotherm Graphs - Modelled

The modelling results were much easier to depict in an isotherm graph since the geochemical speciation model, MINTEQA2, offers a mass balance on precipitated, adsorbed and dissolved species. The modelling output presents the percent of each component (ie, Pb,Cu,Zn) bound in precipitated, adsorbed and dissolved phases. The total retention can be determined by adding the adsorbed and precipitated percents together. To determine the concentration associated with each phase the percentage is multiplied by the initial total component concentration and divided by 100.

The summation of the estimated precipitation and adsorption curves should result in the retention curve.

APPENDIX B

Tabulated Experimental and Modelling Results

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								Hypothetical	/Estimated
Samples	Lead Added	Lead Retained	Final	Initial	Ca Released	Mg Released	Ca + Mg Released	Adsoption	Precipitation
-	(meq/100g)	(meq/100g)	pН	pН	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(maq/100g)
1.00	9.64	9.64	6.37	4.71	7.60	1.71	9.51	0.10	0.38
2.00	9.63	9.63	6.62	4.71	6.48	1.62	8.10	0.10	0.38
3.00	9,63	9,63	7.12	4.71	7.14	1.73	8.88	0.10	0.38
4.00	4.62	4.82	7,32	4.86	4.20	0.90	5,10	1.20	1.21
5.00	4.81	4.81	7,32	4.86	4.41	0.90	5.31	1.20	1.21
6.00	4.82	4.82	7.19	4.86	4.31	0.95	5.28	1.20	1.21
7.00	2.41	2.41	7,46	5.11	3,32	0.39	3.71	4.80	0.01
8.60	2.41	2.41	7.32	5.11	3.43	0.35	3.78	4.80	0.02
9.00	2.41	2.41	· 7.58	5.11	3.64	0.51	4.16	4.80	0.02
1.00	24.97	24.97	8.61	6.61	13.11	9.76	22.88	7.13	2.49
2.00	49.95	49.95	6.48	6.46	40.37	15.68	56.04	5.89	3.74
3.00	74.95	74.95	6.40	6.40	62.97	24.64	87.60	7.81	1.64
7.00	99.87	86.82	4.96	4.50	66.04	26.73	92.77	36.72	13.23
4.00	99.94	65.71	4.56	4.50	69.20	30.97	100.17	83.64	3.18
5.00	199.83	96.71	4.32		60.85	36.25	117.11	83.77	1.94
6.00	299.69	94.82	4.42	4.12	76.95	29.91	106.88	66.83	27.99

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Lead Batch Equilibrium Experimental Results Performed Using Unadjusted Initial pH

Lead Batch Equilibrium Modelling Results Performed Using Unadjusted Initial pH Solutions

Lead Added	Dissolvad	Adsorbed	Precipitated	Retained
(meg/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meq/100g)
4.81	0.01	4.28	0.54	4.60
4.82	0.01	4.27	0.54	4.81
4.62	0.01	4.27	0.54	4.81
9.63	0.02	6.52	3.09	9.61
9.63	0.02	6.52	3.09	9.61
9.64	0,02	6.53	3.10	9.63
49.95	0.15	17.98	31.87	49.85
74.95	0.22	21.96	52.77	74.73
99.87	7.49	92.38	0.00	92.38
99.94	7.50	92.44	0.00	92.44
199.63	99.52	100.32	0.00	100.32
299.69	201.09	98.60	0.00	98.60

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Lead Batch Equilibrium Experimental Results Performed Using Adjusted Initial pH 3 Solutions

								Hypothetical/	Estimated
Samples	Lead Added	Lead Retained	Initial	Final	Ca Released	Mg Released	Ca + Mg Released	Adsorbed	Precipitation
	(meq/100g)	(meq/100g)	ρН	рН	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100y)	(meq/100g)
41.00	10.00	10.00	2.99	7.50	5.10	4.07	9.17	5.00	5.00
40.00	25.00	25.00	3.05	7.23	12.05	8.23	20.28	6.00	19.00
39.00	50.00	50.00	2.99	6.94	22.02	11.78	33.80	30.40	19.60
38.00	75.00	75.00	2.99	6.72	54.77	15.05	69.83	20.00	55.00
37.00	100.00	97.29	3.04	5.36	64.50	20.29	84.79	80 38	16.91
22.00	200.00	140.48	2.90	4.80	45.67	34.62	80.29	120.48	20.00
21.00	300.00	118.74	3.01	4.63	71.32	38.79	110.11	80.65	38.09

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Lead Batch Equilibrium Modelling Results Performed Using Adjusted Initial pH 3 Solutions

Lead Added	Dissolved	Adsorbed	Precipitated	Retained
(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
10	0	0.13	9.87	10
25	0	0.45	24.55	25
50	0	1.7	48.3	50
75	0.075	4.575	70.35	74.925
100	7.9	92.1	0	92.1
200	97.2	102.8	0	102.8
300	198.9	101.1	0	101.1

Copper Batch Equilibrium Experimental Results Performed Using Unadjusted Initial pH Solutions

								Hypothetical/f	Estimated
Samples	Copper Added	Retained Initial	Final	Ca Released	Mg Reteased	Ca + Mg Released	Adsorbed	Precipitated	
	(meq/100g)	(meq/100g)	рН	pН	(meq/100g)	(meq/100g)	(meq/100g)		
4.000	7.850	7.855	4.870	7.08	8.848	5.07	13.91	0.00	7.82
3.000	15.721	15.723	4.590	6.93	16,660	7.46	24.12	0.14	15.59
2.000	31.461	31.446	4.390	6.47	34.695	10.68	45.38	0.47	30.97
11.00	49.885	50.000	4.40	6.60	38.652	12.33	50.98	0.10	49.90
1.000	62.915	62.881	4.230	6.16	54.816	14.21	69.02	0.03	62.85
10.00	74.978	74.983	4.29	6.37	63.583	14.39	77.97	0.08	74.90
9.00	99.887	98.826	4.12	6.00	75.026	16.05	91.07	0.00	100.00
13.00	199.455	147.457	3.97	4.70	76.283	25.76	102.04	64.79	82.67
15.00	299,471	94.225	3.94	4.44	75.438	17.97	93.41	. 0.00	123.15

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Copper Batch Equilibrium Modelling Results Performed Using Unadjusted Initial pH Solutions

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Adsorbed	Precipitated	Retained	Dissolved
(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
0.05	7.80	7.85	0.00
0.09	15.63	15.72	0.00
0.47	30,96	31.43	0.00
0.60	49.09	49.89	0.00
3.08	59.77	62.85	0.13
6.19	93.49	99.69	0.20
90.55	59.64	150.19	49.27
93.14	98.83	191.96	107.51
	Adsorbed (meq/100g) 0.05 0.09 0.47 0.80 3.08 6.19 90.55 93.14	Adsorbed Precipitated (meq/100g) (meq/100g) 0.05 7.80 0.09 15.63 0.47 30.96 0.80 49.09 3.08 59.77 6.19 93.49 90.55 59.64 93.14 98.83	AdsorbedPrecipitatedRetained(meq/100g)(meq/100g)(meq/100g)0.057.807.850.0915.6315.720.4730.9631.430.6049.0949.893.0859.7762.856.1993.4999.6990.5559.64150.1993.1498.83191.96

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Copper Batch Equilibrium Experimental Results Performed Using Adjusted Initial pH 3 Solutions

								Hypothetical/E	Estimated
Sample	Initial	Retained	Initial	Final	Ca Released	Mg Released	Ca + Mg Released	Adsorbed	Precipitated
	(meq/100g)	(meq/100g)	рН	pН	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
31.00	10.00	10.00	2.97	7.13	7.52	4.90	12.42	0.04	9 96
30.00	25.00	25.00	2.98	6.76	19.09	7.24	26.33	0.25	24.75
29.00	50.00	49.99	2.99	6.51	25.17	11,16	36.33	0.14	49.85
28.00	75.00	74.99	2.99	6.44	61.97	13.69	75.66	0.14	74.85
27.00	100.00	99.93	2.95	5,78	85.96	17.94	103.90	9.96	89.96
12.00	200.00	180.43	2.97	4.67	84.53	18.77	103.30	87.76	92.67
14.00	300.00	262.25	2.98	4.50	71.18	13.65	64.83	123.79	138.46

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Copper Batch Equilibrium Modelling Results Performed Using Adjusted Initial pH 3 Solutions

initial	Adsorbed	Precipitated	Retained	Dissolved
(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
10.00	0.07	9.92	9.99	0.00
25.00	0.40	24.60	25.00	0.00
50.00	1.25	48.70	49.95	0.00
75.00	1.73	73.28	75.00	0.00
100.00	27.00	72.30	99.30	0.60
200.00	96.60	48.60	145.20	54.80
300.00	96.30	116.70	213.00	87.00



Tables B 5

Zinc Batch Equilibrium Test Experimental Results Performed Using Unadjusted Initial pH Solutions

								Hypothetical/E	stimated
Sample	Zinc Added	Retained	Initial	Final	Ca Released	Mg Released	Ca + Mg Released	Adsorbed	Precipitation
•	(meg/100g)	(meg/100g)	ρН	рH	(meq/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meq/100g)
16.00	6.11	5.16	6.62	7.20	5.34	3.32	8.67	3.44	1.74
17.00	. 6.12	5.29	6.73	7.53	5.18	3.33	8.51	3.17	2.12
15.00	15.29	14.44	6.38	7.06	11.02	3.67	14 69	7.80	6.64
14.00	15.29	14.27	6.38	6.66	10.05	3.74	13.79	7.98	6.29
13 00	15.29	14.40	6.42	6.93	9.73	3.61	13.54	7.75	6.64
12.00	30.56	26.17	6.20	6.46	17.35	4.99	22.33	18 92	9.18
11.00	30.56	27.35	6.22	6.32	17.35	5.33	22.68	21.17	6.19
10.00	30.58	26.04	6.28	6.39	18.33	5.06	21.39	20.33	7.71
16.00	49.87	38.40	5.77	6.14	20.18	7.87	28.05	35.53	0.87
17.00	74.61	45.83	5.72	6.00	31.14	6.24	36.38	45 82	0.01
18.00	99.67	53.36	5.51	6.00	35.40	6.33	43.73	51.78	1.60
8 00 8	152.66	82.23	5.72	5.65	60.31	7.97	74.29	81.37	0.88
7.00	152.87	79.01	5.77	5.66	62.89	7.48	70.38	78.15	0.67
9.00	152.87	79.82	6.73	5.50	65.29	7.54	72.83	78.95	0.87
19.00	299.21	105.55	5.53	5.58	54.98	9.73	64.69	105.47	2.21
4.00	305.65	110.35	5.57	5.40	67.67	B.48	76.15	83.70	26.65
6.00	305.68	108.34	5.64	5.44	60.63	7.97	68.60	97.65	8 68
5.00	305 88	104.80	5.53	5.40	65.32	6.49	73.61	95.92	8.88

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Zinc Batch Equilibrium Test Modelling Results Performed Using Unadjusted Initial pH Solutions

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Initial	Dissolved	Adsorbed	Precipitated	Retained
(meg/100g)	(meg/100g)	(meg/100g)	(ineq/100g)	(meq/100g)
6.11	0.75	1.85	3.48	5.38
6.12	0.75	1.88	3.49	5.30
15.29	5.41	9.88	0.00	9.88
30.56	13.11	17.45	0.00	17.45
30.58	13.12	17.46	0.00	17.46
49.87	25.14	24.74	0.00	24.74
74.81	43.24	31.57	0.00	31.57
99.67	63.09	36.58	0.00	36.58
152.86	108.99	43 87	0.00	43.87
152.87	109.00	43.87	0.00	43 37
299.21	245.05	54.16	0.00	54.15
305.65	251.25	54.41	0.00	54.41
305.68	251.27	54.41	0 00	54.41
305.68	251.43	54.45	0.00	54.45

Test B.6

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Zinc Batch Equilibrium Test Experimental Results Performed Using Adjusted Initial pH 3 Solutions

								Hypothetical/E	stimated
Sample	Initial	Retained	Initial	Final	Ca Released	Mg Released	Ca + Mg Released	Adsorbed	Precipitated
	(meq/100g)	(meq/100g)	pН	pН	(meq/100g)	(meq/100g)	(maq/100g)	(meq/100g)	(meq/100g)
36.00	10.00	1.99	2.99	6.76	6.35	3.62	9.97	0.00	5.00
35.00	25.00	22.41	3.05	6.41	16.59	5.80	22.39	14.41	8.00
34,00	50.00	39.60	2.97	6.14	19.30	7.62	26.92	36.60	3,00
33.00	75.00	48.38	2.99	5.96	25.65	7.70	33.35	47.38	1.00
32.00	100.00	53.14	3.00	5.87	25.63	8.60	34.23	52.14	1,00
20.00	, 300.00	87.78	2.95	5.58	44.61	8.69	53.31	84.78	3.00

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Zino Batch Equilibrium Test Modelling Results Performed Using Adjusted Initial pH 3

Initial	Dissolved	Adsorbed	Precipitated	Retained
(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meg/100g)
10.00	0.40	5,90	0.00	5.90
25.00	12.63	12.38	0,00	12.38
50.00	30.45	19.65	0.00	19.55
75.00	50.78	24.23	0.00	24.23
100.00	72.40	27.60	0.00	27.60
300.00	260.70	39,30	0.00	39,30



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Table B.7

Copper and Load Batch Equilibrium Tests Experimental Results Performed Using Unadjusted Initial pH

											Hypothesized/	Estimated	
	Initial	Initial	Retained	Retained	Released	Released	Released	Initial	Final				
Samples	Lead	Copper	Lead	Copper	Calcium	Magnesium	Ca + Mg	рН	pН	Lead	Copper	Lesd	Copper
	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(maq/100g)	(meq/100g)	(meq/100g)			Adsorption	Adsorption	Precipitation	Precipitation
8.00	9.96	9.96	9.96	9.98	12.24	7.42	19.66	4.69	6.95	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
9.00	24.99	24.95	24.99	24.91	41.86	10.88	52.72	4.50	6.65	2.59	1.58	7.41	8.42
10 00	49.94	49.98	49.21	23.62	48.84	10.96	59.79	4.48	5.02	8.62	1.98	16.18	22.99
20.00	74.99	74.91	72.61	11.96	68.57	11.67	80.24	4.34	4.75	43.27	19.64	6.00	4 00
6.00	74.78	74.99	72.93	12.11	63.71	11.39	75.09	4.25	4.76	72.62	7.25	0 00	4 82
11.00	74.90	74.78	72.83	3.02	64.40	12.02	76.42	4.34	4.75	73.18	7.27	0.00	4 85
5.00	99.73	99.87	90.62	29.13	69.44	11.65	81.30	4.24	4.61	72.93	0.00	0.00	4 82
12.00	99.81	99.73	85.08	10.32	65.14	12.02	77.15	4.24	4.68	63.39	19.65	7.50	9.61
23.00	99.73	99.81	66.21	13.97	67.94	12.47	60.40	4.24	4.65	77.07	0.68	8.20	9 93
										78 67	4.37	7.90	9.80

Copper and Lead Batch Equilibrium Test Modelling Results Unadjusted Initial pH

Initial	Initial	Dissolved	Dissolved	Retained	Retained	Precipitated	Precipitated	Adsorbed	Adsorbed
Lead	Copper	Lead	Copper	Lead	Copper	Lead	Copper	Lead	Copper
(meg/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
10.00	10.00	0.01	0.00	9.99	10.00	8.92	10.00	1.07	0.00
25.00	25 00	0.05	0.00	24.95	25.00	20.85	25.00	4.10	0.00
50.00	50.00	2.25	18.35	47.75	31.65	0.00	31.65	47.75	0.00
75.00	75.00	9.68	44.85	65.33	30.15	0.00	30.15	65.33	0.00
100.00	100.00	25.10	69.70	71.90	40.30	0.00	40.30	71.90	0.00



Sample

12.00

18.00

14.00

15.00

8.00

18.00

7.00

17.00

100.00

Table B.8

Copper and Lead Batch Equilibrium Tests Experimental Results Performed Using Adjusted Initial pH 3

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Initial intial Copper Released Released Released Initial Final Lesd Leod Copper Lead Copper Lead Copper pН pН Retained **Retained** Celcium Magnesium Ca + Mg Adsorption Adsorption Precipitation Precipitation (meg/100g) (meg/100g) (meg/100g) (meg/100g) (meq/100g) (meg/100g) (meg/100g) (meg/100g) (meg/100g) (meg/100g) (meg/100g) 10.00 10.00 2.97 6.96 9.96 10.00 13.85 6.19 20.04 2.53 1.53 2.48 1.53 24.90 25.00 25.00 3.03 6.39 25.00 25.62 9 61 35.23 11.70 11.70 2.97 2.99 25.00 25.00 3.00 6.53 25.00 24.98 25.68 9.78 35.48 10.15 2.46 10.15 2.44 50.00 50.00 3.02 5.16 49.50 46.44 59.97 9.33 69.30 13.08 39.95 35 40 12 61 75.00 75.00 2.92 4.61 73.29 59.69 66.68 10.81 77.47 75.00 89.98 54 67 73 29 75.00 4.69 58.68 66.38 75.00 2.95 73.40 9.61 75.97 75 00 70.39 54 08 73.40 78.55 72.88 100.00 100.00 2.97 4.62 89.01 12.96 85.85 92.40 90.34 81.41 68 89

74.19

9.90

84.09

Copper and Lead Batch Equilibrium Tests Modelling Results Adjusted Initial pH 3

100.00

Initial	Initial	Dissolved	Dissolved	Retained	Retained	Precipitaled	Precipitated	Adsorbed	Adsorbed
Lead	Copper	Lesd	Copper	Lead	Copper	Lesd	Copper	Lead	Copper
(meg/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meg/100g)	(meq/100g)	(meq/100g)
10.00	10.00	0.01	0.01	9.97	9.99	5.63	9.60	4.34	0.39
25.00	25.00	0.13	0.03	24.85	24.95	14.85	24.08	10.03	0.90
50.00	50.00	8.15	11.15	41.85	38.85	0.00	4.00	41.85	34.85
75.00	75 00	31.20	38.10	43.80	38.90	0.00	0.00	43.80	35.90
100.00	100.00	58.60	62.70	43.40	37.30	0.00	0.00	43.40	37.30

4.62

69.64

79.97

Hypothesized/Eshmated

90.34

92.40

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Hypothesized/Estimated

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Table 8.9

Lead and Zinc Batch Equilibrium Tests Experimental Results Performed Using Unadjusted Initial pH

Sample	Initial Lead (meq/100g)	Initial Zinc (meq/100g)	Relained Lead (meq/100g)	Retained Zinc (meq/100g)	Initial pH	Final pH	Released Calcium (meq/100g)	Released Magnesium (meq/100g)	Released Ca + Mg (meq/100g)	Adsorbed Lead (meq/i00g)	Adsorbed Zinc (meq/100g)	Precipitation Lead (meg/100g)	Precipitation Zinc (meq/100g)
15.00	9.99	9.99	9.99	8.01	4.73	6.72	13.18	5.91	19.09	5.19	7.72	981	5.30
14.00	24.99	24.99	24.99	12.47	4.68	6.18	27.72	6.31	34.03	20.59	0.49	16.91	24 50
16.00	49.95	49.95	49.95	11.20	4.62	6.02	45.78	11.03	58.79	43.00	11.25	32 00	25 00
19.00	74.60	74.80	74.77	7.14	4.61	5.92	73.09	13.00	66.09	43.66	0.71	68 82	44.13
17.00	74.98	74.98	74.93	6.76	4.61	5.92	67.38	13.37	80.75	43.64	0.15	68 82	44.13
18.00	99.67	99.67	90.29	3.80	4.54	5.28	62.48	16.64	79.13	77.34	0 82	63.27	53.40

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Lead and Zinc Batch Equilibrium Tests Modelling Results Unadjusted Initial pH

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Indal	Initial	Retained	Retained	Dissolved	Dissolved	Adsorbed	Adsorbed	Precipitated	Precipitated
Lead	Zinc	Lead	Zinc	Lead	Zinc	Lead	Zinc	Lead	Zinc
(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meg/100g)	(meq/100g)	(məq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
10.00	10.00	10.00	0.00	0.00	10.00	10.00	0.00	0.00	0.00
25.00	25.00	25.00	0.00	0.00	25.00	25.00	0.00	0.00	0.00
50.00	50 00	49.95	0.00	0.05	50.00	49.95	0.00	0.00	0.00
75.00	75 00	74.78	0.00	0.23	75.00	74.78	0.00	0.00	0.00
100.00	100.00	82.60	0.00	17.40	100.00	82.60	0.00	0.00	0.00





Lesd and Zinc Batch Equilibrium Tests Experimental Results Adjusted Initial pH 3

Hypothesized/Estimated

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	Initial	Initial	Initial	Final	Relained	Retained	Released	Related	Refeased	Adsorbed	Adsorbed	Precipitation	Precipitation
Sample	Lesd	Zinc	pН	pН	Lesd	Zinc	Calcium	Magnesium	Ca + Mg	Lead	Zinc	Lead	Zinc
	(meq/100g)	(mag/100g)			(meq/100g)	(meq/100g)	(meq/100g)	(meg/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meg/100g)	(meq/100g)
7.00	10.00	10.00	2.99	6.55	10.00	0.00	10.22	5.30	15.52	5.60	0.00	4.40	0 30
8.00	25.00	25.00	3.05	6.32	25.00	11.76	17.04	7.69	2 73	17.18	0.84	7.84	10 92
9.00	50.00	50.00	3.04	6.15	49.99	9.18	27.01	9.40	35.42	37.74	8 38	12.25	080
10.00	75.00	75.00	3.00	5.97	74.93	5.74	57.38	13.14	70.60	44.89	0.00	30.04	7.02
11.00	100.00	100.00	3.04	5.27	93.16	4.07	59 90	13.07	72.97	82.48	1.53	10.70	2.74

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Lead and Zinc Batch Equilibrium Tests Modelling Results Adjusted Initial pH 3

initia?	Initial	Retained	Retained	Dissolved	Dissolved	Adsorbed	Adsorbed	Precipitated	Precipitated
Lead	Zinc	Lead	Zinc	Lead	Zinc	Lesd	Zinc	Lead	Zinc
(meq/100g)	(meg/100g)	(meq/100g)	(meg/100g)	(meg/100g)	(meg/100g)	(meq/100g)	(maq/100g)	(meq/100g)	(maq/100g)
10.00	10.00	10.00	0.00	0.00	10.00	10.00	0.00	0.00	0.00
25.00	25.00	24.98	0.00	0.03	25.00	24.98	0.00	0.00	0.00
50.00	50.00	49.90	0.00	0.10	50.00	49.90	0.00	0.00	0.00
75.00	75.00	72.45	0.00	2.63	75.00	72.45	0.00	0.00	0.00
100.00	100.00	70.00	0.00	30.00	100.00	70.00	0.00	0.00	0 00



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Copper and Zinc Batch Equilibrium Tests Experimental Results Performed Using Unadjusted pH

Samples	Initial	Initial	Retained	Relained	Initial	Final	Released	Released	Released	Adsorbed	Adsorbed	Precipitated	Precipitated
	Copper	Zinc	Copper	Zinc	рH	рН	Calcium	Magnesium	Ca + Mg	Copper	Zinc	Copper	Zinc
	(meq/100g)	(meq/100g)	(@001\pem)	(meq/100g)			(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
25.00	10.00	10.00	9.97	8 92	4.91	6.82	14.11	5.24	19.38	2.98	7.20	7.00	1.73
24.00	25.00	25.00	24.95	18.72	4.61	6.24	38.02	8.62	46.63	3.64	15.19	21.14	3 54
26.00	50.00	50.00	49.88	22.02	4.50	5.92	62.91	11.35	74.20	4.35	14.26	45.59	7.60
23.00	50.00	50.00	49.85	17.25	4.50	5.91	65.69	11.69	67.78	4.84	9.54	45 31	7.75
22.00	75.00	75.00	74.53	11.35	4.48	5.68	68.26	12 89	81.15	6.41	1.96	68 20	9.42
21.00	100.00	100.00	95.25	1.57	4.27	5.17	75.70	7.60	63.30	10.58	0.00	84.62	2 66

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Copper and Zinc Batch Modelling Tests Experimental Results Unadjusted pH

Initial	Initial	Retained	Retained	Dissolved	Dissolved	Adsorbed	Adsorbed	Precipitated	Precipitated
Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc
(meg/100g)	(meq/100g)	(meg/100g)	(meq/100g)						
10.00	10.00	9.99	0.00	0.01	10.00	9.99	0.00	. 0.00	.0.00
25.00	25.00	24.98	0.00	0.03	25.00	24 96	0.00	0.00	0.00
50.00	50.00	49.90	0.00	0.10	50.00	49.90	0.00	0.00	0.00
75.00	75.00	74.55	0.00	0.45	75.00	74.55	0.00	0.00	0.00
100.00	100.00	93.80	0.00	8.20	100.00	65.30	0.00	7.50	0.00

Hypothebcal/Estimated

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Table 8.12

Copper and Zinc Batch Equilibrium Tests Experimental Results Adjusted pH 3

8ampie	initia Contra	Initial	Initial	Final	Retained	Retained	Released	Released	Released	Adsorbed	Adsorbed	Precipitated	Precipitated
	Çopper	2.mc	pri	рп	Copper	L ING	Calcum	ZINC	Ca + Mg	Copper	Linc	Copper	2 inc
	(meg/100g)	(meq/100g)			(meq/100g)	(m#q/100g)	(meq/100g)	(maq/100g)	(meq/100g)	(n.eq/100g)	(meq/100g)	(meq/100g)	(meg/100ე)
1.00	10.00	10.00	3.01	6.66	10 00	7.60	11.63	4 86	18.69	3.00	6.10	7.00	1 51
2.00	25.00	25.00	2.97	6.19	24.99	18 28	21.13	7.55	25.68	4 06	13.16	20.91	3.12
3.00	50.00	50.00	2 95	6.03	49.99	17.29	51.43	9.40	60.84	1.79	8 29	48 20	9 OO
4.00	75 00	75.00	3 00	5.74	74.94	14 01	68.32	11.78	80.05	7.49	3 85	67.45	10 16
5.00	100.00	100.00	3.06	5 33	99.45	7.75	75 57	14.67	90.25	11.94	2 25	87.50	5 50
6.00	100.00	100.00	3.07	5 31	99.24	1.39	70.39	14.65	85 07	12 07	0.00	87.17	5 14

Copper and Zinc Batch Equilibrium Tests Modelling Results Adjusted pH 3

Initial	Initial	Retained	Retained	Dissolved	Dissolved	Adsorbed	Adsorbed	Precipitated	Precipitated
Copper	Zinc	Cooper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc
(meq/100g)	(meq/100g) -	(meg/100g)	(meg/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)	(meq/100g)
10.00	10.00	9.99	0.00	0.01	10.00	9 99	0.00	0.00	0.00
25.00	25.00	24.96	0.00	0.03	25.00	24.98	0.00	0.00	0.00
50.00	60.00	49 90	0 00	0.10	50.00	49.90	0.00	0.00	0 00
75.00	75.00	74.55	0.00	0.45	75.00	74.65	0.00	0.00	0.00
100.00	100.00	93.60	0.00	6.20	100.00	86.30	0.00	7.50	0.00

Hypothebcal/Estimated





Lead, Copper, and Znic Batch Equilibrium Texus Experimental Readits Performed Uring Adjusted Infeat pH 3

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Hypothatical/Estmated

Samples	h Kal	inital	Final	Retained	Retained	Retained	Fieldshed	Related	Reisand	Advorbed	Aliorbed	Adiorbed	Precipitated	Precipitaled	Precipitad
£	Q. Z	£	£	P	Copper	2NG	Calcium	Integration	Ca + 15	Lead	Copper	Zhe	Leid	Copper	21/10
	(Bool/bew)			(meq/100g)	(6001/beu)	(meq/100g)	(meq/100g)	(meq/100g)	(med/100g)	(b001/perr)	(Eco)/baw)	(foot/peu)	(pool/peri)	(peed) (00g)	(meq/100g)
21 (3)	8 00	8	3	89	12 8	101	15 01	5 61	21.53	0.70	0 97	4	0 7 0	8	7.59
2300	8	207	2	88	21.00	950	88	9 27	62.78	8	0.12	8	8	020	12 70
8.2	8	3.21	5.18	49 43	28.77	6.47	56.61	11 67	70.48	21.74	11.70	8	16.52	21 99	96
8	25 80	2.97	4 64	72.40	16.37	7.08	59.85	22	74 07	51 29	8	3.48 C	56 65	48 60	7140
8	10 8 10 8	294	8	F 2.78	41.79	4 64	70.15	15 08	22 (3	55 03	235	164	1261	81 78	8 6
Lead, Copper, and	Zine Baich Equili	brium Tests Moc	delling Results	Adjusted Inital g	614										

Lend, C

Dissolved Znec (nec) (009) 25 00 25 00 26 00 28 00 20 00 200 2
Disolved Copper (med/100g) 0.02 0.03 0.03 30 53 53 00
Dissolved Lead (rreq/ 1002) 0.07 0.03 0.03 33.15 60.60
Rekined Zna (med 1002) 0 00 0 00 0 00 0 00 0 00 0 00 0 00
Retatived Copper (med/1009) 21 93 21 93 40 60 41,48
Returned Level (med/1003) 3 94 24 55 41,15 11,15 11,15 12 30
Precipita wd Zhec (med/102) 0 00 0 00 0 00 0 00 0 00
Precipita wed Copper (med. 1009) (med. 1009) 9 08 21:95 0 00 0 00 0 00
Precipiture (meg/100g) 2.47 0.50 0.50 0.50 0.50
Adisorbed Zone (meq.)(00) (00) 0.00 0.00 0.00 0.00
Ad Acrited Copper (mac) (002) (002) 2 85 2 86 40 80 41 48 41 48
Maorbad Land (may 1009) 1.47 21.05 41.15 41.15 39.30
hiti P. C. 7 (me) 1001 1002 2500 7500 7500 7500 7500

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Lood, Copper, and Zine Barch Equilibrium Texts Experimental Readin Performed Uning Unadjusted Initial pH

Laid, Coper, I	nd Zne Buch E	quatrium fests	Esperimental Re	suits Parlomed U	, basu(bant) gris	Hq lette						Ŧ	hpothe Keal East			
Sample	Invited	Relatived	Retained	Resided	In fee	Final	Reissed	Refet ted	Relation of		Adioched	Advorbed	Adiorbed	Precipitated	Precipitated	Precipe and
	P. C. Z	P	Copper	Zine	Ŧ	£	Calcium	Magnet	2 2		Lead	Copper	Š	Lead	Copper	ž
	(B001/baan)	(meq/100g)	(B00)/ber/j	(g001/perr)			(B001/Dem)	(p001/pem)	(6001/pem)		(6001/beut)	(500)/hand	(6001/pem)	(meq/100g)	(meq/100g)	(pool/pen)
8	8 9 9	21	81	8	RŢ	2	9 6	1.15	27.11		20	80	8	8	8	8
88	2 8	2.1	82	7.01	87¥	89	43.04	101	5.2		8	0.17	8	5 N 11	22	10 24
88	88	10.01	38	2.87	404	4.71	54.32	20 03	74 35		227	66 23	80	17.10	13 15	5.97
84	8	0113	117.02	110	8	3	52 20	12 09	62°10		24 M	10 21	8	2002	17.40	8
5 8 9	1500	22	11.11	2.14	385	477	1465	2.2	10 73		51.13	8	80	15 48	21 59	3
8	338	12.14	\$ 8	89	164	4.62	88	4 T	21		5104	8	8	212	88	8
5 8 8	100 00	1210	92.0	8	30	121	/1 59	8	11.10		69.78	80	8	27.41	37 90	82
1,00	100 DD	64.07	15.99	10.11	4.27	4 80	80 84	15.13	10 50		47.62	8	N.7	40.18	63.67	8
Leid, Copper, I	nd Zne Batch E	quillibrium feste.	Modelling Result	Its Performed Using	livi betrujpev() g	ia pł										
Inital	Adaorbed	Adiorhed	Ad extrad	Precipits ted	Precipita ted	Precipitated	Relained	Retained	Returned	Dissolved	Dis solved	Dissolved				
Pb. CJ. ZV	2	Copper	ай Г	2	Copper	Zinc	Leed	Copper	эч Х		Copper	ž				
(meq/100g)	(meg/100g)	(meq/100g)	(fuo) /bew)	(Boo)/bem)	(600)/bew)	(meq/100g)	(pool/perr)	(B001/peru)	(mec.100g)	(boo! ->+u)	(meq/100g)	(Bco1/bew)				
800	90.0	80	80	9.57	8	8	6 8	2	8	001	0 02	8 9				
8	1 71	8	80	20	16 N	8	24.55	19 12	8	0.45	80	8				
89	38	8	80	80	97. 9 7	8	21.15	9. 9	8	818	10 60	88				
88	20.45	80	80	80	\$. 8	8	202	9: 9	80	8.8	. 10.80	8				
75.00	39	80	8	8	17.40	80	38	17.40	80	10.11	57.60	75 00				
75 00	24.16	80	80	8	17.40	80	38	17.40	8	36.18	57.60	75 00				
80,001	4140	8	8	8	05 GJ	800	8	49.50	8	88	99 99 95	100 CO				
881	41.40	8	000	80	49.50	8	41.80	1 5	8	8	202	100 00				

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APPENDIX C



Figures C.23a,b - Pb batch equilibrium test (unadjusted initial pH) isotherm a) based on experimental results b) based on modelling results.



Figures C.24a,b - Pb batch equilibrium test (adjusted initial pH 3) isotherm a) based on experimental results b) based on modelling results.

Isotherm Graphs



Figures C.25a,b - Cu batch equilibrium test (unadjusted initial pH) isotherm a) based on experimental results b) based on modelling results.



Figures C.26a,b - Cu batch equilibrium test (adjusted initial pH 3) isotherm a) based on experimental results b) based on modelling results.



Figures C.27a,b - Zn batch equilibrium test (unadjusted initial pH) isotherm a) based on experimental results b) based on modelling results.



Figures C.28a,b - Zn batch equilibrium test (adjusted initial pH 3) isotherm a) based on experimental results b) based on modelling results.



Figures C.29a,b - Pb and Cu batch equilibrium test (unadjusted initial pH) Pb isotherm a) based on experimental results b) based on modelling results.



Figures C.30a,b - Pb and Cu batch equilibrium test (adjusted initial pH 3) Pb isotherm a) based on experimental results b) based on modelling results.



Figures C.31a,b - Pb and Cu batch equilibrium test (unadjusted initial pH) Cu isotherm a) based on experimental results b) based on modelling results.



Figures C.32a,b - Pb and Cu batch equilibrium test (adjusted initial pH 3) Cu isotherm a) based on experimental results b) based on modelling results.



Figures C.33a,b - Pb and Zn batch equilibrium test (initial unadjusted pH) Pb isotherm a) based on experimental results b) based on modelling results.



Figures C.34a,b - Pb and Zn batch equilibrium test (initial adjusted pH 3) Pb isotherm a) based on experimental results b) based on modelling results.



Figures C.35a,b - Pb and Zn batch equilibrium test Zn isotherm based on a) experimental results initial unadjusted pH tests b) experimental results initial pH 3.



Figures C.36a,b - Cu and Zn batch equilibrium test (unadjusted initial pH) Cu isotherm a) based on experimental results b) based on modelling results.

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Figures C.37a,b - Cu and Zn batch equilibrium test (adjusted initial pH 3) Cu isotherm a) based on experimental results b) based on modelling results.



Figures C.38a,b - Cu and Zn batch equilibrium test Zn isotherms based on a)experimental results unadjusted pH b) experimental results initial pH 3 tests.



Figures C.39a,b - Pb, Cu and Zn batch equilibrium tests (unadjusted initial pH) Pb isotherm a) based on experimental results b) based on modelling results.



Figures C.40a,b - Pb, Cu and Zn batch equilibrium tests (adjusted initial pH 3) Pb isotherm a) based on experimental results b) based on modelling results.

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Figures C.41a,b - Pb, Cu and Zn batch equilibrium tests (unadjusted initial pH) Cu isotherms a) based on experimental results b) based on modelling results.



Figures C.42a,b - Pb, Cu and Zn batch equilibrium tests (adjusted initial pH 3) Cu isotherms a) based on experimental results b) based on modelling results.



Figures C.43a,b - Pb, Cu and Zn batch equilibrium tests Zn isotherms based on experimental results a) unadjusted pH b) adjusted initial pH 3.

APPENDIX D

Initial and Final pH Graphs



Figures D.44a,b - Initial and Final supernatant pH of Pb batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.45a,b - Initial and Final supernatant pH of Cu batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.46a,b - Initial and Final supernatant pH of Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.47a,b - Initial and Final supernatant pH of Pb + Cu batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.48a,b - Initial and Final supernatant pH of Pb + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.49a,b - Initial and Final supernatant pH of Cu + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.



Figures D.50a,b - Initial and Final supernatant pH of Pb, Cu + Zn batch equilibrium tests a) unadjusted initial pH b) adjusted to initial pH 3.

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