

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Modelling and Analysis of Leaching of Copper from Volcanic Ash Soil

A thesis presented in partial fulfilment of the
requirements for the degree of **Master of Technology**
in **Environmental Engineering**

by **Dali He**

Institute of Technology and Engineering

Massey University

Palmerston North, New Zealand

1999

ABSTRACT

Soil contaminated by heavy metal ions has become a global problem. Besides legislation to restrict the input of heavy metals, remediation of contaminated soil is also essential. The most common means of remediation is leaching. There have been many studies published in this field, some of which relate to development of mathematical models. Volcanic ash soil is common in New Zealand. Developing a model to predict the process of leaching heavy metal from volcanic ash soil is important for New Zealand. No model was found for predicting the process of leaching heavy metal from volcanic ash soil.

Heavy metal soil contamination can not be remedied by microorganisms, so the heavy metals will inevitably accumulate in soils over time. Once heavy metals have accumulated in soil to exceed a threshold, they will be released and then be taken up by plants, entering the food chain or moving into the groundwater system. Therefore, it is necessary to leach the heavy metals from the contaminated soil. The batch stirred process is a fast and convenient method, and it is easily used in the field. The main purpose of this study is to develop a model that can predict the bulk liquid concentration of heavy metal in the stirred vessel.

In the present study, the internal model is pore diffusion model. The explicit method is used to translate a partial differential equation to a finite difference equation. The results from thermodynamic and kinetic experiments agree with the model. With the exception of the equilibrium parameters for Freundlich isotherm derived by experiment, all other parameters were obtained from literature on volcanic ash soil. Therefore, the model can be used for leaching of other heavy metals from volcanic soil under similar conditions.

The leaching of heavy metals from volcanic soil is shown to be an internal diffusion controlled process, so increasing the agitating speed in a stirred reactor is of no use for improving the mass transfer. Decreasing the size of volcanic soil

aggregates by breaking them clearly increases the rate of the leaching process. The equilibrium relationships of the adsorption process and the desorption process are different for the system, and there is a hysteresis.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my chief supervisor Prof. S. M. Rao Bhamidimarri for his assistance, valuable advice and guidance during this study, and writing of this thesis.

I am very grateful also to my co-operative supervisor Ken Butler for valuable assistance in experiments, literature review and writing of this thesis.

Thanks to John Sykes for valuable help on using Atomic Absorption Spectrophotometer.

Finally, I would like to thank all of those people who have helped with this project.

CONTENTS

Abstract	II
Acknowledgment	IV
List of figures	X
List of tables	XIII
Chapter 1. Introduction	1
1.1 Background	1
1.2 Remediation technologies	2
1.3 Objectives of the project	3
Chapter 2. Literature review	4
2.1 Introduction	4
2.2 Volcanic ash soil	4
2.2.1 Volcanic soil genesis.....	5
2.2.2 Volcanic soil classification.....	6
2.2.3 Volcanic soil structure	7
2.2.4 Volcanic soil constituents.....	8
2.2.4.1 Inorganic constituents.....	8
2.2.4.2 Organic constituents.....	10
2.2.5 Mineralogical characteristics of volcanic soil.....	10
2.2.5.1 Primary minerals.....	11
2.2.5.2 Secondary minerals.....	12
2.2.6 Chemical characteristics of volcanic soil.....	14

2.2.6.1 Ion exchange equilibrium.....	14
2.2.6.2 Sorption of heavy metal ions.....	15
2.2.7 Physical characteristics of volcanic soil.....	16
2.2.7.1 Density.....	16
2.2.7.2 Aggregate porosity (ϵ).....	17
2.2.7.3 Aggregate tortuosity (τ).....	18
2.2.7.4 Aggregate size.....	19
2.2.7.5 Specific surface area.....	19
2.3 Mathematical model.....	19
2.3.1 Process description.....	20
2.3.2 Model selection.....	21
2.3.3 Simplifying assumption.....	23
2.3.3.1 Constant particle size.....	23
2.3.3.2 Constant temperature.....	24
2.3.3.3 Spherical aggregates.....	24
2.3.4 Mathematical expression.....	24
2.3.4.1 External diffusion control.....	25
2.3.4.2 Internal diffusion control.....	27
2.3.4.3 Interface solubilizing control.....	31
2.3.4.4 Combination control.....	31
2.3.5 Parameters for the model.....	32
2.3.5.1 Diffusion coefficient.....	32
2.3.5.1.1 External diffusion coefficient.....	32
2.3.5.1.2 Pore diffusion coefficient.....	37
2.3.5.1.3 Surface diffusion coefficient.....	38
2.3.5.1.4 Overall diffusion coefficient.....	38
2.3.5.2 Mass transfer coefficient.....	38
2.3.5.3 Specific surface area.....	41
2.3.6 Equilibrium model and its parameters.....	41

2.3.6.1 Linear model.....	42
2.3.6.2 Langmuir model.....	42
2.3.6.3 BET model.....	43
2.3.6.4 Gibbs model.....	43
2.3.6.5 Freundlich model.....	44
2.4 Conclusion.....	45
Chapter 3. Materials and methods.....	47
3.1 Background.....	47
3.2 Collection and preparation of volcanic soil sample.....	47
3.3 Analysis.....	48
3.4 Experimental procedures.....	49
3.4.1 Preliminary experiments.....	49
3.4.2 Thermodynamic experiments.....	50
3.4.3 Kinetic experiments.....	51
3.4.4 Stirred vessel experiments.....	51
3.5 Mathematical methods.....	52
Chapter 4. Thermodynamic and kinetic model.....	55
4.1 Introduction.....	55
4.2 Thermodynamic model.....	56
4.3 Kinetic model.....	57

4.3.1 Diffusion model for a single aggregate.....	57
4.3.2 Diffusion model for stirred vessel.....	63
4.4 Algorithm.....	64
4.4.1 Finite difference equation.....	64
4.4.1.1 For volcanic soil aggregates.....	64
4.4.1.2 For stirred vessel.....	68
4.4.2 Solution stability.....	68
4.5 Summary.....	69
Chapter 5. Results and discussion.....	72
5.1 Introduction.....	72
5.2 Thermodynamic process.....	72
5.2.1 Adsorption process.....	73
5.2.2 Desorption process.....	75
5.3 Kinetic process.....	80
5.3.1 Adsorption process.....	80
5.3.2 Desorption process.....	82
5.4 Leaching process.....	85
5.5 Desorption efficiency.....	87
5.6 Control step.....	88

Chapter 6. Conclusions and recommendations.....	91
6.1 Conclusions.....	91
6.2 Recommendations.....	92
Reference.....	94
Appendices.....	102
A1 Liquid film diffusion model.....	102
A2 Concentration conversion.....	105
A3 Derivation of partial derivative.....	106
A4 Relationship between porosity and densities.....	108
A5 Relationship of porosities.....	110

LIST OF FIGURES

2-1	Concentrations of Cd, Pb, Cu and Zn vs. time for a leaching process. The aqueous:solid ratio was 51:1.....	20
2-2	According to the progressive conversion model, leach proceeds continuously throughout the soil aggregate.....	21
2-3	According to the shrinking unleached core model, an unleached core of material which shrinks in size during reaction.....	21
2-4	Sketch of Untreated-core Model.....	22
2-5	Mass transport mechanism in a soil aggregate.....	27
2-6	Effect of concentration on diffusivity of electrolytes in aqueous solution at 18.5 °C. Solid lines calculated by using Eq (2-38).....	34
2-7	The relation of the three velocities.....	41
2-8	Types of equilibrium sorption separations: q_e = amount sorbed and C_e = amount in solution.....	41
3-1	Sketch of stirred process.....	52
4-1	Sketch of mass transport in a aggregate.....	58
4-2	Sketch of mass transport at center node.....	66
4-3	Mass transport at node j.....	67
4-4	Mass transport at surface node.....	68
5-1	Adsorption equilibrium for CuSO_4 in volcanic soil of 600-800 μm aggregate size.....	73
5-2	Adsorption equilibrium for CuSO_4 in volcanic soil of 500-600 μm aggregate size.....	74
5-3	Adsorption equilibrium for CuSO_4 in volcanic soil of 425-500 μm	

aggregate size.....75

5-4 Desorption equilibrium for CuSO₄ in volcanic soil of 600-800 μm
 aggregate size.....76

5-5 Desorption equilibrium for CuSO₄ in volcanic soil of 500-600 μm
 aggregate size.....77

5-6 Desorption equilibrium for CuSO₄ in volcanic soil of 425-500 μm
 aggregate size.....78

5-7 Sketch of equilibrium curves of adsorption and desorption..... 79

5-8 Sketch of energy path for adsorption and desorption..... 79

5-9 Adsorption process for 2.5g volcanic soil of 600-800 μm
 aggregate size in 50ml CuSO₄ solution..... 80

5-10 Adsorption process for 2.5g volcanic soil of 500-600 μm
 aggregate size in 50ml CuSO₄ solution.....81

5-11 Adsorption process for 2.5g volcanic soil of 425-500 μm
 aggregate size in 50ml CuSO₄ solution..... 82

5-12 Desorption process for 1.0g volcanic soil of 600-800 μm
 aggregate size in 50ml deionized water..... 83

5-13 Desorption process for 1.0g volcanic soil of 500-600 μm
 aggregate size in 50ml deionized water..... 84

5-14 Desorption process for 1.0g volcanic soil of 425-500 μm
 aggregate size in 50ml deionized water..... 84

5-15 Leaching process for 100g volcanic soil of 600-800 μm
 aggregate size in 5.0 l deionized water..... 85

5-16 Leaching process for 100g volcanic soil of 500-600 μm
 aggregate size in 5.0 l deionized water..... 86

5-17 Leaching process for 100g volcanic soil of 425-500 μm
 aggregate size in 5.0 l deionized water..... 86

5-18 Desorption efficiency of different mass of volcanic soil
 of 600-800 μm size by 50 ml deionized water.....88

5-19 Influence of different stirring speeds on the leaching process.....89

LIST OF TABLES

2-1	Spectrographic analyses of volcanic soils.....	9
2-2	Content of major elements in fresh tephras from Japan.....	9
2-3	Ionic conductances in water at 25 °C.....	33
2-4	B values of some salts at 25 °C.....	35
3-1	Soil physical characteristics.....	47
5-1	Inputted kinetic parameters for 600-800 µm aggregate size volcanic soil sample about adsorption equilibrium.....	74
5-2	The adsorption equilibrium constants for different soil aggregate sizes.....	75
5-3	Inputted kinetic parameters for 600-800 µm aggregate size volcanic soil sample about desorption equilibrium.....	77
5-4	The desorption equilibrium constants for different soil aggregate sizes.....	78
5-5	Inputted kinetic parameters for 600-800 µm aggregate size volcanic soil sample about adsorption kinetic process.....	81
5-6	Inputted kinetic parameters for 600-800 µm aggregate size volcanic soil sample about desorption kinetic process.....	83
5-7	Inputted kinetic parameters for 600-800 µm aggregate size volcanic soil sample about stirred vessel leaching process.....	85
5-8	Comparison of mass transfer coefficient and effective internal diffusion coefficient of CuSO ₄ in aqueous solution.....	89

CHAPTER 1

INTRODUCTION

1.1 Background

The distribution of soils derived from volcanic materials closely parallels the global distribution of active and recently active volcanoes. It is estimated that soils derived from volcanic ejecta are distributed over approximately 124 million hectares or 0.84% of the earth's surface (Leamy, 1984). Approximately 60% of volcanic ash soils occur in tropical countries. In some countries with high volcanic activity, there may be a higher distribution of volcanic ash soils such as Japan, Melanesia, and Philippines.

Volcanic ash soil is also common in New Zealand. Most of the region south from Auckland to Wanganui on the west coast, and to Napier on the east coast, has a mantle of volcanic ash deposits more than 18 inches thick (Gibbs, 1968). The occurrence of volcanic soil is shown by the numerous particles of volcanic glass found in most soils of the North Island. The presence of volcanic ash soil has made New Zealand a favourable country for the production of food, timber, and water.

With wide application of sewage sludge and some chemical products including pesticides and herbicides to agricultural land, the risk and extent of soil contamination has increased. The pollutants in contaminated soils can be divided into two groups, organic matter and heavy metals. Organic pollutants include pesticides and herbicides. They can be degraded or decomposed by microorganisms in soil. However, microorganisms can not decompose heavy metals. Therefore, heavy metals will inevitably accumulate in soils over time. Once heavy metals have accumulated to exceed a threshold, they will be released and then be taken up by plants, entering the food chain

or moving into the groundwater system. Consequently, human health and the environment in which human lives may be seriously imperiled. It may be necessary to leach heavy metals from contaminated soil.

1.2 Remediation technologies

There are many technologies to remedy contaminated soil. Koustas and Fischer (1998) indicated that the various available treatment options for remediation fall into three broad categories: containment-immobilization, separation-concentration, and destruction. Each category can be classified by different ways in which technique can be used as in situ, a prepared bed, and in tank (Boulding, 1995).

- In situ treatment consists of treating contaminated soil in place, i.e., the contaminated soil is not moved from the ground. Although the treatment method is the best way in economic terms, there are some restricting conditions and potential new damage to soil for this method.
- In a prepared bed system, the contaminated soil may be either (1) physically moved from its original site to a newly prepared area, which has been designed to enhance treatment and/or to prevent transport of contaminants from the site; or (2) removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where treatment is accomplished. The advantages and disadvantages of the method are not conspicuous.
- In tank treatment involves removing the contaminated soil and treating it in a vessel or other system designed to optimize treatment efficiency. The method needs more operation cost, but there is no potential of new pollution to soil and fewer restricting requirements.

The heavy metals in contaminated soil cannot be destroyed by thermal treatment and microorganism because their ions can not be degraded. Therefore, just containment-

immobilization and separation-concentration can be considered. However, soil immobilization may result in the significant change on physical and chemical properties of soil. The result is that soil loses its agricultural function. Because soil is a limited resources on earth, the economical factor of soil remediation may be no longer a restrictive aspect for mankind in the near future. Thus, the method of separation-concentration in tank may become a principal aspect in soil remediation.

The main principle of remedying soil contaminated by heavy metal is leaching using a solvent. The solvent may be water, organic or inorganic reagent. There are many processes, which can be used to leach heavy metals from contaminated soil. For example, there are fixed bed or fluidized bed systems, continuous or batch processes. This work uses a batch stirred process.

1.3 Objectives of the project

The main purpose of this study is to develop a model that can predict the bulk liquid concentration of heavy metal in the stirred tank reactor. During the operation of leaching heavy metals from contaminated soil, monitoring heavy metal concentration in the bulk liquid is a regular practice in order to determine whether the bulk liquid concentration of heavy metal has achieved the required value. However, a large amount of monitoring work in the field is neither economical nor convenient. On the contrary, using a model to predict the concentration can be very easy, and only the initial concentrations of heavy metal in the bulk liquid need to be determined during the experiment.

A mathematical model has been developed. Experimental work on adsorption and desorption parameter determination and leaching in a stirred tank reactor is presented. The reliability of the models is discussed.