



The effectiveness of steel foundry by-products in the treatment of stormwater

Jiyang Ren

A thesis submitted in partial fulfilment of the
degree of Master of Applied Science

Auckland University of Technology
Auckland
New Zealand

June 2006

Acknowledgements

This study is completed with the support of many people, one way or another, over the last two years. I am very grateful to my wife and daughter for their understanding and support, and wish to convey my gratitude to:

- ♦ My primary supervisor, Dr. John Robertson (Auckland University of Technology), for his advice on experiment design, assistance in the laboratory and the finalization of the report
- ♦ Professor John Buckeridge (Auckland University of Technology), who had been my primary supervisor, for his invaluable support and guidance
- ♦ Dr. Kevin Tilbrook (Auckland University of Technology) who had been my secondary supervisor and helped me to design the field experiments
- ♦ The SteelServ Ltd. who propose the project and provide aggregate for testing. Special thanks to Mr. Bill Bourke and Mr. Hendrik Wortman for their suggestions and support
- ♦ Mr. Christopher Whyburd and Ms. Yan Wang (Auckland University of Technology) for their assistance with the Flame Atomic Absorption Spectrometer and other instruments
- ♦ Mr. Michael Lindgreen (Metro Water Limited), Ms. Jane Puddephatt and Ms. Danielle Hancock (Auckland Regional Council) for their suggestions on stormwater sample collection

Abstract

The capacity and efficiency of melter slag (provided by New Zealand Steel) to remove heavy metals and suspended solids from stormwater samples are studied in this thesis. A series of batch tests were carried out to investigate the adsorption-desorption mechanism of the slag to remove heavy metals (Cd^{2+} , Zn^{2+} and Cu^{2+}) from working solutions. The results showed that all the tested metallic ions could be removed by mixing the melter slag with the working solutions. Adsorption and ion exchange are the dominant mechanisms in this process. The adsorption capacity follows the descending order of $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+}$. Varied binding energy of different metallic ions to the slag resulted in competitive adsorption between ions.

A variety of substances: inorganic salts (KCl, NaCl, KNO_3 and sea water), organic acids (citric and tartaric) and inorganic acids (nitric and carbonic), were tested as desorbing agents to recover the used slag. Citric acid in sea water was found to be the best in terms of desorption efficiency and cost-effectiveness.

The column tests were carried out to simulate the filtration bed in laboratory conditions. Stormwater samples were collected from residential and commercial areas in Auckland. The synthetic stormwater samples were prepared from clay and metallic ion solution. Both samples were used as feeding solutions in the tests. The removal efficiencies of suspended solids and metallic ions (Zn^{2+} , Cd^{2+} and Cu^{2+}) vary depending on different operation conditions. They are in inverse proportion to the grain size of the melter slag and the influent flow rate. The higher removal efficiency of Zn^{2+} than that of suspended solids infers that metallic ions are removed by both precipitation and adsorption.

Table of Contents

Acknowledgements.....	i
Abstract.....	ii
Table of Contents.....	iii
List of Figures.....	v
List of Tables.....	vii
Statement of Originality.....	ix
 Chapter 1 Introduction.....	 1
1.1 Overview.....	1
1.1.1 Stormwater.....	1
1.1.2 Slags.....	5
1.2 Background.....	7
1.3 Research aims and objectives.....	9
1.4 Literature review.....	9
 Chapter 2 Materials and Methods.....	 12
2.1 Selection of metal analyzing instruments.....	12
2.2 Stock standard solutions preparation.....	13
2.3 Calibration curve.....	14
2.4 Slag aggregate.....	14
2.5 Adsorption kinetics.....	16
2.6 Adsorption isotherm.....	17
2.7 Desorption.....	18
2.8 Column experiments.....	20
2.8.1 Stormwater sampling.....	20
2.8.2 Sample conservation:.....	21
2.8.3 Sample analysis.....	21
2.8.4 Column tests with stormwater samples.....	22
2.8.5 Column tests with synthetic stormwater samples.....	24
 Chapter 3 Results.....	 26
3.1 Adsorption kinetics.....	26
3.2 Alkalinity effect of the slag.....	29
3.3 Competitive effect of the metallic ions.....	30

3.4 Adsorption isotherm.....	32
3.4.1 Adsorption capacity	32
3.4.2 Adsorption isotherm	33
3.5 Desorption.....	39
3.6 Column test	42
3.6.1 Stormwater sample analysis	42
3.6.2 Effect of nitric acid digestion	43
3.6.3 Removal efficiency of metallic ions in column test	44
3.6.4 Column test results with synthetic stormwater samples	49
Chapter 4 Discussion	55
4.1 Metallic ion removal efficiency	55
4.1.1 Adsorption kinetics.....	55
4.1.2 Heavy Metal ion removal mechanism.....	57
4.1.3 Competitive adsorption	58
4.1.4 Adsorption isotherm.....	60
4.2 Desorption of metallic ions from slag.....	61
4.2.1 Ion exchange	61
4.2.2 Complexes with ligands	62
4.2.3 Chelating.....	64
4.3 Column tests with stormwater sample	66
4.3.1 Chemical analysis of the stormwater samples	66
4.3.2 Pollutants removal efficiency in columns	68
4.3.3 Perspective of the application.....	72
Chapter 5 Conclusions	74
References.....	77
Abbreviations.....	83
Glossary	84
Appendix A Adsorption Batch Tests Results	
Appendix B Desorption Batch Tests Results	
Appendix C Column Tests Results	
Appendix D Cost analysis of desorption tests	

List of Figures

Figure 1-1	Stormwater development, collection and treatment	3
Figure 1-2	Mechanical screening of slag at NZ Steel (<i>Auckland</i>)	6
Figure 2.1	The Perkin-Elmer 3110 flame atomic absorption spectrometer used for all metal analysis conducted at AUT	13
Figure 2.2	The melter slag samples in three particle sizes used as adsorbent in the study	15
Figure 2.3	Adsorption batch experiments	16
Figure 2.4	Desorption of metallic ions by carbonic acid	19
Figure 2.5	Layout of column experiment	23
Figure 2.6	Spectrum of stormwater sample	25
Figure 2.7	Relationship between suspended solids and absorbance of synthetic stormwater sample	25
Figure 3.1	Trends of Zn^{2+} removal over time by melter slag (50g)	26
Figure 3.2	Trends of Cu^{2+} removal over time by melter slag (50g)	27
Figure 3.3	Trends of Zn^{2+} removal over time by marble (50g)	27
Figure 3.4	Trends of Cu^{2+} removal over time by marble (50g)	28
Figure 3.5	Trends of Zn^{2+} removal over time by melter slag (100g)	28
Figure 3.6	Metallic ions removal by slag (fine) from multi-ion solution	29

Figure 3.7	Adsorption isotherm of slag to each metallic ion (single-ion solution)	35
Figure 3.8	Adsorption isotherm of slag in different grain size (single-ion solution)	36
Figure 3.9	Adsorption isotherm of slag to each metallic ion (multiple-ion solution)	37
Figure 3.10	Adsorption isotherm of slag in different grain size (multiple-ion solution)	38
Figure 3.11	Variation of pH in the solutions with the change of Ca^{2+} concentration	40
Figure 4.1	Porous structure of the slag (fine) viewed from microscope (Scale with 1 mm intervals)	56

List of Tables

Table 2.1	Atomic spectrometric detection limits	12
Table 2.2	Chemical composition of the slag	15
Table 2.3	Description of stormwater sampling sites	20
Table 2.4	Concentration of each element in the synthetic stormwater samples	24
Table 3.1	Change of Ca^{2+} and pH in the solution	30
Table 3.2	Cu^{2+} removal by slag which is saturated with Zn^{2+}	31
Table 3.3	Zn^{2+} removal by slag which is saturated with Cu^{2+}	31
Table 3.4	Adsorption capacity of melter slag to each ion	32
Table 3.5	Adsorption efficiency of melter slag to each ion	32
Table 3.6	Adsorption isotherm of the slag to each ion	34
Table 3.7	Relationship between pH and equilibrium concentration of Ca^{2+}	39
Table 3.8	Recovery of used slag with inorganic salts (0.01M)	40
Table 3.9	Recovery of used slag with inorganic salt and organic acid	40
Table 3.10	Recovery of used slag with seawater and organic acid	41
Table 3.11	Recovery of used slag with carbonic acid	42
Table 3.12	Recovery of used slag with nitric acid	42
Table 3.13	Characteristics of the stormwater samples	43
Table 3.14	Efficiency of nitric acid digestion	44
Table 3.15	Metal ion removal efficiency by slag (fine size)	45
Table 3.16	Metal ion removal efficiency by slag (medium size)	46
Table 3.17	Metal ion removal efficiency by slag (coarse size)	47
Table 3.18	Results of the control lane in the column test	48
Table 3.19	Chemical analysis of synthetic stormwater samples	49

Table 3.20	Measurement errors of the AAS	50
Table 3.21	Suspended solids and metal ions removal efficiency by fine slag (0.6-1.0 mm) from synthetic stormwater samples	51
Table 3.22	Suspended solids and metal ions removal efficiency by medium slag (1.0-2.0 mm) from synthetic stormwater samples	52
Table 3.23	Suspended solids and metal ions removal efficiency by coarse slag (2.0-3.35 mm) from synthetic stormwater samples	53
Table 3.24	Results of the control lane in the column test with synthetic stormwater samples	54
Table 4.1	Water Quality Standards	72

Statement of Originality

‘I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person or material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgements is made in the acknowledgments.’

.....Signed

Jiyang Ren

.....Date

Chapter 1 Introduction

1.1 Overview

1.1.1 Stormwater

The engineering design of stormwater management systems, even though relatively sophisticated in some situations (Gribbin, 1997), still has much need of improvement (Ng, 2004).

Both water quantity and quality need to be considered in the design and operation of stormwater systems (Auckland City Council, 2002). Urban stormwater, in terms of its pollution, has often been considered less of a problem than domestic sewage, which has been given considerable attention from collection, treatment and reuse perspectives (Henze *et al.*, 2001). City planning and administrative authorities have worked extensively to build up separate collection systems to isolate the stormwater from sewage which is directed to and treated at wastewater treatment plants (Salvato *et al.*, 2003). Stormwater, on the other hand, is mostly discharged directly to natural water systems (e.g. rivers, lakes, streams and wetlands, groundwater, harbours as well as coastal waters) without any treatment (Mara *et al.*, 2003; Ng, 2004).

A number of local and international studies on water quality have identified stormwater discharges as one of significant sources of water pollution (USPEA, 1993; Auckland Healthcare Services Ltd., 2000). An investigation made in Auckland (ARC Stormwater Liaison Group, 1998; Ng, 2004) identified that the pollutants in stormwater derive from:

- Vehicle uses and emissions;
- Runoff from roads, car parks, paved surfaces and roofs;
- Sedimentation from earthworks during urban development;
- Infiltration of stormwater into sewerage systems and subsequent overflows;

- Runoff from poorly managed industrial and commercial sites;
- Poor domestic chemical disposal practices; and
- Landfill leachates.

The awareness of pollution from stormwater was initially raised following deposition of sediment in waterways. The elevated suspended solids in runoff after heavy rainfall, either from erosion by stormwater or run-off from paved surfaces, are regarded as one of the major sources for sediments in receiving waters. Blocked, leaking and illegally connected sewage pipes, together with inadequate sewer capacity and pump failures add wastewater contaminants to the mix (ARC, 2004).

Suspended solids increase the turbidity of receiving water bodies, thereby reducing the penetration of light, resulting in decreased activity and growth of photosynthetic organisms. The increased turbidity also detracts from the aesthetics of natural waters. Solids that settle in the receiving water pose long-term threats resulting from their oxygen demand and gradual accumulation of toxic substances (Adams *et al.*, 2000; Ng and Buckeridge, 2000).

The increased application of fertilizers and pesticides on farmland, the expansion of artificial pavement accompanied by urbanization and the change of land use with the industrialization have led to heavy metal accumulation in soils (Ng and Buckeridge, 2002).

Studies in the United States and Canada indicate that heavy metals, including lead, zinc, and copper, were the most prevalent toxic contaminants found in urban runoff. Other toxic pollutants found in stormwater include phthalate esters (plasticizer compounds), phenols and creosols (wood preservatives), pesticides and herbicides, oils and greases, and polycyclic aromatic hydrocarbons (PAHs) (Adams *et al.*, 2000; Ng, 2004).

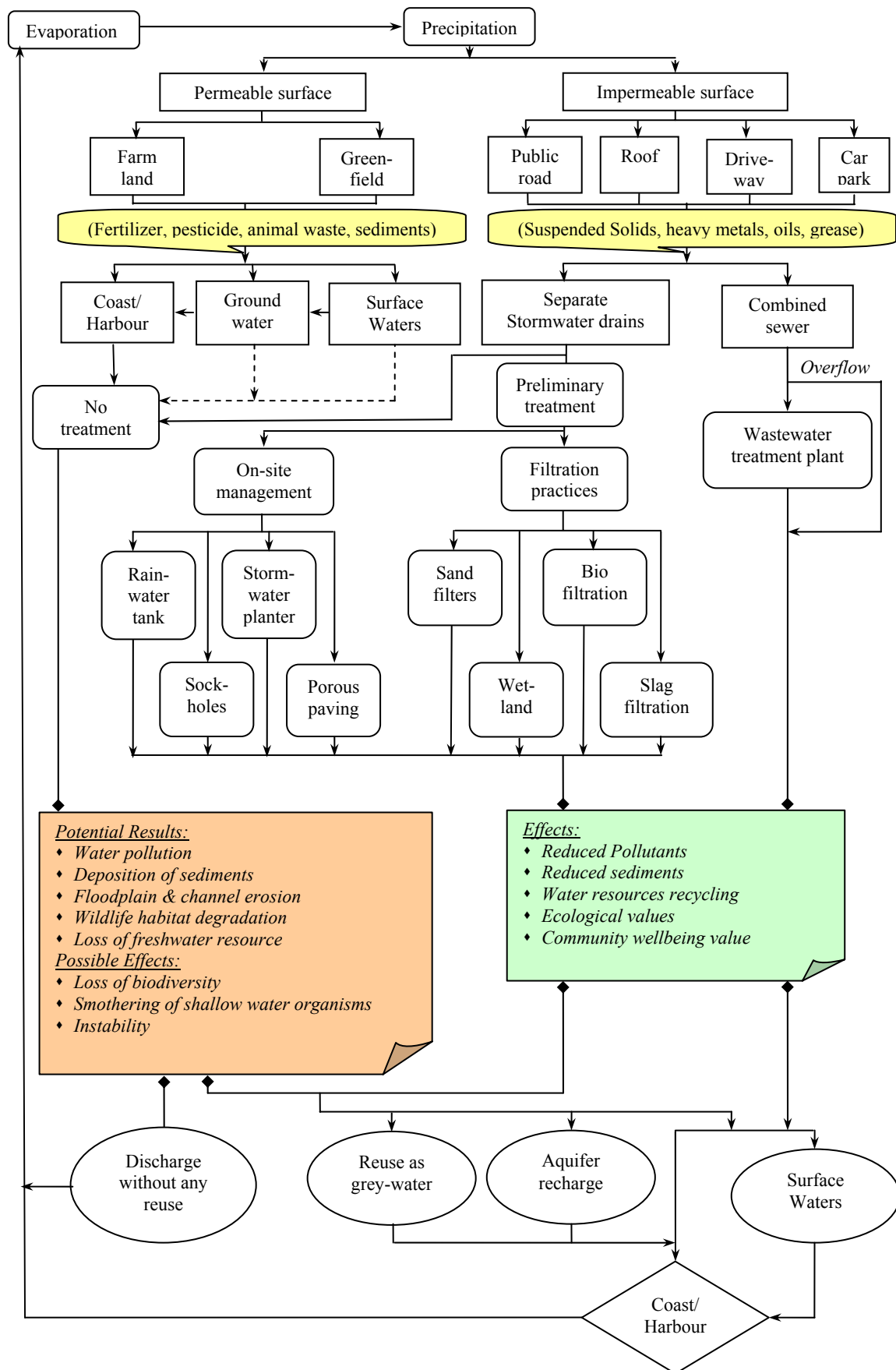


Figure 1-1 Stormwater development, collection and treatment

The primary sources of heavy metals in urban area are traffic-related activities (eg exhaust from motor vehicles) and atmospheric fallout (Sorme and Lagerkvist, 2002) as well as the wear and tear of the road pavement (Ng, 2004).

An investigation in Auckland (Williamson and Kelly, 2003) applied environmental response criteria (ERC) to evaluate the pollution by each element. The red, amber and green ERC represent unhealthy, degraded health and healthy environments respectively. The report showed that zinc exceeded the Red more frequently than lead or copper. However, copper and lead fell within the Amber range more frequently than zinc. Zinc and copper concentrations are generally increasing in estuarine sediments whereas lead concentrations are decreasing. The latter is believed to be the result of following an international trend by introducing lead-free petrol in 1996 (Kingett Mitchell Limited, 2003). PAH levels were Green except at some sites with older catchments such as Meola Stream (sewage overflows) and Motions Creek (overflows from combined drainage system), and sites near historic gas works (Chelsea, Little Shoal Bay).

Even though the implementation of source control is often more cost-effective than traditional end-of-pipe approaches, the residual solids and toxic substances collected in the runoff still need to be removed in order that appropriate (e.g. Local Authority) water quality standards be achieved against the standard or quote to eliminate the potential hazard to the receiving water bodies.

In the United States, most stormwater discharges are considered point sources and have been regulated under the *National Pollutant Discharge Elimination System* (NPDES) since 1994.

A traditional approach where stormwater is collected in underground pipes and disposed of as soon as possible at some convenient downstream location is, given the subsequent flooding and pollution problems is not acceptable in developed countries and in many cases, no longer acceptable in developing countries (Nathanson, 2000).

Potable water shortage is now a global problem due to the increased water demand as well as the deterioration of ecosystems. It was found (Kingsley, 2005) that the flow

into catchments in the Perth area had been decreased by two-thirds in the last 30 years and that Perth, which now survives on fossil water, will run out of its available sustainable natural water resources by 2015 if nothing is done to slow usage rates. In fact, stormwater is increasingly being viewed as a natural resource for use in a beneficial manner, rather than as a waste material to be disposed of quickly. For example, the stormwater in on-site storage or detention basins can percolate to the groundwater and help to recharge an aquifer (Nathanson, 2000).

Environment-friendly management of stormwater has been included in the agenda of local authorities such as Auckland City Council (ACC). It is generally recognized that a high percentage of heavy metals and toxic contaminants have a strong affinity for the suspended sediments present in runoff. This association is fortuitous in terms of control and treatment of runoff since it is relatively straightforward to separate suspended solids and hence the pollutants attached to them (Adams *et al.*, 2000). Ng (2004) studied the particle size distribution in stormwater in Auckland and concluded that particles larger than 100 μm make up around 90% of the total road sediment load. The removal of coarse sediments (size over 100 μm) would ensure removal of 75% to 90% of all deleterious metal contaminants.

The ACC plans to remove 27% of the suspended sediments in 70% of stormwater catchments by 2020. The detention pond in Waiatarua Basin and mechanical filtration systems at Central Park in Penrose have been built up to facilitate the achievement of the goal (Auckland City Council, 2005).

1.1.2 Slags

From the metallurgical point of view, slag is not just an unwanted by-product in most metallurgical processes (Bramming and Wikstram, 2002). It is used in the smelting furnaces to separate the impurities, such as gravel, sand, clay and stones, from the molten iron (Clair, 1964). It plays an important role in all metal smelting processes and the slag composition must ensure satisfactory composition of the metal being produced (Davies and Oelmann, 1985). The functions of a slag in molten metal processing are as follows:

- 1) To protect the melt from contamination from the furnace atmosphere;
- 2) To take up (and remove) unwanted impurities present in the melt;
- 3) To control the supply of refining agents to the melt through additions to the slag; and
- 4) To insulate the melt.

Smelting slags are usually dominated by silicates, but may also contain calcium, magnesium, aluminium, phosphorous and iron etc.

Slag can be classified as basic or acidic according to its nature. A basic slag is one which contains an excess of basic oxide, while an acidic slag contains excess acidic oxide. The characteristics of a slag are to some extent a function of the alkalinity of the slag, which is expressed as the ratio of the mass of basic oxides to that of acidic oxides in the slag. The most important basic oxide is CaO, and the principal acidic oxide is SiO₂.



Figure 1-2 Mechanical screening of slag at NZ Steel (*Auckland*)

Considering the energy crisis, global warming and the environmental deterioration, a large effort has been made in modern metallurgical industries to minimize heat loss, slag consumption and evolution of waste slag (Emi and Seetharaman, 2000). Slag volume reduction has always been an important part in the development of the operation of blast furnace. The low slag volume operation in blast furnaces requires a tight control over both raw material quality and process. The improved efficiency of the process could, on the other hand, result in a number of advantages such as lower cost of production, higher productivity and improved hot metal quality (Bramming and Wikstram, 2002).

Blast furnace slag has been put to many commercial uses (Dennis, 1963). According to the manner in which it is cooled from the molten state, three general types may be recognized.

Air-Cooled slag: This is the normal product from smelting. The slag is simply poured from the ladle car on to the slag dump. After crushing and screening, it may be used for railway ballast, road-making or as aggregate for cement.

Granulated slag: This is prepared either by running the molten slag into water, or the slag is subjected to a high pressure water jet as it falls into the pit. The principal use is for making cement or concrete blocks.

Foamed or expanded slag: This is the product obtained by running slag into a controlled amount of water or by blowing steam through the molten slag. The amount of water used is less than that required for granulation. The result is relatively dry cellular product. It is an effective non-conductor of heat and sound and is used for thermal and acoustic insulation.

1.2 Background

It was estimated in 2004 (U.S. Geological Survey, 2005) that the iron and steel slag output was on the order of 220 to 380 million tonnes in the world, based on typical ratios of slag to crude iron and steel output. Almost 2×10^7 tonnes of slag were

consumed in the U.S in 2004. The major uses were in construction sector as aggregates for asphaltic paving, fill, and road bases, and as a feed for cement kilns. Some slags were also returned to the furnaces as ferrous and flux feed.

A certain portion of slag is disposed of, either as land fill or stock-piled outdoors, besides those consumed or recycled. Research on the application of iron and steel making slags in wastewater treatment provides another option for using this material. The mechanisms and efficiency of the removal of heavy metals like arsenic (Ahn *et al.*, 2003), lead (Dimitrova and Mehandgiev, 1998; Dimitrova, 2002) copper (Feng *et al.*, 2004), dye removal/decolorization (Konduru *et al.*, 1997; Gupta *et al.*, 2003) from different sources had been studied.

SteelServ Ltd. of Auckland, as part of the *Multiserv* international group of companies, requested the University to examine the use of iron and steel making slags as a media for assisting the removal of suspended solids and heavy metals from stormwater. It is recognized that this is an international problem – not unique to New Zealand – and one that may provide an outlet and constructive end use for surplus steel industry co-products.

As a by-product from metallurgical industry, most slags contain pollutants to some extent, especially the heavy metals. However, the *SteelServ* melter slag is a by-product of titanomagnetite. Leaching trials have shown that there is no release of heavy metals from this material when it is subjected to prolonged leaching (New Zealand Steel, 1992). Therefore it is likely to be a non-toxic aggregate for the treatment of stormwater.

More recently, the removal of heavy metal contaminants from stormwater has become a strategic imperative for Territorial and Regional councils, through heightened awareness of their impact on the environment. It is contended here that the slag should be regarded as a candidate to assist with these initiatives.

A field test carried out by *SteelServ* in a filtration bed showed that the zinc concentration of the effluent from the industry dropped from 100 mg L⁻¹ to 10 mg L⁻¹ after draining through the two-step beds, i.e. over 90% of zinc can be removed from

the effluent of the factory. However, a batch test carried out recently (Menzlin, 2005) showed that the *SteelServ* melter slag was no better than river sand or silica sand (which were used as controls in the test) to remove Zn (up to 3 ppm) from feeding water at low concentration. The hydroxide precipitation plays a key role in the process.

As constructed wetlands have been widely used to process the sewage and stormwater (Cameron *et al.*, 2003), the massive land coverage makes them unsuitable for use in urban areas. The availability of a cheap, compact, efficient heavy metal adsorbing, and environmentally-safe aggregate is seen as a solution to the problem.

1.3 Research aims and objectives

The overall research aim of the project is:

To develop a better understanding of the nature and ability of slag to remove solids and heavy metals from stormwater without any deleterious side effects on the water quality.

Following objectives are designed to achieve the above aim:

- 1) Build on previous scientific study undertaken in New Zealand and internationally with these materials;
- 2) In conjunction with *SteelServ Ltd.*, determine where and in what role slag-based products may play a part in assisting with improving storm water quality;
- 3) Organise, trials and experiments. Monitor and report on their outcomes;
- 4) Confirm the safety and suitability of these materials for such end uses.

1.4 Literature review

The ability of removing heavy metals from contaminated water by metallurgical industry slags has been investigated in a number of studies.

Kang *et al.* (2004) used steel slag as an adsorbent to remove lead from wastewater. The impact of temperature and pH on the kinetic and equilibrium characteristics of Pb adsorption on the slag was also studied.

Dimitrova (2002) carried out a column test which used granular blast furnace slag as an adsorbent for lead removal. It was found that the presence of Na and Ca could impede the uptake of Pb. The fact revealed that ion exchange played a dominant role in the process. Solubilisation and hydrolysis of the calcium silicates and aluminosilicates of the slag is accompanied by the adsorption of metals presented in the solution.

The adsorption of nickel from wastewater by steel converter slag is considered to be enhanced by the presence of magnetite (Ortiz *et al.*, 2000). It works under a wide range of conditions in terms of initial metal concentration, retention time, adsorbent dosage and temperature.

Feng *et al.* (2004) compared the iron and steel making slag in terms of their capacity to remove copper and lead from aqueous solutions. The iron slag presents higher efficiency due to its higher surface area, porosity and ion-exchange ability.

There is little research on desorption of heavy metal from saturated aggregates. EDTA, which is able to chelate metals, was proved to desorb lead rapidly from the adsorbent (Kang *et al.*, 2004).

Desorption of heavy metals from contaminated soils can be achieved by applying organic acids, which function as chelating agents, e.g. citric, malic, acetic, tartrate acids (Gao *et al.*, 2003; Qin *et al.*, 2004), or inorganic salts like sodium nitrate (Arias *et al.*, 2005) and calcium chloride (Qin *et al.*, 2004). In general, the organic acids showed higher ability to desorb metals than inorganic salts. However the disposal of the solution following desorption, and the cost, are key considerations of promoting the application. These aspects were not discussed in the above papers.

The side effect of introducing such aggregates (which are usually regarded as waste) into environment is always a concern. Kozanoglou *et al.* (1997) found that higher

levels of Fe and Cr in biota from the sampling sites situated near the ferro-nickel smelting plant or the dumping site of the metalliferous slag in contrast with the obviously lower levels of the more distant sites. Molluscs showed generally higher concentrations of Fe and Cr in their tissues than plants.

The leaching trials were conducted on melter slag by New Zealand Steel (1992). Water with different pH's for a period of over two years was used to leach the slag continuously. The results showed that there were no major impact on water quality when the test rig feed water was neutral or basic. Iron and manganese were leached out under acid conditions. The investigation on the reaction of slag to a marine environment (New Zealand Steel, 2002) showed the medium extraction concentration of Ca, S, K, B, Mg initially and dropped to below detection levels rapidly. Mo, Cu, Mn, Zn, Pb, Cd and Ni were below detection levels from the beginning. Fe and Al showed low but consistent discharge value even after ten cycles.

It can be concluded from the review that the capacity of heavy metal removal by slag has been verified by many studies. It is currently applied in constructed wetland systems as an adsorption substrate. However, the application of melter slag in stormwater purification is under-researched in terms of heavy metal and suspended solids removal. These, and an evaluation of the recovery of the used aggregates, are the basis of this study.

Chapter 2 Materials and Methods

2.1 Selection of metal analyzing instruments

The analysis of the metallic elements in solution was one of the essential tasks in this study. Spectroscopic techniques, which process the samples in a rapid and effective way (Rouessac, 2000), are now widely used in laboratories for analyzing metal elements. Both flame atomic absorption spectrometer (Flame AAS, Perkin-Elmer 3110) and Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES, Varian Liberty AX-Sequential) were available in the AUT chemistry laboratory. The AAS was selected in this study for the following considerations:

- ♦ acceptable detection limit;
- ♦ simplicity; and
- ♦ lower operational cost

Table 2.1 Atomic spectrometric detection limits ($\mu\text{g L}^{-1}$)

<i>Element</i>	<i>Flame AAS</i>	<i>ICP-AES</i>
Ca	1	0.08
Cd	0.5	1
Cu	1	0.9
Zn	0.8	1

Source: Modern Methods for Trace Element Determination (Vandecasteele and Block, 1993; Oguz, E. 2005)

Varied detection limit can be achieved by using different instrument. They are, nevertheless, in the ppb level.

One of the advantages of ICP-AES was the ability of simultaneous multi-element analysis. However due to the limited budget of this study only three metallic elements were considered. The increased workload through using AAS, which processes the

sample at a wavelength that is specific and characteristic of the element under consideration, was acceptable.



Figure 2.1 The Perkin-Elmer 3110 flame atomic absorption spectrometer used for all metal analysis conducted at AUT

2.2 Stock standard solutions preparation

Stock standard solutions were used for making the standards to calibrate the measurement of metallic ions by AAS. They were also used to prepare the working solutions for the batch tests and column tests. The nominal concentration of the stock solutions used in the study was 1000 mg L^{-1} .

The standard solutions are preferably to be prepared by metals (User Manual of AAS). However considering the absence of the metals in the laboratory, the metallic salts (reagent grade) were used as alternative in this study. The stocks for each element were prepared as follows:

- a) Cadmium

Dissolve 2.283 g of reagent grade cadmium chloride into a 1L volumetric flask to volume with 1% hydrochloric acid.

b) Copper

Dissolve 2.953 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ (reagent grade) into a 1L volumetric flask to volume with 1% nitric acid.

c) Zinc

Dissolve 1.000 g of Zinc metal (reagent grade) in 40 mL hydrochloric acid and dilute into a 1L volumetric flask to volume with deionized water.

d) Calcium

Dissolve 2.497 g of dried calcium carbonate CaCO_3 in a volume of 1:4 nitric acid. Dilute into a 1L volumetric flask to volume with deionized water.

The stock solutions were made from nitric or hydrochloric acid and stored in a sealed volumetric flask. All the working solutions and standards hereafter were diluted from these stock solutions to ensure the consistency of the results.

2.3 Calibration curve

A set of standards ranging $0.2 \sim 20 \text{ mg L}^{-1}$ for each element were prepared and measured by AAS. Three standards for each element were selected for making calibration curve. They were determined by the following criteria:

- ♦ The reading from the spectrometer should be within $0.1 \sim 0.8$
- ♦ Linear response of the reading to the concentration

2.4 Slag aggregate

The original melter slag sample provided by SteelServ had a grain size range of 5 – 10 mm. It was then crushed by Wiley mill and sieved in a sieve stack into the following three grain size categories:

0.60 ~ 1.00 mm (fine)

1.00 ~ 2.00 mm (medium)

2.00 ~ 3.35 mm. (coarse)

The sieved slag was then washed by deionized water to remove the small particles and dried in the oven (Wilton Utility) at 105°C for 24 hours. The samples were stored in large uncovered beakers until required in the experiments.

Table 2.2 Chemical composition of the slag

<i>Component</i>	<i>Weight percentage (%)</i>	<i>Component</i>	<i>Weight percentage (%)</i>
Fe	0 ~ 10	MgO	11 ~ 15
CaO	12 ~ 20	P ₂ O ₅	<0.005
SiO ₂	9 ~ 15	V ₂ O ₅	0.1 ~ 0.5
TiO ₂	27 ~ 42	MnO	0.5 ~ 1.7
Al ₂ O ₃	15 ~ 21	Cr ₂ O ₃	0.2 ~ 0.6

Source: *Results of Leaching Trials Conducted on Melter Slag*, NZ Steel, 1992



Figure 2.2 The melter slag samples in three particle sizes used as adsorbent in the study

2.5 Adsorption kinetics

The first experiment was designed to verify the capacity of the slag to remove heavy metals.

Hypothesis 1 *That melter Slag has the capacity to remove zinc and copper ions from wastewater, and that this ability is not simply a function of the alkalinity of the slag.*

A working solution (around 20 mg L^{-1}) containing known levels of zinc or copper was prepared by diluting the stock solution with deionized water. Mix 150 mL of this “synthetic wastewater” with slag samples of different grain size in 250 mL conical flask. A magnetic stirrer was used to homogenize the solution. The concentrations of Cu^{2+} and Zn^{2+} in the solution were measured by AAS at intervals of 15 minutes. The trial was stopped when equilibrium was reached, i.e. at the point of saturation of the aggregate or the end point of the adsorption. The experiment was conducted at 23°C .



Figure 2.3 Adsorption batch experiments

Since the batch tests on slag were supposed to be conducted under acidic or neutral surroundings, the marble (92.4% of CaCO_3), which is considered to be a more

alkaline material, was used in a series of control tests. The control tests were carried out under the same conditions as those on slag in terms of particle size, initial pH and concentration of the working solution and the liquid/solid ratio.

The pH of the solution was measured by a pH meter (MeterLab PHM201) at the time of AAS analysis. The initial and final concentrations of calcium (Ca^{2+}) in the solution were also measured.

Background to Experimental Procedure

The adsorption capacity of the aggregate depends on the temperature (Oguz, 2005), the nature of the adsorbate (such as pH, concentration, and turbidity) (Ricou *et al.*, 1999; Pan *et al.*, 2003; Oguz, 2005) and the nature of adsorbent (such as grain size and specific surface area) (Sansalone, 1999).

2.6 Adsorption isotherm

Batch adsorption tests were then carried out to investigate the nature of adsorption.

The equilibrium relationship between the amount of substance adsorbed and that remaining in solution is defined for a given set of conditions by an equation known as an adsorption isotherm. Depending on the theory used to model the adsorption, Langmuir and Freundlich are most commonly used for the application of adsorbent in water treatment (Binnie *et al.*, 2002; Pan *et al.*, 2003).

Hypothesis 2 *That the Freundlich theory applies to the adsorption isotherm, i.e. that the equation for adsorption is:*

$$x/m = Kc_q^{1/n}$$

where:

x = weight of material adsorbed

m = weight of adsorbent

c_q = concentration of material remaining in solution once equilibrium has been reached

K and n are constants.

The adsorption capacity of different aggregates or the same aggregate in different particle sizes can be evaluated by comparing the constants in each isotherm. It will be discussed in Chapter 4.

The analytes include Zn^{2+} , Cu^{2+} and Cd^{2+} . Samples of about 1.0, 2.0, 3.0, 4.0 and 5.0g of melter slag at different particle sizes were prepared for testing. The “synthetic wastewater” solutions which contain 20 mg L^{-1} of one of the metallic ions were adjusted to pH=4 with 10% NaOH or 10% HNO_3 . The slags were mixed with 150 mL of the metal solutions in 250 mL conical flasks at room temperature (23°C) and stirred on magnetic stirrer for 24 hours. The concentrations of metallic ion and calcium were measured by AAS before and after the test. The pH of the solutions was also measured using pH meter. All batch tests were carried out three times.

2.7 Desorption

The batch tests were conducted to confirm whether or not the adsorption process is reversible.

Hypothesis 3 *That adsorption is a reversible process and that used slag can be recovered by exposing the slag to inorganic acid salts or organic acids.*

The used slag that was saturated by Cd^{2+} , Zn^{2+} and Cu^{2+} ions in the batch tests was washed with deionized water and dried in oven at 105°C for 3 hours. The slag was then weighed.

There is little study on desorption of heavy metals from slag aggregate. Low-molecular-weight organic acids had been used for desorbing copper, cadmium and lead from contaminated soils (Qin *et al.*, 2004). Although synthetic chelators such as diethylenetriaminepentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) had the verified capacity to extract heavy metals from soils (Feng *et al.*, 2005; Jeon *et al.*, 2005), they were not selected in this study due to

the toxicity of the formulated chelate complex to the receiving water bodies (Knepper, 2003).

Potassium chloride, sodium chloride, sodium nitrate, nitric acid (ion exchange) citric acid, tartaric acid (chelators) and carbonic acid (generated by blowing carbon dioxide into deionized water) and solutions in different concentration were prepared from corresponding salt or acid solid (AR grade). Sea water, which is supposed to be one alternative desorption agent was collected at Herne Bay (Auckland). The supernatant¹ was used for the tests. The inorganic salts were used for comparison since they were main background electrolytes in environment (Qin *et al.*, 2004).

The desorption mechanism of each agent is to be discussed in Chapter 4.

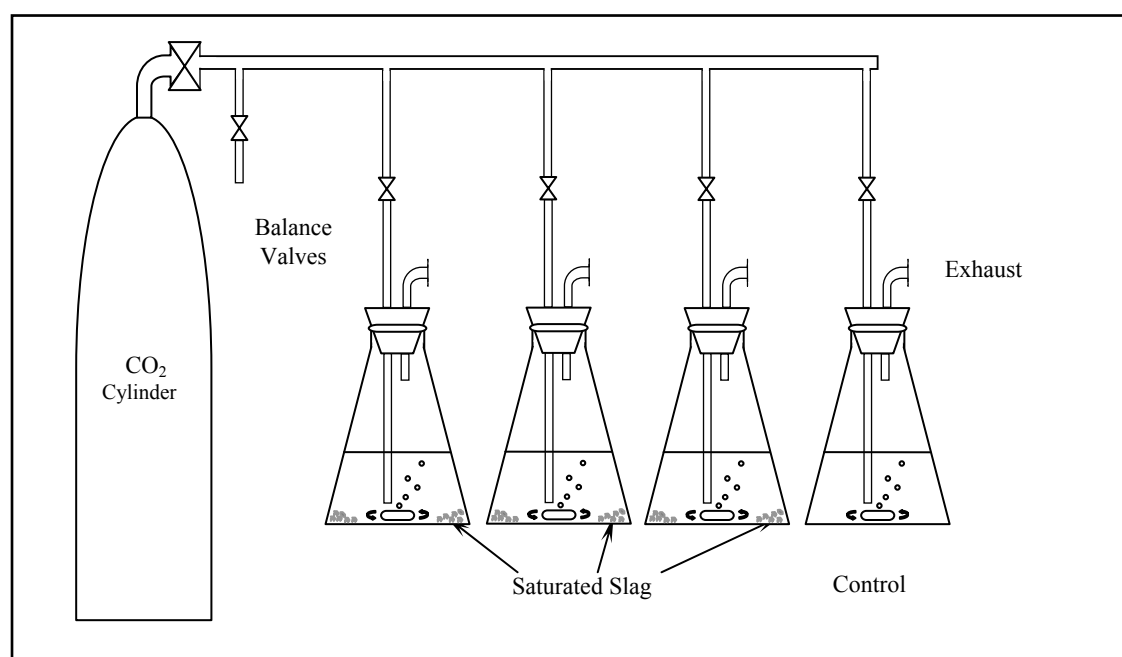


Figure 2.4 Desorption of metallic ions by carbonic acid

The slag was mixed with 150 mL of the test solutions or the combination of these for 24 hours. The concentrations of metallic ions released to the aqueous phase were measured thereafter. As the adsorbed ions in the slag was known, the desorption

¹ The seawater sample was kept at 4°C for one night and the fluid above the sediment was siphoned off.

efficiency in the first 24 hours (first run, η_1) can be expressed as the percentage of released ions in the adsorbed metals in the slag.

Similar to the above process, the second run was repeated except for extending the retention time to 96 hours. The accumulative efficiency (η_2) was calculated and the effectiveness of the first run can be given as the percentage of η_1 in η_2 . The results are given in Section 3.5 (P.39).

2.8 Column experiments

2.8.1 Stormwater sampling

The working solutions used in the batch experiments differed from real stormwater runoff due to the absence of solids. The presence of solids, composed of both organic and inorganic substances, could change the characteristics of the solution from the physical, chemical and biological point of view (Asaf *et al.*, 2004; Zanders, 2005). The stormwater samples collected from different function areas were used in the column experiments. Since the first flush is regarded as containing elevated level of pollutants (Lee *et al.*, 2002; Ng, 2004), collection of such runoff is essential to the analysis in the study.

As the study was carried out during a wet winter (July and August) in Auckland, it was only possible to collect on two “first flush occasions”.

Table 2.3 Description of stormwater sampling sites

<i>Site</i>		<i>Function area</i>	<i>Sampling point</i>	<i>Days since last storm</i>
Oakley Creek	Site 1	Residential	Outfall of stormwater drains	2
	Site 2	Construction site with unpaved surface		
Hobson St. (CBD)		Commercial and high traffic	Gratings before entering the drainage	3

2.8.2 Sample conservation:

Plastic collection containers, which had been rinsed with deionized water and diluted nitric acid, were used for sampling. Considering the formulation of unsoluble oxides by some metals at high pH, it was recommended (Eaton *et al.*, 1995) that conservation of the samples be carried out at pH 2 (adjustment with nitric acid). However such conservation may mobilize the metallic components that are attached to the organic and/or inorganic particles. On the other hand, more metallic ions in the sample without conservation may be attached to the solids during the storage (Arias *et al.*, 2005). The allocation of heavy metals between solution and suspended solids may therefore be changed from the original status. The determination of the removal efficiency of heavy metals by slag will, as a result, be affected. The problem is minimized by analyzing the sample immediately after the sampling. Also the presence of nutrients and microorganisms in the stormwater sample (Ng, 2004) may change both the physical and chemical properties; the sample was therefore kept at 4°C to reduce the biological reaction by microorganisms. The column test was carried out within 24 hours of sampling to minimize the possible error.

2.8.3 Sample analysis

The method of nitric acid digestion accompanied by sample dry ashing was applied to metallic elements analysis in the study (Hseu, 2004).

- ♦ 200 mL of stormwater sample was filtered through pre-weighted filter paper (Whatman, No.42). The filtrate was kept for the analysis of soluble metallic elements.
- ♦ The filter paper is then dried at $105\pm 2^{\circ}\text{C}$ in drying oven for 16 hours. The SS content is determined by comparing the increase of the weight of the filter paper.
- ♦ Place the filter paper (ash-less) in the muffle furnace (McGregor NL-200), which is set to 200°C and raise the temperature by 50°C increment until the temperature reaches 350°C and there is little or no smoking. Finally set the

temperature to 450°C and ash about 16 hours.

- ♦ Remove the samples from the furnace and allow them to cool. Wet the ash with DI water and add 4 mL of HNO₃ (70%, reagent grade) to cover the ash. Cover with a watch glass and reflux on a hot plate for about 1 hour. Then move the watch glass and reduce the heat to gently evaporate the acid. Return the samples to the furnace and ash at 375°C for 1 hour until a white ash is obtained. This ash represented the suspended solids in the sample.
- ♦ Add 5 mL 10% hydrochloric acid and gently boil the solution, cool and make up to 25 mL with deionized water.

A blank was prepared in the same manner.

The Cd²⁺, Zn²⁺ and Cu²⁺ concentrations in the digested sample and filtrate were measured by AAS.

The same samples were also measured directly by AAS without any filtration and digestion to show the efficiency of the digestion method.

2.8.4 Column tests with stormwater samples

The column experiments were carried out to determine whether other components within the slag had caused adsorption.

Hypothesis 4 *Removal of heavy metals from stormwater by slag is not simply through precipitation of cations as hydroxides and/or subsequent particle settlement*

The glass columns (5 mm ID) which were packed with melter slag were used in these experiments. The columns were in U-shaped to ensure that the aggregate was submerged throughout the experiment (Figure 2.5). Three different particle sizes of slag (0.6 – 1.0, 1.0 – 2.0 and 2.0-3.35 mm) were tested. The bulk densities of each

size of slag were 1.67, 1.64 and 1.44 g/cm³ respectively. The slag bed height for each size of slag was 19.2, 19.6 and 22.2 cm respectively at the weight of 6 g.

The stormwater sample, which was stirred by magnetic stirrer to mix the solution, was stored in a 1L beaker and pumped by peristaltic pump (Alitea) through the column with the linear flow rates of 1.96, 3.92 and 8.92 cm/min.

A blank column was used as control in the experiment.

The effluent samples from each column were collected at intervals of 1 hour for 4 hours and analyzed without previous filtration. The influent was also analyzed.

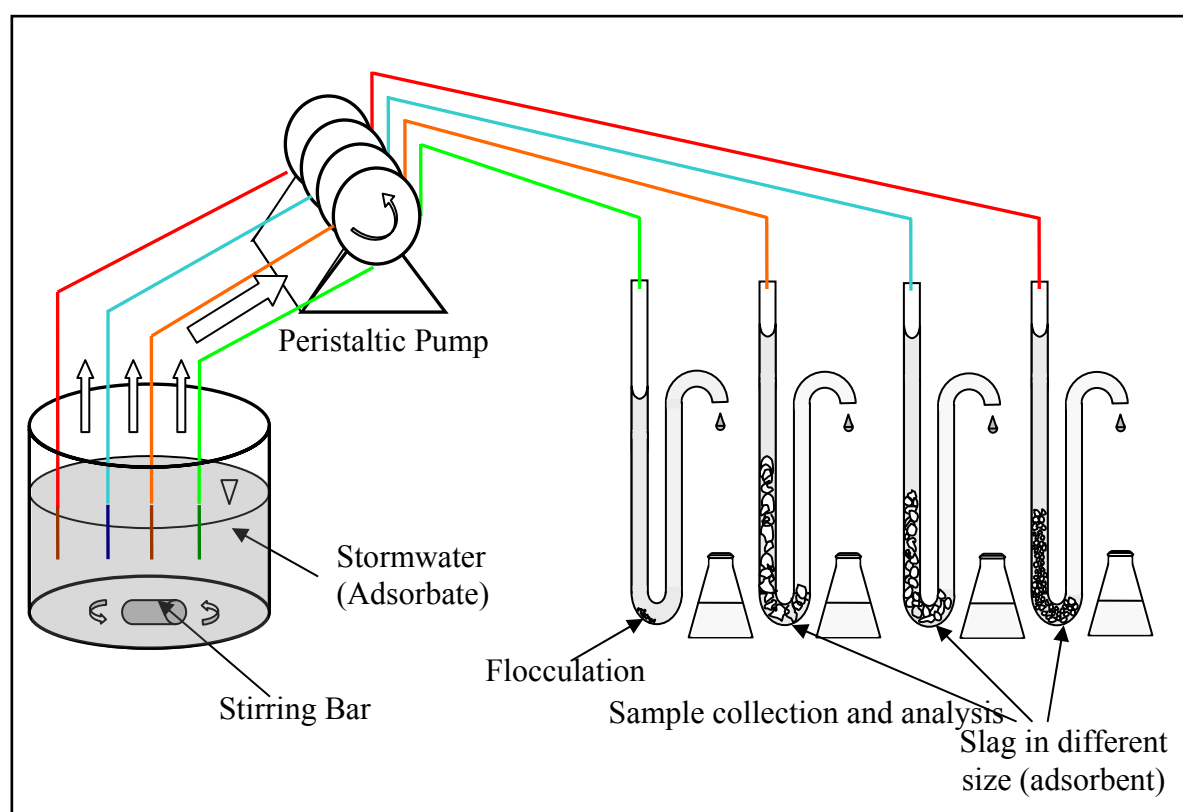


Figure 2.5 Layout of column experiment

The analysis of the sample showed that the concentrations of Cu²⁺ and Cd²⁺ are extremely low (Table 3.13). It was hard to determine the removal efficiency of

metallic ions from the stormwater samples. Therefore a set of supplementary column tests which used synthetic stormwater samples as filtrate were carried out.

2.8.5 Column tests with synthetic stormwater samples

The synthetic stormwater samples were prepared by mixing clay ($29\pm 2\%$ of moisture) with deionized water and metallic solutions which were originated from stock standard solutions. The clay is quite easily mixed to give a uniform milky suspension. The concentrations of SS and metallic ions were adjusted as follows:

Table 2.4 Concentration of each element in the synthetic stormwater samples

Sample	SS(mg/kg)	Cd ($\mu\text{g L}^{-1}$)	Zn ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)
1	100	100	400	200
2	200	100	600	200
3	400	100	800	200

The sample was stabilized at room temperature for 1 hour before it was used in the column test. The variables in the supplementary tests include the particle size of the slag (0.6 ~ 1.0, 1.0 ~ 2.0 and 2.0 ~ 3.35 mm), flow rate of the feeding sample (1.96, 3.92 and 8.92 cm/min) and the concentration of each element in the samples.

The efficiencies of the SS and heavy metal removal were evaluated by comparing the difference between the influent and effluent.

Although turbidity is the typical parameter for evaluating the clarity of the water sample, the scattering of the sample creates an apparent absorbance which can be measured by spectrophotometer (Ultrospec 2100 pro). It was applied in this study as an alternative due to its simplicity.

The wave scanning of the sample is shown in Figure 2.6.

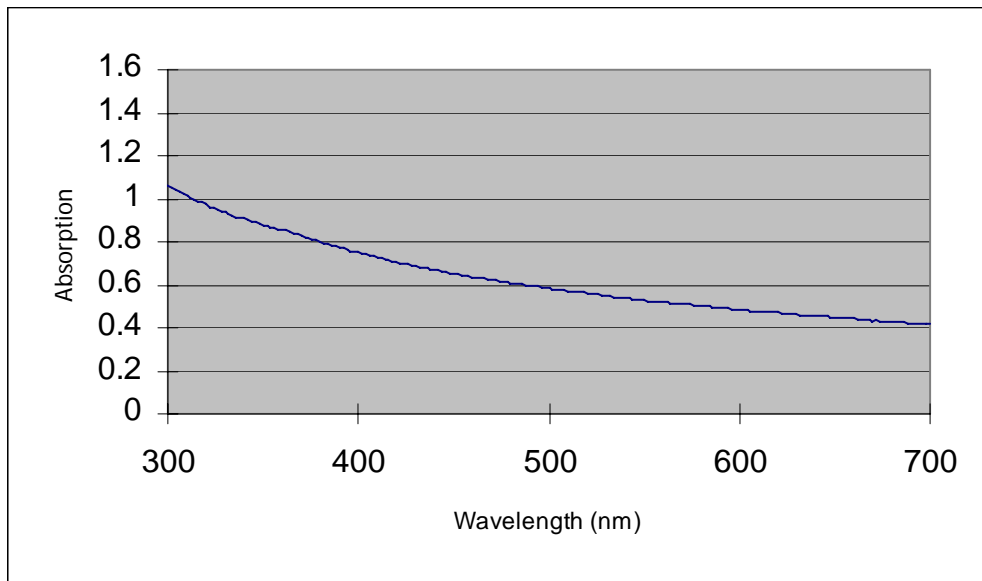


Figure 2.6 Spectrum of stormwater sample

The wavelength was set to be 400 nm to measure the absorption of the samples. The linear regression of the absorbance of the samples to the corresponding SS (mg/kg) showed that they are closely related ($R^2=0.9965$) within the tested SS region. Therefore the absorbance was used to represent the SS level in this study.

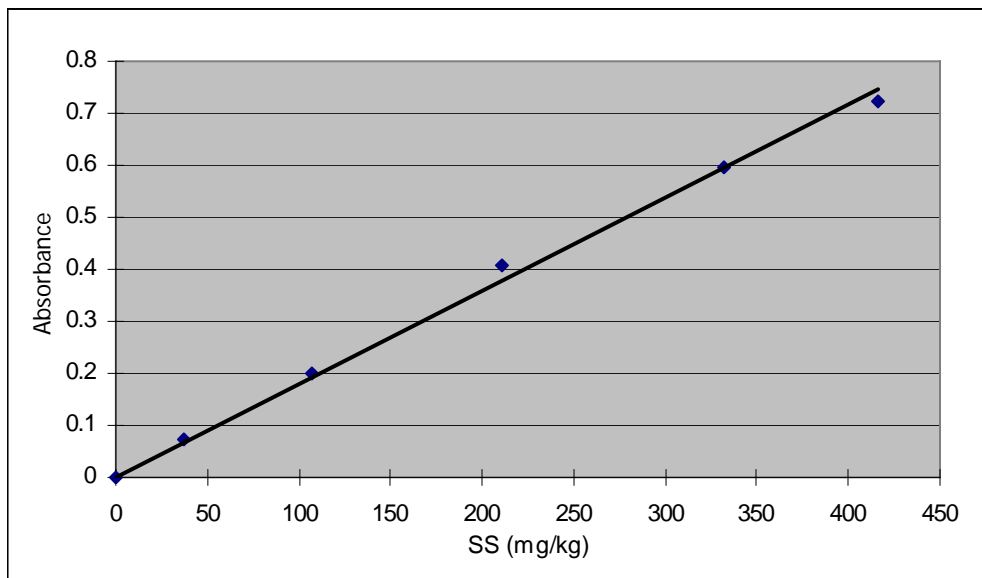


Figure 2.7 Relationship between suspended solids and absorbance of synthetic stormwater sample

The tests followed the same process described in the above section.

Chapter 3 Results

3.1 Adsorption kinetics

It was observed (Oguz, 2005) that the adsorption capacity of metallic ion on adsorbent was proportional to active sites on its surface. Adsorption kinetics describes the temporal rate of solute adsorption. It is one of the key characteristics in evaluating the efficiency of adsorption.

Figure 3.1 and 3.2 are composite results, showing the removal efficiency of Zn^{2+} and Cu^{2+} from working solutions by melter slag at different grain sizes (Fine – Φ 0.6 ~1.0 mm; Medium – Φ 1.0 ~2.0 mm and Coarse – Φ 2.0 ~3.5 mm). The mass of slag used in the tests was 50g.

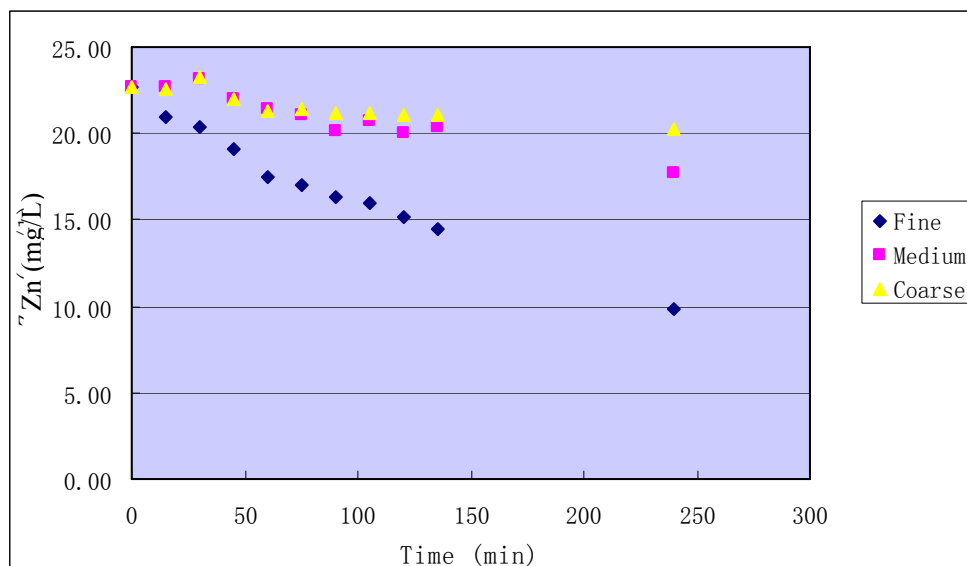


Figure 3.1 Trends of Zn^{2+} removal over time by melter slag (50g)

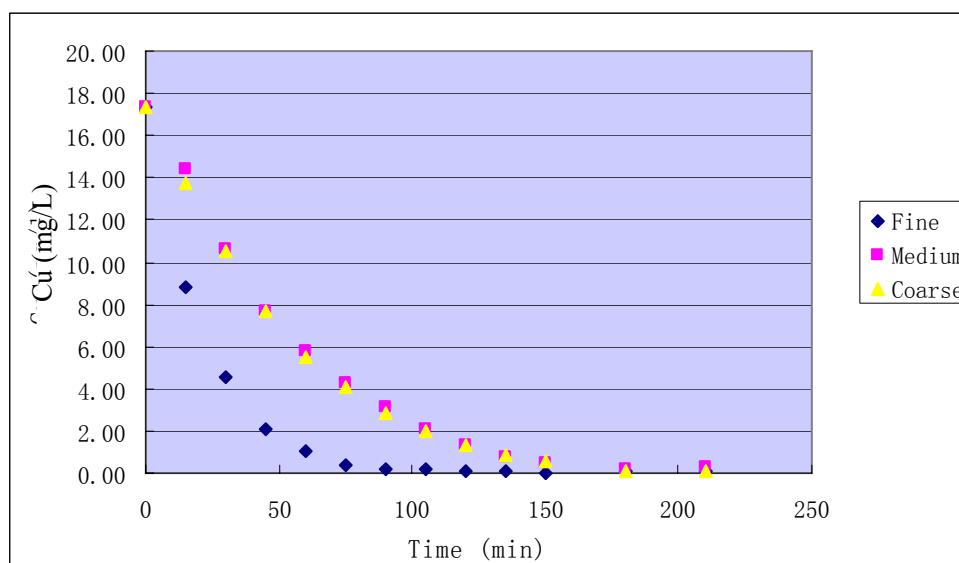


Figure 3.2 Trends of Cu^{2+} removal over time by melter slag (50g)

Figure 3.3 and 3.4 show the results of control tests which used marble as adsorbent under the same conditions as slag.

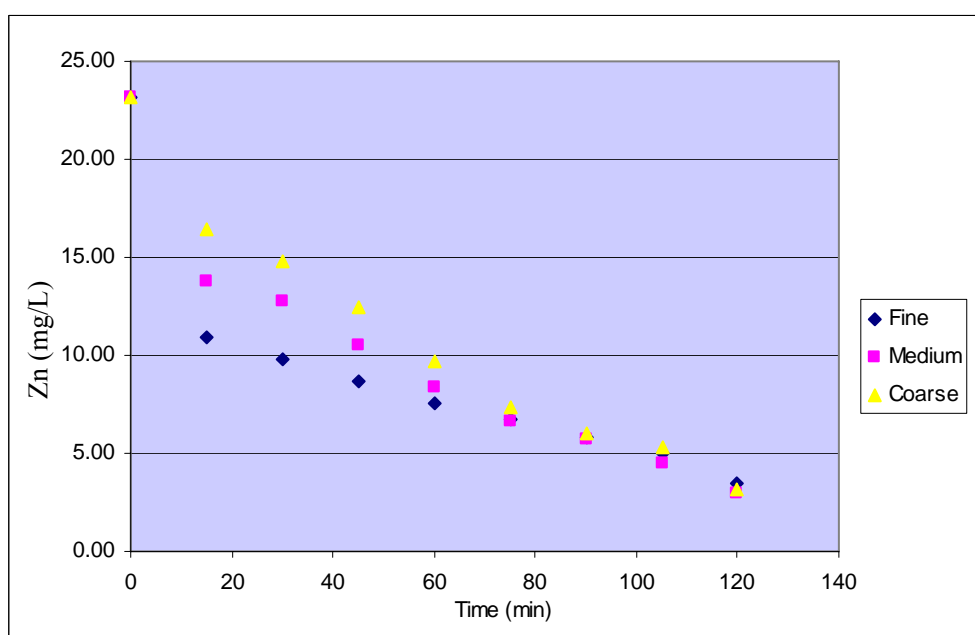


Figure 3.3 Trends of Zn^{2+} removal over time by marble (50g)

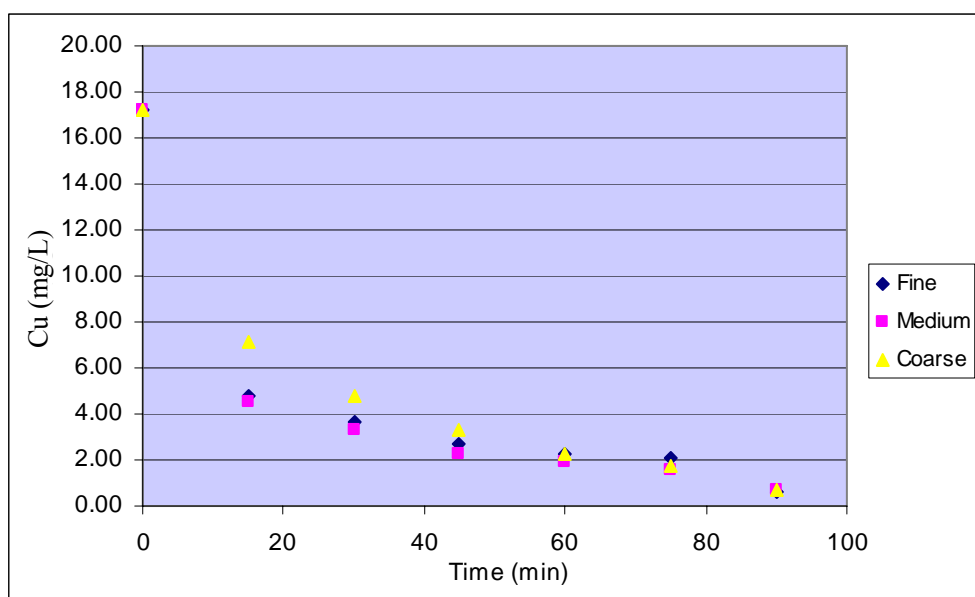


Figure 3.4 Trends of Cu^{2+} removal over time by marble (50g)

The removal efficiencies for Zn^{2+} by fine, medium and coarse slag in 4 hours were 56%, 22% and 11% respectively, while over 99% of Cu^{2+} can be removed by slag at all tested grain sizes. A second experiment which increased the mass of slag to 100g was carried out (Figure 3.5) to see whether more Zn^{2+} can be adsorbed by elevated amount of slag.

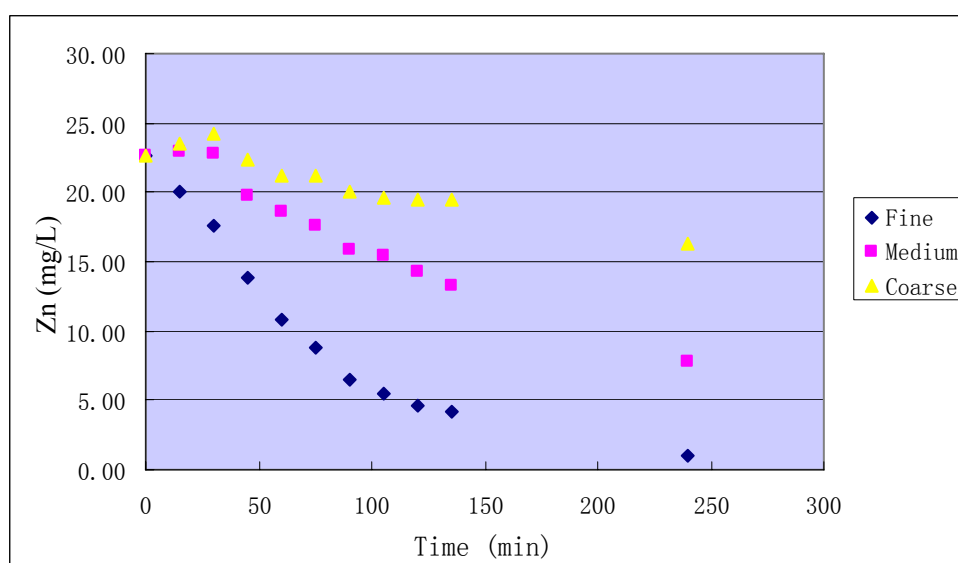


Figure 3.5 Trends of Zn^{2+} removal over time by melter slag (100g)

The Zn^{2+} removal efficiency was raised to 95%, 66% and 28% respectively for fine, medium and coarse slag in the test.

A solution consisting around 20 mg L^{-1} of Cd^{2+} , Zn^{2+} and Cu^{2+} respectively was mixed with 3g of slag (fine size). The removal of each ion from this multi-ion solution over time was shown in the following figure.

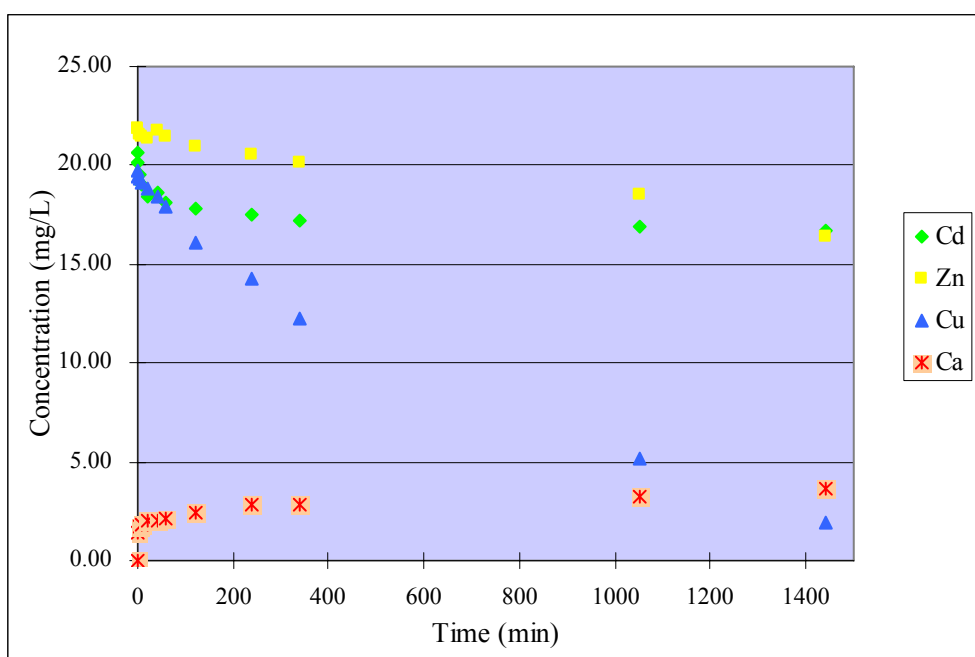


Figure 3.6 Metallic ions removal by slag (fine) from multi-ion solution

3.2 Alkalinity effect of the slag

The melter slag tested in the study can be classified as alkaline due to the dominant composition of basic oxide, i.e. CaO (12%) and MgO (13.1%) over that of acidic oxide, i.e. SiO_2 (14%).

It was detected that the pH of the solution had been increasing during the adsorption process, accompanied by an increase of Ca^{2+} in solution. The concentrations of Ca^{2+} and pH of the solution before and after the tests were given in Table 3.1.

Table 3.1 Change of Ca^{2+} and pH in the solutionUnit: mg L^{-1}

<i>Analyte</i>	<i>Mass of Slag (g)</i>	<i>Items</i>	<i>Fine</i>		<i>Medium</i>		<i>Coarse</i>	
			<i>Initial</i>	<i>Final</i>	<i>Initial</i>	<i>Final</i>	<i>Initial</i>	<i>Final</i>
Cu^{2+}	50	Ca^{2+}	0.14	11.13	0.14	9.46	0.14	6.82
		pH	3.03	5.87	3.03	5.63	3.03	5.35
Zn^{2+}	50	Ca^{2+}	0.34	25.61	0.34	19.74	0.34	8.95
		pH	3.14	5.98	3.14	4.91	3.14	4.45
	100	Ca^{2+}	0.34	48.74	0.34	39.49	0.34	24.06
		pH	3.14	6.52	3.14	6.36	3.14	5.92

The cause of the alkalinity effect by the slag will be further discussed in Section 4.1.2 (Page 56).

3.3 Competitive effect of the metallic ions

Since the affinity to adsorbent differs between each ion, it is assumed that the competitive effect between different ions exist during the adsorption process. The adsorption of Cu^{2+} by the slag that was saturated with Zn^{2+} is shown in Table 3.2.

The competitive effect of the elements for adsorption was verified by a reverse test which mixed the Zn^{2+} solution with the slag that was saturated with Cu^{2+} . The results are shown in Table 3.3.

It was shown that the slag still had the ability to remove Zn^{2+} even though it had been saturated by Cu^{2+} . However there was no Cu^{2+} released from the slag at any instance.

Table 3.2 Cu^{2+} removal by slag which is saturated with Zn^{2+}

Mass of slag (g)	Items	Fine		Medium		Coarse	
		Initial	Final	Initial	Final	Initial	Final
50	pH	3.04	4.72	3.04	4.47	3.04	4.35
	Cu^{2+} (mg L ⁻¹)	17.32	1.17	17.32	3.39	17.32	3.07
	Zn^{2+} (mg L ⁻¹)	0	1.91	0	1.73	0	1.12
	Ca^{2+} (mg L ⁻¹)	0.07	1.04	0.07	0.36	0.07	0.27
	Cu^{2+} adsorbed (mg)	2.42		2.09		2.14	
	Zn^{2+} released (%)	8.51		12.87		21.03	
100	pH	3.04	6.30	3.04	4.91	3.04	4.66
	Cu^{2+} (mg L ⁻¹)	17.32	0.29	17.32	1.10	17.32	1.68
	Zn^{2+} (mg L ⁻¹)	0	1.21	0	1.99	0	2.08
	Ca^{2+} (mg L ⁻¹)	0.07	4.37	0.07	2.98	0.07	1.50
	Cu^{2+} adsorbed (mg)	2.55		2.43		2.35	
	Zn^{2+} released (%)	5.35		8.81		9.38	

Note: A parallel sample using deionized water as control should have been included in these early tests. However the later desorption tests of the study showed that deionized water had little effect on the release of adsorbed metal ions from slag. Therefore the presence of Zn^{2+} in the solution can be expressed as the effect of ion-exchange by Cu^{2+} which has stronger affinity to the slag.

Table 3.3 Zn^{2+} removal by slag which is saturated with Cu^{2+}

Mass of slag (g)	Items	Fine		Medium		Coarse	
		Initial	Final	Initial	Final	Initial	Final
25	pH	4.15	5.74	4.15	5.62	4.15	5.20
	Cu^{2+} (mg L ⁻¹)	0	0	0	0	0	0
	Zn^{2+} (mg L ⁻¹)	18.65	3.50	18.65	6.00	18.65	10.16
	Ca^{2+} (mg L ⁻¹)	0	5.47	0	5.29	0	2.85
	Zn^{2+} adsorbed (mg)	2.27		1.90		1.27	
	Cu^{2+} released (%)	0		0		0	
50	pH	4.15	6.53	4.15	6.43	4.15	5.99
	Cu^{2+} (mg L ⁻¹)	0	0	0	0	0	0
	Zn^{2+} (mg L ⁻¹)	18.65	1.42	18.65	1.75	18.65	4.16
	Ca^{2+} (mg L ⁻¹)	0	13.07	0	12.78	0	7.90
	Zn^{2+} adsorbed (mg)	2.59		2.54		2.17	
	Cu^{2+} released (%)	0		0		0	

3.4 Adsorption isotherm

The results of the adsorption experiments are presented in Appendix A.

3.4.1 Adsorption capacity

The capacity of slag aggregate to remove metallic ions from a working solution can be calculated from the reduction of ion concentration in the solution after the adsorption tests. The working solutions containing each metallic ion and the mixture of the three elements in the same concentration were used in the batch tests.

Table 3.4 Adsorption capacity of melter slag to each ion

<i>Items</i>		<i>Metallic ions Adsorption Capacity in 24 hours (mg/g)</i>	
		<i>Single-ion solution</i>	<i>Multi-ion solution</i>
Cd ²⁺	Fine	0.19 ± 0.02	0.07 ± 0.02
	Medium	0.15 ± 0.02	0.07 ± 0.01
	Coarse	0.09 ± 0.02	0.04 ± 0.01
Zn ²⁺	Fine	0.28 ± 0.03	0.22 ± 0.06
	Medium	0.14 ± 0.04	0.14 ± 0.03
	Coarse	0.09 ± 0.02	0.09 ± 0.04
Cu ²⁺	Fine	0.66 ± 0.09	1.00 ± 0.27
	Medium	0.79 ± 0.19	0.90 ± 0.17
	Coarse	0.46 ± 0.08	0.64 ± 0.08

Table 3.5 Adsorption efficiency of melter slag to each ion

<i>Items</i>		<i>Metallic ions Adsorption efficiency in 24 hours (%)</i>	
		<i>Single-ion solution</i>	<i>Multi-ion solution</i>
Cd ²⁺	Fine	19 ± 6	6 ± 2
	Medium	12 ± 3	6 ± 1
	Coarse	8 ± 2	3 ± 1
Zn ²⁺	Fine	24 ± 6	19 ± 5
	Medium	12 ± 3	12 ± 4
	Coarse	9 ± 3	8 ± 4
Cu ²⁺	Fine	69 ± 13	79 ± 8
	Medium	70 ± 12	76 ± 11
	Coarse	46 ± 13	60 ± 14

3.4.2 Adsorption isotherm

The equilibrium relationship between the amount of substance adsorbed and that remaining in solution is defined for a given set of conditions by an equation known as an adsorption isotherm. Depending on the theory used to model the adsorption, Langmuir and Freundlich formulae are most commonly used for the application of adsorbent in water treatment (Binnie *et al.*, 2002).

The Freundlich theory assumes that the equation for adsorption is:

$$x/m = K \times c_q^{1/n} \quad (1)$$

where

x = weight of material adsorbed

m = weight of adsorbent

c_q = concentration of material remaining in solution once equilibrium has been reached

K and n are constants.

Logarithmic transformation of equation (1) gives following equation.

$$\ln(x/m) = \ln K + (1/n) \times \ln c_q \quad (2)$$

Plotting $\ln(x/m)$ against $\ln c_q$ on graph paper will give a straight line with a slope of $1/n$ and an intercept of $\ln K$ where $\ln c_q = 1$.

The results of metallic ion concentrations from three duplicates for each element (Zn^{2+} , Cu^{2+} and Cd^{2+}) are averaged respectively and used for plotting the isotherm curves. The linear isotherm derived from the curves is shown in Table 3.6.

Table 3.6 Adsorption isotherm of the slag to each ion

Items			Freundlich isotherm	
			Formula	R^2
Single-ion solution	Cd	Fine	$\ln(x/m) = -0.96 - 0.26 \times \ln Cq$	0.4205
		Medium	$\ln(x/m) = -4.39 + 0.82 \times \ln Cq$	0.6062
		Coarse	$\ln(x/m) = -16.97 + 4.90 \times \ln Cq$	0.3614
	Zn	Fine	$\ln(x/m) = -3.61 + 0.83 \times \ln Cq$	0.5660
		Medium	$\ln(x/m) = -7.82 + 2.01 \times \ln Cq$	0.2577
		Coarse	$\ln(x/m) = -1.36 - 0.35 \times \ln Cq$	0.0127
	Cu	Fine	$\ln(x/m) = -0.71 + 0.20 \times \ln Cq$	0.8816
		Medium	$\ln(x/m) = -0.93 + 0.41 \times \ln Cq$	0.7776
		Coarse	$\ln(x/m) = -1.07 + 0.12 \times \ln Cq$	0.1991
Multi-ion solution	Cd	Fine	$\ln(x/m) = -24.70 + 7.44 \times \ln Cq$	0.3220
		Medium	$\ln(x/m) = -49.13 + 15.48 \times \ln Cq$	0.7578
		Coarse	$\ln(x/m) = -31.32 + 9.48 \times \ln Cq$	0.1585
	Zn	Fine	$\ln(x/m) = -32.49 + 10.50 \times \ln Cq$	0.9608
		Medium	$\ln(x/m) = -6.59 + 1.54 \times \ln Cq$	0.6308
		Coarse	$\ln(x/m) = 14.54 - 5.68 \times \ln Cq$	0.4906
	Cu	Fine	$\ln(x/m) = -56.64 + 19.17 \times \ln Cq$	0.9168
		Medium	$\ln(x/m) = -0.55 + 0.32 \times \ln Cq$	0.6623
		Coarse	$\ln(x/m) = -0.63 + 0.08 \times \ln Cq$	0.0943

Note: x -- mass of metal adsorbed by slag (mg)

m -- mass of slag (g)

Cq - concentration of metal remaining in solution once equilibrium has been reached

The adsorption isotherm curves under cross conditions are shown in Figure 3.4 to 3.7.

Note: $\ln(x/m)$ – Logarithmic transformation of the weight of metallic ion adsorbed by unit mass of slag

$\ln(Cq)$ – logarithmic transformation of concentration of metal remaining in solution once equilibrium has been reached

The analysis of the isotherms under different conditions is given in Section 4.1.4

(Page 60).

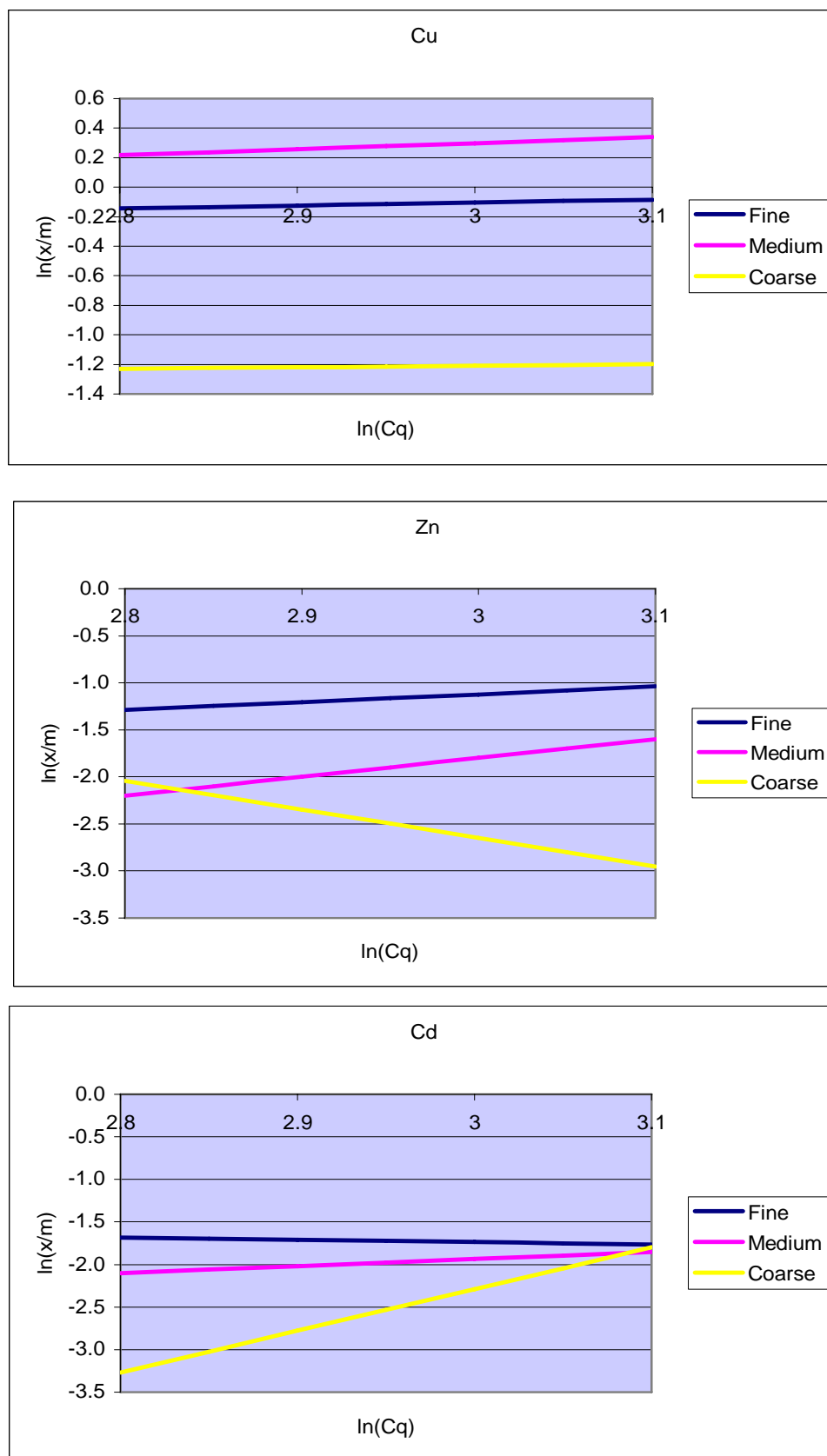


Figure 3.7 Adsorption isotherm of slag to each metallic ion (single-ion solution)

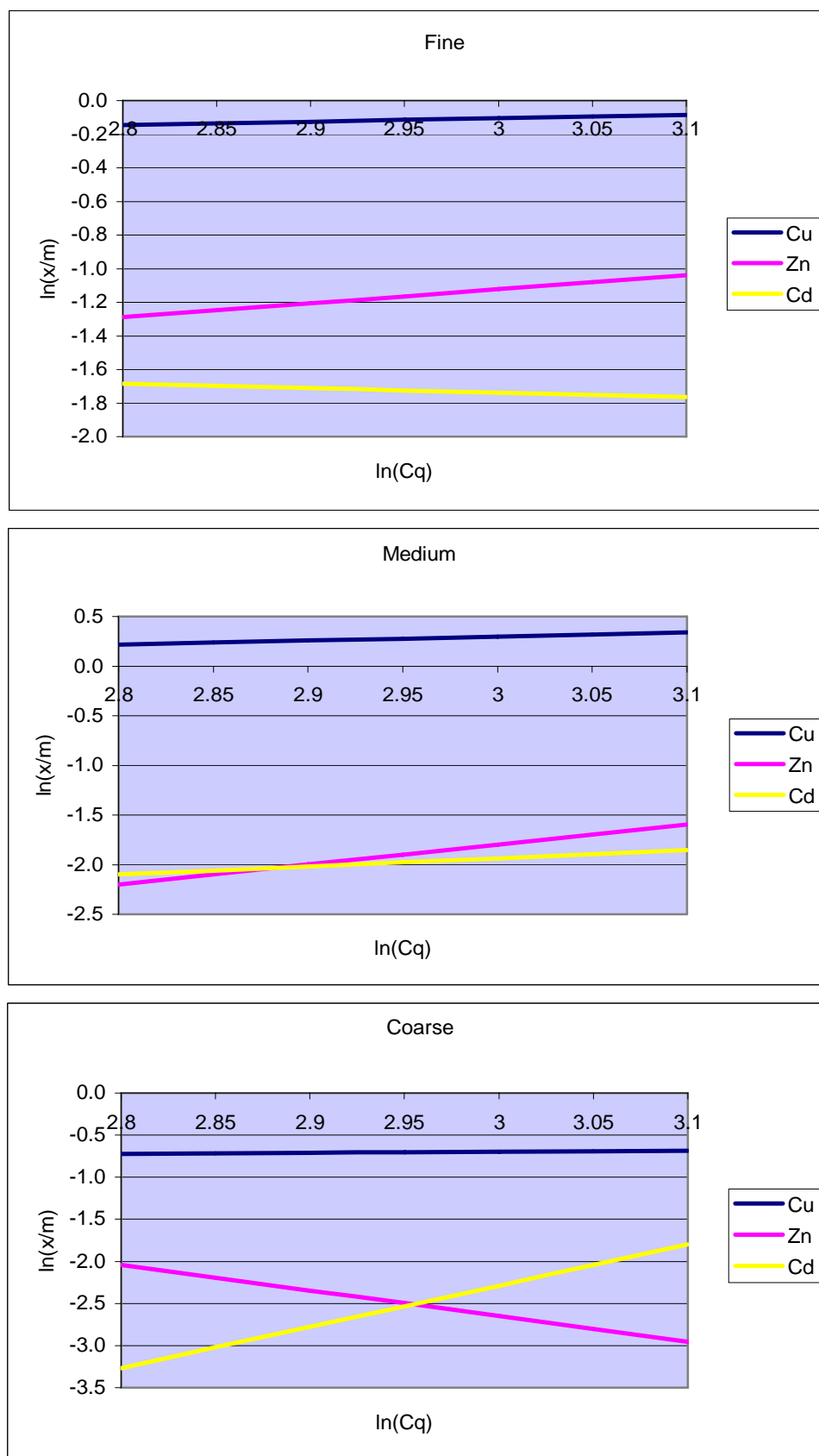


Figure 3.8 Adsorption isotherm of slag in different grain size (single-ion solution)

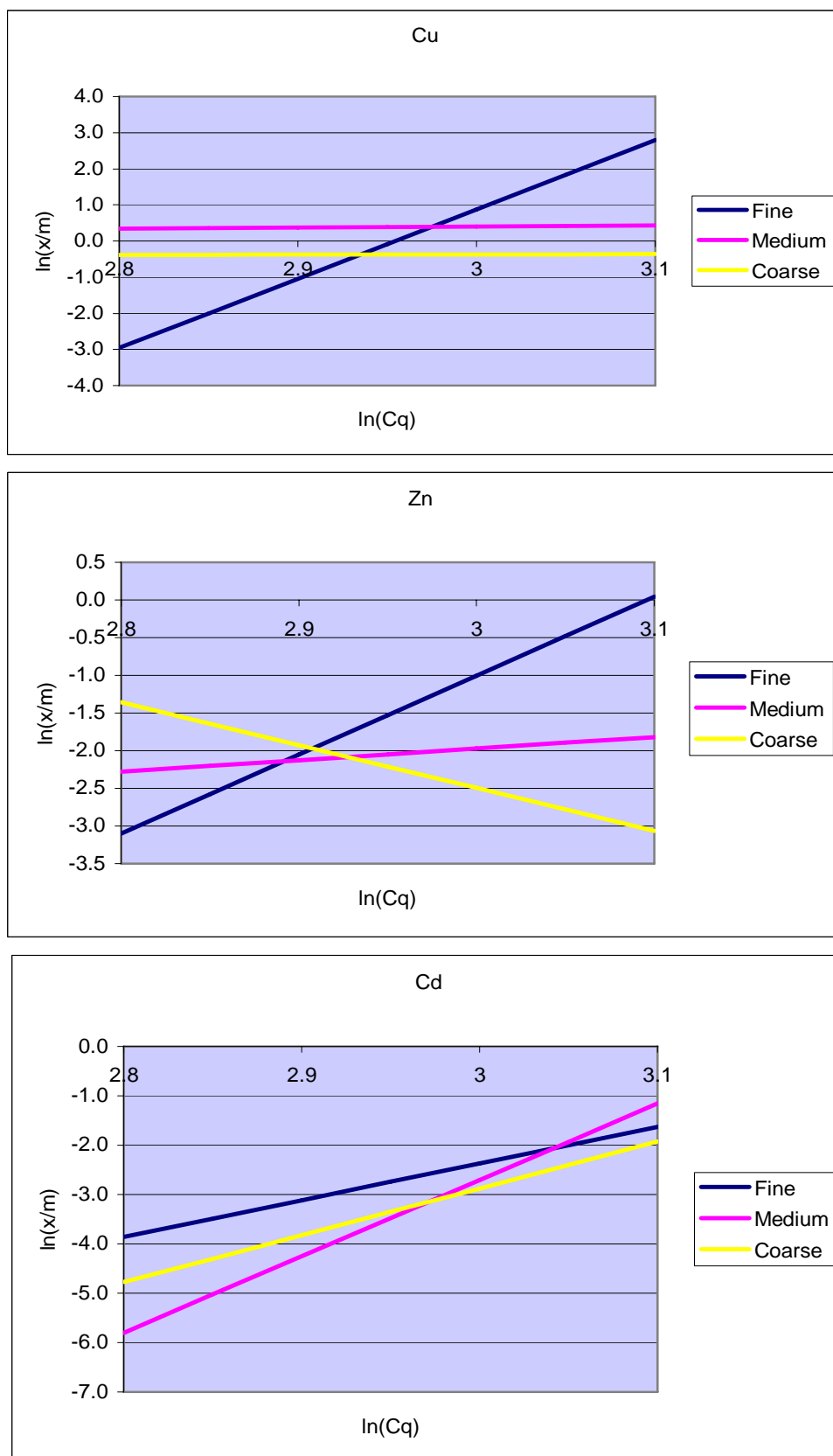


Figure 3.9 Adsorption isotherm of slag to each metallic ion (multiple-ion solution)

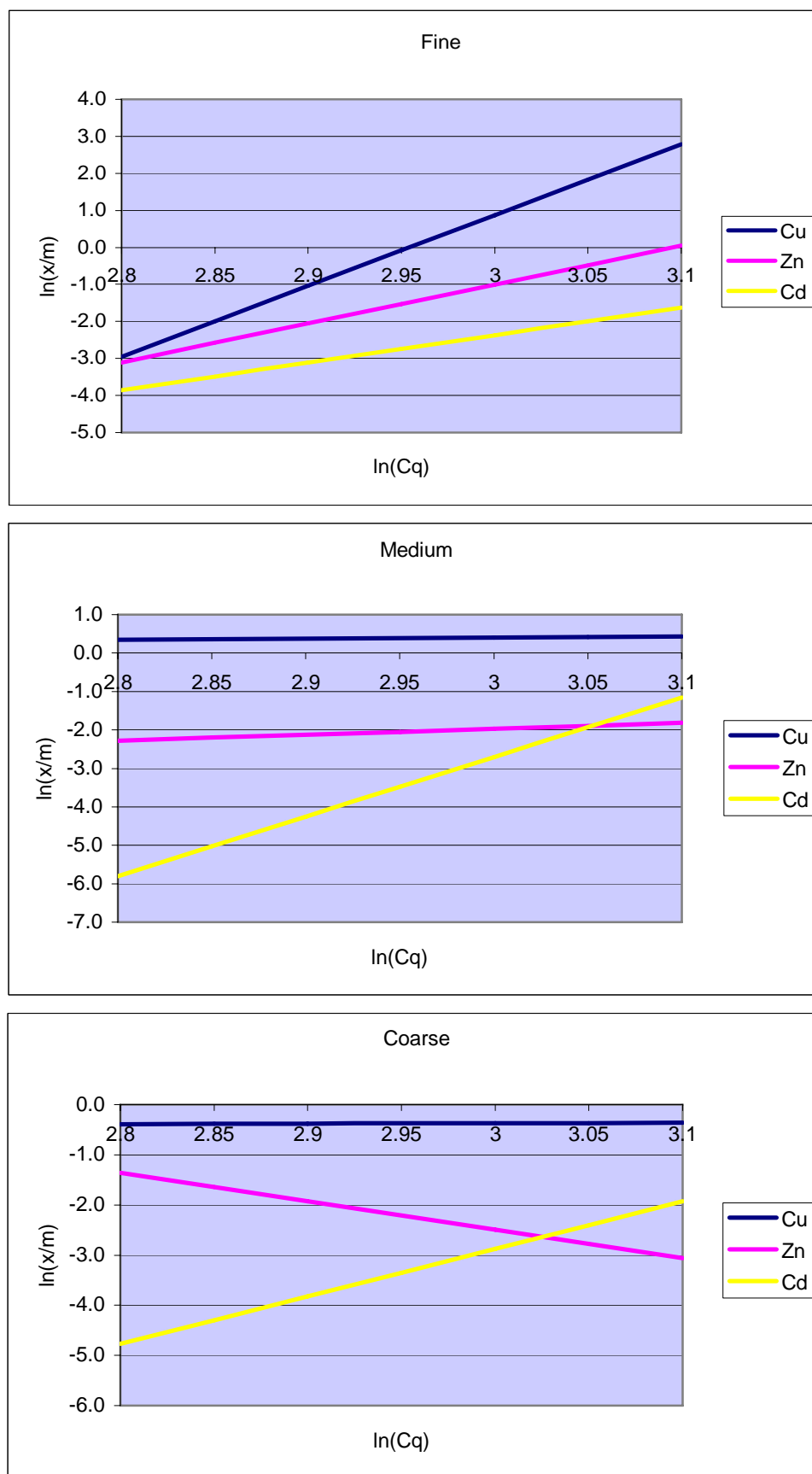


Figure 3.10 Adsorption isotherm of slag in different grain size (multiple-ion solution)

It was found that pH and Ca^{2+} concentrations in the solution at equilibrium are mutually dependent. This follows an exponential distribution under most conditions within the tested pH range.

Table 3.7 Relationship between pH and equilibrium concentration of Ca^{2+}

<i>Adsorbate</i>	<i>Grain size</i>	<i>Formula</i>	<i>R²</i>
Zn^{2+}	Fine	$b = 5.91a^{0.06}$	0.9829
	Medium	$b = 5.65a^{0.10}$	0.9749
	Coarse	$b = 5.76a^{0.09}$	0.9661
Cd^{2+}	Fine	$b = 6.32a^{0.04}$	0.9699
	Medium	$b = 5.86a^{0.07}$	0.9839
	Coarse	$b = 5.74a^{0.11}$	0.9720
Cu^{2+}	Fine	$b = 4.77a^{0.03}$	0.5973
	Medium	$b = 4.53a^{0.03}$	0.5696
	Coarse	$b = 4.71a^{0.01}$	0.8154

Note: a – calcium concentration in solution
b – pH of the equilibrium solution

The alkaline effect of the aggregate is discussed in Section 4.1.2 (Page 57).

3.5 Desorption

Desorption is the reverse process to adsorption. The used slag can be recovered by separating the adsorbed ions from the adsorbent with the assistance of desorption agent. The most commonly applied mechanisms for desorption are:

- ♦ Competitive adsorption
- ♦ Ion-exchange
- ♦ Chelation

A range of inorganic salt, sea water, organic and inorganic acid was selected as desorbent. The efficiencies of each substance or the combination to recover the used slag are shown in the following tables.

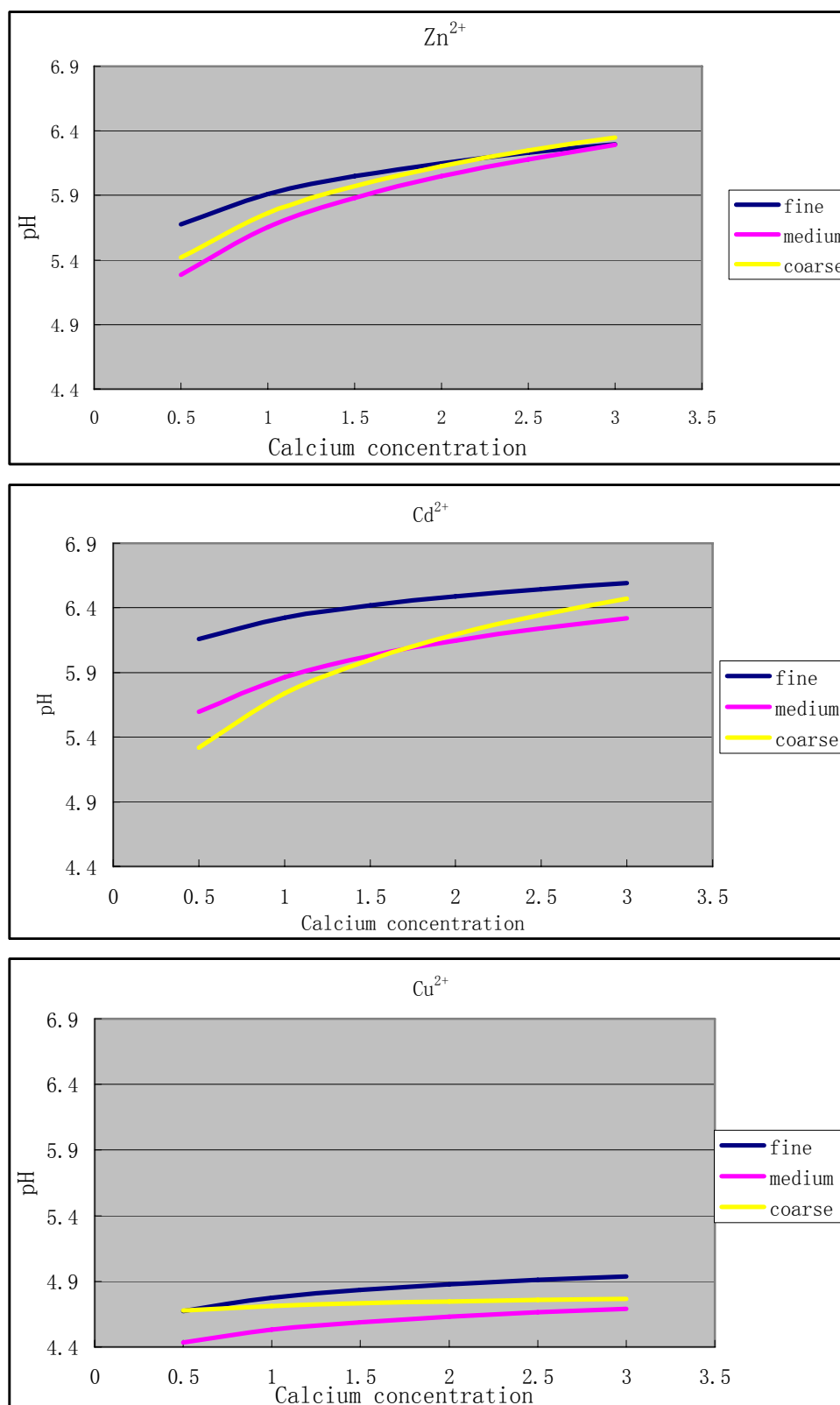
Figure 3.11 Variation of pH in the solutions with the change of Ca^{2+} concentration

Table 3.8 Recovery of used slag with inorganic salts (0.01M)

<i>Metallic ion</i>	<i>Cd</i>			<i>Zn</i>			<i>Cu</i>		
<i>Desorption Agent</i>	<i>KCl</i>	<i>NaCl</i>	<i>NaNO₃</i>	<i>KCl</i>	<i>NaCl</i>	<i>NaNO₃</i>	<i>KCl</i>	<i>NaCl</i>	<i>NaNO₃</i>
η_1 (%)	41 ± 6	40 ± 9	46 ± 22	10 ± 5	9 ± 3	7 ± 1	0	0	0
η_2 (%)	48 ± 8	47 ± 12	50 ± 23	11 ± 6	10 ± 3	8 ± 1	0	0	0
η_1/η_2 (%)	85 ± 4	84 ± 3	90 ± 2	93 ± 2	88 ± 4	88 ± 4	–	–	–

In which: η_1 = Recovery in 24 h (1st run, %)
 η_2 = Accumulative recovery in 96 h (2nd run, %)
 η_1/η_2 = Efficiency of the 1st run (%)

Table 3.9 Recovery of used slag with inorganic salt and organic acid

<i>Metallic ion</i>	<i>Cd</i>			<i>Zn</i>			<i>Cu</i>		
<i>Desorption Agent</i>	<i>KCl</i>	<i>0.02 M Citric Acid</i>	<i>KCl + 0.02M Citric Acid</i>	<i>KCl</i>	<i>0.02 M Citric Acid</i>	<i>KCl + 0.02M Citric Acid</i>	<i>0.02 M Citric Acid</i>	<i>KCl + 0.02M Tartaric Acid</i>	<i>KCl + 0.02M Citric Acid</i>
η_1 (%)	19 ± 4	46 ± 13	46 ± 5	8 ± 3	65 ± 26	108 ± 12	23 ± 15	27 ± 12	32 ± 10
η_2 (%)	26 ± 8	52 ± 12	52 ± 5	10 ± 3	69 ± 29	118 ± 10	35 ± 23	39 ± 19	39 ± 12
η_1/η_2 (%)	72 ± 5	88 ± 7	88 ± 5	81 ± 4	94 ± 3	92 ± 3	69 ± 18	70 ± 8	81 ± 15

Table 3.10 Recovery of used slag with seawater and organic acid

<i>Metallic ion</i>	<i>Cd</i>			<i>Zn</i>			<i>Cu</i>		
<i>Desorption Agent</i>	<i>SW</i>	<i>SW + 0.02M Citric Acid</i>	<i>SW + 0.02M Tartaric Acid</i>	<i>SW</i>	<i>SW + 0.02M Citric Acid</i>	<i>SW + 0.02M Tartaric Acid</i>	<i>SW</i>	<i>SW + 0.02M Citric Acid</i>	<i>SW + 0.02M Tartaric Acid</i>
η_1 (%)	41 ± 16	50 ± 15	49 ± 15	3 ± 1	56 ± 21	97 ± 21	4 ± 1	50 ± 9	49 ± 13
η_2 (%)	50 ± 18	55 ± 16	53 ± 17	5 ± 2	61 ± 22	106 ± 23	6 ± 2	54 ± 11	52 ± 13
η_1/η_2 (%)	81 ± 5	92 ± 3	94 ± 2	56 ± 9	91 ± 3	91 ± 2	64 ± 2	94 ± 2	94 ± 2

Note: SW – Seawater

Table 3.11 Recovery of used slag with carbonic acid

Items	Cd		Zn		Cu	
	DI + CO ₂	SW + CO ₂	DI + CO ₂	SW + CO ₂	DI + CO ₂	SW + CO ₂
Recovery in 1 h (%)	33	39	42	27	11	18
Recovery in 4 h (%)	44	51	66	42	16	23
Recovery in 24 h (%)	61	66	124	84	18	25

Note: DI – Deionized water

Table 3.12 Recovery of used slag with nitric acid

Items	Cd		Zn		Cu	
	5% HNO ₃	10% HNO ₃	5% HNO ₃	10% HNO ₃	5% HNO ₃	10% HNO ₃
Recovery in 24 h (%)	50 ± 31	65 ± 28	63 ± 40	54 ± 26	85 ± 47	60 ± 5

3.6 Column test

The column tests were conducted to determine the removal efficiency of suspended solids and metallic ions by slag which is used as filtrate in the glass column. Stormwater samples from residential and commercial areas were collected and tested as analyte in this study. Also the column tests which used synthetic stormwater samples as filtrate were carried out to determine the removal efficiency of SS, Cd²⁺, Zn²⁺ and Cu²⁺ which were adjusted to higher level (Cd²⁺ and Zn²⁺) or similar to actual stormwater sample (SS and Cu²⁺).

3.6.1 Stormwater sample analysis

The concentrations of suspended solids and metallic ions in the stormwater samples are as follows:

Table 3.13 Characteristics of the stormwater samples

Items	SS (mg/kg)	Cd ²⁺ (μg L ⁻¹)		Non- digestion	Zn ²⁺ (μg L ⁻¹)		non- digestion	Cu ²⁺ (μg L ⁻¹)		Non- digestion
		Digested			Digested			Digested		
		Cs	Cx		Cs	Cx		Cs	Cx	
Oakley Creek Site 1	4.98	0	1	0	61	99	53	0	4	0
		1			160			4		
Oakley Creek Site 2	79.01	0	2	0	142	172	154	0	42	32
		2			314			42		
Hobson St.	431.81	0	0	0	193	689	386	0	134	67
		0			882			134		

Note: Cs = soluble ions in the solution

Cx = extractable ions attached to suspended solids

3.6.2 Effect of nitric acid digestion

The suspended solids, either organic or inorganic, in the sample may adsorb part of the metallic ions (McFarlane *et al.*, 2005). For the tested elements (Cd^{2+} , Cu^{2+} and Zn^{2+}) there are few significant chemical interference effects for environmental samples in the air-acetylene flame (Haswell, 1991). The physical characteristics of the samples are different from those of standards in terms of the surface tension and viscosity. The solids exist in the droplets of the sample after nebulization and may cause physical interferences (Lajunen, 1992). Also the elements attached to the solids may not be atomized in the flame of AAS due to the low temperature (2450 K) and short residence time. Therefore it is accurate to digest the sample to obtain the actual concentration of the elements in the samples. The filtrate of the column test was analyzed with and without nitric acid digestion. The comparisons of the results are as follows:

Table 3.14 Efficiency of nitric acid digestion

Items		Stormwater	Control column		Coarse slag		Medium slag		Fine slag	
			C.	η	C.	η	C.	η	C.	η
pH		7.00	7.30		7.31		7.37		7.46	
Cd ²⁺	N/D	0.000	0.000	/	0.000	/	0.000	/	0.000	/
	DGT	0.000	0.000	/	0.000	/	0.000	/	0.000	/
Zn ²⁺	N/D	0.386	0.346	10.29	0.267	30.88	0.182	52.94	0.125	67.65
	DGT	0.882	0.681	22.74	0.341	61.37	0.346	60.73	0.204	76.82
Cu ²⁺	N/D	0.067	0.067	0.00	0.067	0.00	0.067	0.00	0.034	50.00
	DGT	0.134	0.134	0.00	0.067	49.95	0.067	49.95	0.000	100.00

Note: C = concentration of the elements (mg L⁻¹)

η = removal efficiency (%)

N/D = non-digestion

DGT = nitric acid digested

3.6.3 Removal efficiency of metallic ions in column test

Although there are differences between the analysis with and without digestion of the filtrate, the analysis of the sample was conducted without digestion for the following considerations:

- ♦ There is insufficient space in the muffle furnace in the lab to process that much analyte (16 samples in one batch);
- ♦ The removal efficiency obtained from the digestion analysis are in consistent with those without digestion, i.e. the finer the slag, the smaller the difference in removal efficiency.

The removal efficiency of each stormwater sample in the column experiments are presented in the following tables. The interpretation of the results are given in Section 4.3.

Table 3.15 Metal ion removal efficiency by slag

(fine size 0.6 ~ 1.0 mm)

Items		Removal efficiency (%)		
		Cd^{2+}	Zn^{2+}	Cu^{2+}
Oakley Creek Site 1 (3.9cm/min)	1 st h	—	77.78	—
	2 nd h	—	77.78	—
	3 rd h	—	77.78	—
	4 th h	—	77.78	—
	Average	—	78	—
Oakley Creek Site 2 (3.9cm/min)	1 st h	—	84.62	100.00
	2 nd h	—	76.92	100.00
	3 rd h	—	76.92	100.00
	4 th h	—	76.92	100.00
	Average	—	79 ± 6	100.00
Oakley Creek Site 2 (8.9cm/min)	1 st h	—	65.38	100.00
	2 nd h	—	76.92	100.00
	3 rd h	—	76.92	100.00
	4 th h	—	73.08	100.00
	Average	—	73 ± 9	100.00
Hobson St. (2.0cm/min)	1 st h	—	76.47	100.00
	2 nd h	—	66.18	50.00
	3 rd h	—	64.71	100.00
	4 th h	—	72.06	100.00
	Average	—	70 ± 9	88 ± 40
Hobson St. (3.9cm/min)	1 st h	—	67.65	100.00
	2 nd h	—	55.88	100.00
	3 rd h	—	45.59	0.00
	4 th h	—	45.59	50.00
	Average	—	54 ± 17	/

Note: “—” = amount too small to be determined by this technique

Table 3.16 Metal ion removal efficiency by slag

(medium size 1.0 ~ 2.0 mm)

Items		Removal efficiency (%)		
		Cd^{2+}	Zn^{2+}	Cu^{2+}
Oakley Creek Site 1 (3.9cm/min)	1 st h	—	77.78	—
	2 nd h	—	100	—
	3 rd h	—	88.89	—
	4 th h	—	88.89	—
	Average	—	89 ± 14	—
Oakley Creek Site 2 (3.9cm/min)	1 st h	—	76.92	100.00
	2 nd h	—	65.38	100.00
	3 rd h	—	73.08	100.00
	4 th h	—	73.08	100.00
	Average	—	72 ± 8	100.00
Oakley Creek Site 2 (8.9cm/min)	1 st h	—	50.00	100.00
	2 nd h	—	46.15	100.00
	3 rd h	—	53.85	100.00
	4 th h	—	50.00	100.00
	Average	—	50 ± 5	100.00
Hobson St. (2.0cm/min)	1 st h	—	64.71	100.00
	2 nd h	—	55.88	50.00
	3 rd h	—	48.53	50.00
	4 th h	—	55.88	100.00
	Average	—	56 ± 11	75 ± 46
Hobson St. (3.9cm/min)	1 st h	—	52.94	0.00
	2 nd h	—	48.53	100.00
	3 rd h	—	42.65	0.00
	4 th h	—	30.88	100.00
	Average	—	44 ± 15	/

Table 3.17 Metal ion removal efficiency by slag

(coarse size 2.0 ~ 3.35 mm)

Items		Removal efficiency (%)		
		Cd^{2+}	Zn^{2+}	Cu^{2+}
Oakley Creek Site 1 (3.9cm/min)	1 st h	—	33.33	—
	2 nd h	—	55.56	—
	3 rd h	—	66.67	—
	4 th h	—	66.67	—
	Average	—	56 ± 25	—
Oakley Creek Site 2 (3.9cm/min)	1 st h	—	73.08	0.00
	2 nd h	—	61.54	0.00
	3 rd h	—	69.23	0.00
	4 th h	—	61.54	0.00
	Average	—	66 ± 9	0.00
Oakley Creek Site 2 (8.9cm/min)	1 st h	—	23.08	100.00
	2 nd h	—	38.46	100.00
	3 rd h	—	30.77	100.00
	4 th h	—	34.62	100.00
	Average	—	32 ± 10	100.00
Hobson St. (2.0cm/min)	1 st h	—	35.29	50.00
	2 nd h	—	35.29	50.00
	3 rd h	—	36.76	50.00
	4 th h	—	35.29	50.00
	Average	—	36 ± 1	50.00
Hobson St. (3.9cm/min)	1 st h	—	30.88	0.00
	2 nd h	—	35.29	50.00
	3 rd h	—	29.41	50.00
	4 th h	—	14.71	0.00
	Average	—	28 ± 14	/

Table 3.18 Results of the control lane in the column test

Items		Removal efficiency (%)		
		Cd^{2+}	Zn^{2+}	Cu^{2+}
Oakley Creek Site 1 (3.9cm/min)	1 st h	—	33.33	—
	2 nd h	—	0	—
	3 rd h	—	44.44	—
	4 th h	—	44.44	—
	Average	—	31 ± 33	—
Oakley Creek Site 2 (3.9cm/min)	1 st h	—	30.77	0.00
	2 nd h	—	50.00	0.00
	3 rd h	—	50.00	0.00
	4 th h	—	46.15	0.00
	Average	—	44 ± 15	0.00
Oakley Creek Site 2 (8.9cm/min)	1 st h	—	19.23	50.00
	2 nd h	—	15.38	100.00
	3 rd h	—	26.92	50.00
	4 th h	—	23.08	100.00
	Average	—	21 ± 8	75 ± 46
Hobson St. (2.0cm/min)	1 st h	—	10.29	50.00
	2 nd h	—	11.76	50.00
	3 rd h	—	8.82	50.00
	4 th h	—	20.59	50.00
	Average	—	13 ± 8	50.00
Hobson St. (3.9cm/min)	1 st h	—	10.29	0.00
	2 nd h	—	14.71	50.00
	3 rd h	—	17.65	0.00
	4 th h	—	10.29	50.00
	Average	—	13 ± 6	/

3.6.4 Column test results with synthetic stormwater samples

The synthetic stormwater sample was prepared from clay and metal solutions. The negatively charged surface structure of natural clay is usually compensated for by exchangeable cations, such as Na^+ and Ca^{2+} (Pushpaletha *et al.*, 2005). The ion exchange may occur once the clay is exposed to the solution containing metallic ions, such as Cu^{2+} , Cd^{2+} and Zn^{2+} . The chemical analysis of the samples is shown in Table 3.19.

Table 3.19 Chemical analysis of synthetic stormwater samples

Sample		A	B	C
1	Cd^{2+}	0.095	0.079	0.024
	Zn^{2+}	0.322	0.290	0.076
	Cu^{2+}	0.164	0.143	0.041
2	Cd^{2+}	0.076	0.061	0.015
	Zn^{2+}	0.623	0.508	0.142
	Cu^{2+}	0.122	0.082	0.020
3	Cd^{2+}	0.122	0.081	0.041
	Zn^{2+}	0.859	0.690	0.252
	Cu^{2+}	0.141	0.070	0.018

Note: A = Metallic ions concentration of the original solution which is used to prepare the samples (mg L^{-1});

B = Metallic ions concentration of the prepared samples tested directly by AA (mg L^{-1});

C = Soluble metallic ions concentration in the samples filtrated by filter paper (Whatman, No. 42) (mg L^{-1})

The nominal concentrations of all the elements in synthetic samples are lower than 1 mg L^{-1} . The limited ability of the AAS to measure the sample with low concentration results in a significant error. A set of samples with different known level of metallic ions and 400 mg/kg SS were prepared. The concentrations of each element were measured directly by AAS. The results are shown in Table 3.20.

Table 3.20 Measurement errors of the AAS

Element	Nominal concentration (mg L ⁻¹)	Sample without clay			Sample with clay		
		Measured Conc. (mg L ⁻¹)		Standard deviation (mg L ⁻¹)	Measured Conc. (mg L ⁻¹)		Standard deviation (mg L ⁻¹)
		Average	Range		Average	Range	
Cd	0.1	0.09	0.07~0.11	0.02	0.05	0.04~0.08	0.02
	0.2	0.19	0.17~0.21	0.02	0.12	0.11~0.14	0.02
	0.5	0.54	0.52~0.57	0.02	0.42	0.40~0.45	0.03
	1.0	1.00	0.97~1.03	0.03	0.81	0.80~0.82	0.01
	2.0	2.00	1.96~2.03	0.04	1.72	1.69~1.75	0.03
	5.0	4.78	4.73~4.82	0.05	4.34	4.29~4.39	0.05
Zn	0.1	0.09	0.07~0.11	0.02	0.08	0.07~0.10	0.01
	0.2	0.19	0.17~0.21	0.02	0.16	0.15~0.18	0.01
	0.5	0.53	0.51~0.55	0.02	0.46	0.45~0.48	0.01
	1.0	1.02	1.01~1.04	0.01	0.87	0.86~0.89	0.01
	2.0	2.01	2.00~2.03	0.01	1.90	1.87~1.92	0.03
	5.0	4.87	4.81~4.93	0.06	4.70	4.64~4.79	0.08
Cu	0.1	0.08	0.02~0.14	0.06	0.06	0.00~0.12	0.06
	0.2	0.16	0.10~0.22	0.06	0.14	0.08~0.20	0.06
	0.5	0.47	0.41~0.53	0.06	0.51	0.45~0.57	0.06
	1.0	1.00	0.93~1.06	0.06	0.93	0.87~1.00	0.06
	2.0	2.01	1.95~2.07	0.06	1.97	1.91~2.03	0.06
	5.0	5.00	4.92~5.08	0.08	4.90	4.82~4.98	0.08

It is shown in the above table that the lower the concentration, the larger the error of the measurements. It is valid to the samples with or without clay. The impact of such error on the conclusion will be further discussed in Chapter 4.

The removal efficiencies of SS and metallic ions from synthetic stormwater samples in the column experiments are presented in the following tables.

Table 3.21 Suspended solids and metal ions removal efficiency by fine slag (0.6-1.0 mm) from synthetic stormwater samples

Items		Removal efficiency (%)			
		SS (%)	Cd (%)	Zn (%)	Cu (%)
Sample 1 (44 ml/h)	1 st h	28.49	80.00	90.41	85.71
	2 nd h	21.39	60.00	87.67	85.71
	3 rd h	21.05	70.00	87.67	100.00
	4 th h	11.98	70.00	80.82	85.71
	Average	21 ± 11	70 ± 13	87 ± 7	89 ± 11
Sample 2 (44 ml/h)	1 st h	37.39	50.00	61.29	75.00
	2 nd h	17.17	50.00	70.97	75.00
	3 rd h	14.97	37.50	59.14	75.00
	4 th h	10.95	50.00	58.07	75.00
	Average	20 ± 19	47 ± 10	62 ± 9	75
Sample 3 (22 ml/h)	1 st h	68.40	90.91	86.99	90.00
	2 nd h	45.28	90.91	85.37	80.00
	3 rd h	42.10	90.91	81.30	60.00
	4 th h	36.82	81.82	82.11	80.00
	Average	48 ± 22	89 ± 7	84 ± 4	78 ± 20
Sample 3 (44 ml/h)	1 st h	36.85	90.00	73.81	100.00
	2 nd h	35.02	90.00	73.02	75.00
	3 rd h	19.39	90.00	58.73	75.00
	4 th h	11.29	70.00	46.83	75.00
	Average	26 ± 19	85 ± 16	63 ± 20	81 ± 20
Sample 3 (100 ml/h)	1 st h	20.30	54.55	40.17	90.00
	2 nd h	10.63	54.55	40.17	90.00
	3 rd h	7.90	45.45	29.91	70.00
	4 th h	8.65	36.36	28.21	70.00
	Average	12 ± 9	48 ± 12	35 ± 10	80 ± 18

Table 3.22 Suspended solids and metal ions removal efficiency by medium slag (1.0-2.0 mm) from synthetic stormwater samples

<i>Items</i>		<i>Removal efficiency (%)</i>			
		<i>SS (%)</i>	<i>Cd (%)</i>	<i>Zn (%)</i>	<i>Cu (%)</i>
Sample 1 (44 ml/h)	1 st h	21.51	60.00	65.75	71.73
	2 nd h	14.97	50.00	60.27	71.73
	3 rd h	23.68	50.00	69.86	85.71
	4 th h	23.96	50.00	58.90	85.71
	Average	21 ± 7	53 ± 8	64 ± 8	79 ± 13
Sample 2 (44 ml/h)	1 st h	23.44	50.00	38.71	75.00
	2 nd h	17.47	12.50	43.01	75.00
	3 rd h	16.17	12.50	36.56	75.00
	4 th h	15.68	12.50	35.48	75.00
	Average	18 ± 6	22 ± 29	38 ± 5	75
Sample 3 (22 ml/h)	1 st h	46.45	54.55	63.41	60.00
	2 nd h	38.27	81.82	63.41	70.00
	3 rd h	35.15	72.73	59.35	60.00
	4 th h	32.16	45.45	55.28	60.00
	Average	38 ± 9	64 ± 26	60 ± 6	63 ± 8
Sample 3 (44 ml/h)	1 st h	31.51	90.00	46.83	75.00
	2 nd h	23.70	80.00	39.68	75.00
	3 rd h	13.01	50.00	31.75	75.00
	4 th h	10.09	60.00	26.98	75.00
	Average	20 ± 15	70 ± 29	36 ± 14	75
Sample 3 (100 ml/h)	1 st h	12.62	27.27	23.08	70.00
	2 nd h	7.22	27.27	23.08	70.00
	3 rd h	5.72	27.27	11.11	60.00
	4 th h	5.00	9.09	14.53	50.00
	Average	8 ± 5	23 ± 14	18 ± 9	63 ± 15

Table 3.23 Suspended solids and metal ions removal efficiency by coarse slag (2.0-3.35 mm) from synthetic stormwater samples

<i>Items</i>		<i>Removal efficiency (%)</i>			
		<i>SS (%)</i>	<i>Cd (%)</i>	<i>Zn (%)</i>	<i>Cu (%)</i>
Sample 1 (44 ml/h)	1 st h	12.90	30.00	38.36	71.43
	2 nd h	24.06	20.00	30.14	85.71
	3 rd h	8.42	20.00	50.68	85.71
	4 th h	15.63	20.00	36.99	85.71
	Average	15 ± 10	23 ± 8	39 ± 13	82 ± 11
Sample 2 (44 ml/h)	1 st h	15.73	12.50	22.58	75.00
	2 nd h	17.47	12.50	21.51	75.00
	3 rd h	12.28	0.00	18.28	50.00
	4 th h	10.06	0.00	20.43	50.00
	Average	14 ± 5	6 ± 11	21 ± 3	63 ± 23
Sample 3 (22 ml/h)	1 st h	34.52	45.45	28.46	50.00
	2 nd h	32.78	54.55	35.77	60.00
	3 rd h	33.25	54.55	37.40	50.00
	4 th h	30.26	45.45	30.08	50.00
	Average	33 ± 3	50 ± 8	33 ± 7	53 ± 8
Sample 3 (44 ml/h)	1 st h	22.96	60.00	38.10	75.00
	2 nd h	24.50	70.00	30.95	75.00
	3 rd h	19.52	50.00	24.60	75.00
	4 th h	11.29	50.00	21.43	50.00
	Average	20 ± 9	58 ± 15	29 ± 12	69 ± 20
Sample 3 (100 ml/h)	1 st h	11.66	27.27	7.69	80.00
	2 nd h	11.17	18.18	11.97	80.00
	3 rd h	8.45	9.09	9.40	60.00
	4 th h	1.22	9.09	7.69	40.00
	Average	8 ± 7	16 ± 13	9 ± 3	65 ± 30

Table 3.24 Results of the control lane in the column test with synthetic stormwater samples

Items		Control			
		SS (%)	Cd (%)	Zn (%)	Cu (%)
Sample 1 (44 ml/h)	1 st h	27.42	20.00	19.18	0.00
	2 nd h	21.93	0.00	15.07	14.29
	3 rd h	15.26	0.00	20.55	14.29
	4 th h	7.29	0.00	17.81	42.86
	Average	18 ± 13	/	18 ± 4	/
Sample 2 (44 ml/h)	1 st h	16.91	0.00	8.60	50.00
	2 nd h	16.27	0.00	7.53	25.00
	3 rd h	8.98	0.00	9.68	25.00
	4 th h	12.13	0.00	6.45	0.00
	Average	14 ± 6	0.00	8 ± 2	/
Sample 3 (22 ml/h)	1 st h	30.46	18.18	13.82	0.00
	2 nd h	29.72	27.27	15.45	10.00
	3 rd h	31.73	27.27	13.01	0.00
	4 th h	29.26	0.00	8.13	10.00
	Average	30 ± 2	/	13 ± 5	/
Sample 3 (44 ml/h)	1 st h	14.42	10.00	38.10	75.00
	2 nd h	22.90	10.00	15.87	75.00
	3 rd h	11.16	0.00	5.56	0.00
	4 th h	12.08	0.00	3.17	50.00
	Average	15 ± 8	/	/	/
Sample 3 (100 ml/h)	1 st h	6.45	9.09	4.27	40.00
	2 nd h	7.63	9.09	7.69	30.00
	3 rd h	5.86	0.00	3.42	20.00
	4 th h	6.62	9.09	3.42	20.00
	Average	7 ± 1	/	5 ± 3	/

Chapter 4 Discussion

The results derived from the experiments are discussed in this section in light of existing knowledge and understanding of the issue. The heavy metals removal mechanisms and efficiency by the tested slag are the major concerns of the author as they are the basis for further application of the aggregate in stormwater/wastewater purification practice.

4.1 Metallic ion removal efficiency

4.1.1 Adsorption kinetics

Adsorption is usually composed of two distinct kinetic phases, i.e. a rapid and reversible initial stage followed by a much slower, non-reversible stage (Essington, 2004). The rapid phase usually includes the retention of compounds by easily accessible sites on macro-particles, and on the edges of slag. The slower reaction phase that follows the initial phase generally involves the formation of inner-sphere surface complexes with bonds that have a covalent character.

The batch tests showed that the temporal variations of Zn^{2+} and Cu^{2+} concentration in the working solutions after mixing with the slag were similar, i.e. an initial drop sharply followed by a gentle decreasing slope until becoming stable (Figure 3.1 and 3.2). Cu^{2+} reached equilibrium faster than Zn^{2+} . Also the Cu^{2+} concentration in the solution that reached equilibrium is lower than Zn^{2+} at the same solid/liquid ratio.

The tests on Zn^{2+} adsorption showed that by increasing the mass of slag from 50g/150mL to 100g/150mL (adsorbent/adsorbate ratio), it is possible to shorten the

time to reach equilibrium. Also the removal efficiencies were increased by 70%, 200% and 155% for fine, medium and coarse slag respectively.

The adsorption capacity of adsorbate is proportional to active sites on the surface of the aggregate (Oguz, 2004). Throughout these experiments, the removal capacity of slag is in proportion to its grain size. The fine slag had the greatest capacity to remove both Zn^{2+} and Cu^{2+} at any adsorbent/adsorbate ratio. A surface analysis showed that slag had a porous structure (Figure 4.1). Although the surface area of the slag in different sizes was not measured², the finer size of the slag undoubtedly presented a larger surface area and consequently provided more active sites for reaction.

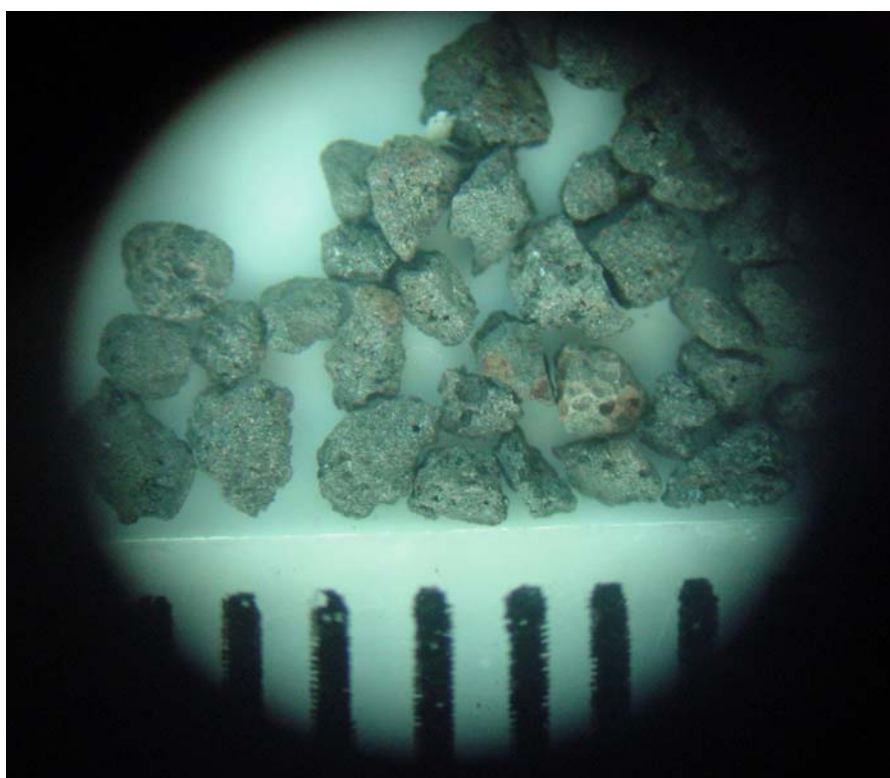


Figure 4.1 Porous structure of the slag (fine) viewed from microscope
(Scale with 1 mm intervals)

² Surface area is determined by gas absorption method. Such facility is not available in AUT chemistry lab

4.1.2 Heavy Metal ion removal mechanism

The leaching tests (New Zealand Steel, 1992) indicated that calcium and silicon were continuously released in water, with a consequent increase of pH of the effluent. The alkaline effect of the slag is a result of the release of hydroxyl ions by components such as gehlenite and $2\text{CaO}\cdot\text{SiO}_2$ (Dimitrova *et al.*, 2000).



The above analysis is supported by the observed parallel increase of pH and Ca^{2+} in the solution (Table 3.7 and Figure 3.11). The extent of the reaction is dependent upon the grain size of the slag and the adsorbent/adsorbate ratio. Thus more OH^- and Ca^{2+} are released when grain size is in the coarse silt/sand range.

The exchange and displacement of the calcium ions in the slag by Cu^{2+} , Zn^{2+} and Cd^{2+} resulted in an increase of Ca^{2+} concentration in the solution and a shift of the above equilibrium to the right due to the binding of OH^- and heavy metal ions to form the complexes (Kang *et al.*, 2004).

One of the concerns of the metallic ions removal by slag is that whether the adsorption effect is simply the reaction of the ions with anions, e.g. to form insoluble hydroxide.

Every dissolved metal ion has a distinct pH at which the optimum hydroxide precipitation will occur (Greenwood and Earnshaw, 1997). The optimum pH for copper and zinc is 8.1 and 10.1 respectively. However the tests on the removal of metallic ions by marble (Table A.13 and 14) showed that:

- The concentration of the tested ions (Zn^{2+} and Cu^{2+}) in working solutions decreased more significantly by mixing with marble than slag in the first 15 minutes.
- The working solutions were shifted from acidic ($\text{pH} \approx 3$) to neutral or alkaline ($\text{pH} = 6.95 \sim 7.11$) instantly by mixing with marble.
- Different grain sizes of marble presented similar removal efficiency (Figure 3.3 and 3.4).
- A definite decrease in metallic ion concentration after filtering the working solution was observed.

From the above observations, it is deduced that chemical reactions, i.e. dissolving CaCO_3 in solution and followed by formulating ionic species (e.g. MCO_3^0 , MHCO_3^+ , M(OH)_n , etc.) with metallic ions, are the major mechanisms for the removal of heavy metals by marble. Hydroxide precipitation may occur under alkaline or even neutral conditions.

However the tests on slag were carried out in acidic solutions (range: 3.1 ~ 5.9), although the pH of the solutions had been increasing throughout the process (Table A.15 and 16). From this it is further deduced that the removal of heavy metals by slag in this instance is not due to metal hydroxide precipitation. This contravenes the conclusions reached by Menzlin (See Page 9).

4.1.3 Competitive adsorption

Adsorption from solution always involves competition between the components of a

liquid mixture for the adsorption sites (Shaw, 1980).

According to the batch tests (Table 3.4) which mixed the slag with each element for adsorption, the adsorption capacity, expressed as the amount of metallic ion removed from the solution by unit mass of slag, differs for each element. It followed the descending order of $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+}$.

When the three tested elements (Cu^{2+} , Zn^{2+} and Cd^{2+}) were mixed in the solution as ions, the Cu^{2+} removal capacity was raised by 51%, 14% and 39% for fine, medium and coarse slag respectively. However both Zn^{2+} and Cd^{2+} adsorption capacities were reduced by 4% ~ 22% and 51% ~ 65% respectively.

The above observations reflect the competitive effect among the elements in the adsorption system. The binding capacity varies among the adsorption sites on the surface of the slag. Competitive effects can be significant even if a small fraction of the surface is occupied, since the sites that are preferentially occupied by one competing adsorbate might be the ones that bind to the other adsorbate most strongly. That is, if there are only a small number of strong binding sites on a solid, a relatively small concentration of strongly competing adsorbates might leave all these sites occupied. In that case, even though there are plenty of sites still available on the surface, the less competitive adsorbate would have to bind to relatively weak sites (Benjamin, 2002).

As shown in section 3.3, Cu^{2+} was a more competitive adsorbate than Zn^{2+} . The stronger binding energy of Cu^{2+} displaced Zn^{2+} and Cd^{2+} through ion-exchange. The higher adsorption capacity of Zn^{2+} as opposed to Cd^{2+} shows that the affinity of the three elements to the slag follows the descending order of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. This assumption accords with the observed elevation of Cu^{2+} adsorption capacity from the multi-ion solutions and the more significant decrease of Cd^{2+} adsorption capacity than Zn^{2+} .

4.1.4 Adsorption isotherm

It has been demonstrated that pH, initial metallic ion concentration, temperature and solid/liquid ratio may have an impact on adsorption efficiency (Ortiz *et al.*, 2001; Ahn *et al.*, 2003; Kang *et al.*, 2004; Dimitrova *et al.*, 1998). In this study the pH, temperature and initial metallic ion concentration were set at 4, 23°C, 20 mg L⁻¹ respectively. The variables included the grain size of the slag and solid/liquid ratio.

The adsorption isotherm describes the equilibrium status of a system. The Freundlich isotherm is summarized under different conditions in Table 3.6. In most instances, the amount of metallic ions removed from the solution by slag at equilibrium increased with the increase of solid/liquid ratio. However, the slopes of the curves ($1/n$) are small, and occasionally even negative. The horizontal lines mean that there is little or no functional dependence between Cq and x/m in these cases. The adsorption capacity, which was measured by metallic ion removal by unit mass of aggregate, decreased as the ratio rose.

Figures 3.5 and 3.6 present the isotherms of each element adsorbed by different size of slag. Usually the larger A and smaller $1/n$ in the Freundlich isotherm refers to a higher adsorption capacity of an adsorbent (Kang *et al.*, 2004). It is hard to draw any definite conclusion, according to the limited data obtained in the experiments, about the removal capacity of the slag under different conditions.

The correlation coefficient (R^2) of the adsorption isotherms in Table 3.6 showed that the Cu adsorption data fitted the Freundlich model better than Zn and Cd. Also the model fitted the adsorption data for fine slag better than those for coarse slag. The stronger binding energy of the element and the greater adsorption capacity of the aggregate dominated the process and masked the other effects such as pH, temperature and competitive elements etc.

The data were derived from batch tests. However the industrial application will be carried out in a continuous-flow system. That would react differently – initially all the substance will be removed, and then the concentration in the treated water will increase steadily with time until there is no removal. Nevertheless, it does permit the comparison of different isotherms.

The distribution of adsorbate between the solution and the adsorbent particles is determined by a number of factors, such as the competition for surface sites among adsorbates, competition for adsorbate between the surface and dissolved ligands, and electrostatic interactions at the surface. The isotherm of the ions adsorbed from multi-ion solution (Table 3.6) ignored the competitive effect among the ions and was excessively simplified. The multi-site Langmuir model, which assumes that the surface has groups of sites with different affinities for an adsorbate, can be applied to in this case (Benjamin, 2002). However it is out of the study objective and no further discussion will be made hereafter on this issue.

4.2 Desorption of metallic ions from slag

4.2.1 Ion exchange

Potassium chloride, sodium chloride and sodium nitrate were used to test desorption of heavy metals from the slag. The experimental results (Table 3.8) showed that about 40% of Cd^{2+} was released by all the salts in 24 hours. Less than 10% of Zn^{2+} was retrieved into aqueous phase from the slag under the same conditions. The inorganic salt had absolutely no effect on the recovery of Cu^{2+} from contaminated slag.

Over 80% of the recoveries happened in the first 24 hours (out of the 96 hours of experimentation).

Ion exchange is regarded as the key mechanism for inorganic salts to recover the used slag (Qin *et al.*, 2004). As the ion exchange abilities of K^+ and Na^+ are similar, there

is no significant difference of recovery efficiency between the salts. The difference in releasing Cd^{2+} , Zn^{2+} and Cu^{2+} from the slag, from 40% to zero, could be attributed to the different binding energy of the complexes of each element to the aggregate (Arias *et al.*, 2005).

The recovery experiments using nitric acid as a desorption agent (Table 3.11) showed that 50%, 63% and 85% of Cd^{2+} , Zn^{2+} and Cu^{2+} were mobilized from the slag respectively by 5% HNO_3 . H_3O^+ presented in the solution worked as competitive ion exchanger to metallic ions on the slag. The increased concentration of HNO_3 from 5% to 10% did not result in an elevation of recovery efficiency. It means that the H_3O^+ ionic strength in 5% nitric acid is high enough for reaching the equilibrium of the ion exchange reaction.

The variance of the results, indicated by the wide confidence level (95%), made it difficult to determine the order of the recovery efficiency among the three elements. Such variance comes from the non-homogeneous physical structure and chemical composition of the slag and the error of the analysis technology.

4.2.2 Complexes with ligands

Metallic ions can combine with numerous other species to form complexes, either dissolved or solid, in aqueous systems (Benjamin, 2002).

(1) Chloride

The presence of Cd^{2+} , Zn^{2+} and Cu^{2+} with Cl^- in solution formed the soluble metal chloride complexes (Pitcher *et al.*, 2004). As these tests were carried out in an acidic environment, the OH^- complexes of metallic ions can be ignored. The stabilities of each complex at equilibrium are as follows:



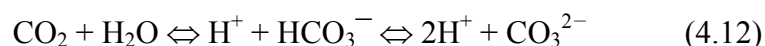


In which K_i – equilibrium constant for a reaction between two dissolved species

The higher the equilibrium constant, the more stable the complex. According to the comparison of the equilibrium constant of the complexes formed by each ion, the stability of the complexes can be ranked as $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. The formulation of more stable complex might reduce the ionic strength of the solution and, as a result, facilitate the release of more metallic ions from solid surface into liquid phase.

(2) Carbonic acid

The carbonic acid in solution was produced by blowing carbon dioxide (Air Liquide, food grade) into desorption agent, either deionized water or sea water.



The results of the desorption tests (Table 3.10) indicated that 66%, 84% and 25% of the bound Cd^{2+} , Zn^{2+} and Cu^{2+} were released by carbonic acid in sea water respectively. As the recovery efficiencies of sea water to each element was 41%, 3%

and 4% respectively, the increased portion of the effect was believed to be due to the carbonic acid.

A number of metallic complexes for each element could be produced in the solution as follows:



In which: β_i – Equilibrium constant for a reaction between an uncomplexed ion and i ligands to form a complex of the type MeL_i .

The higher the equilibrium constant, the more stable the complex. Both competitive adsorption of Na^+ , K^+ , Ca^{2+} and H^+ etc. to displace metallic ions previously adsorbed by slag and the formation of complexes by the mobilized metallic ions with CO_3^{2-} and HCO_3^- contributed to the release of metal ions to aqueous phase.

4.2.3 Chelating

Complexes that contain more than one type of ligand are called mixed-ligand complexes. The anions of low-molecular-weight organic acids have been shown to be

effective in desorbing heavy metals from contaminated soils (Qin *et al.*, 2004; Gao *et al.*, 2003). Citric and tartaric acids, which were presented as background substances in the natural environment, were used here as chelating agents (polydentate ions that form strongly bound ring complexes).

The batch tests (Table 3.8) showed that the desorption efficiencies of Cd^{2+} , Zn^{2+} and Cu^{2+} by citric acid were 46%, 65% and 23% respectively. The presence of K^+ in the citric acid could increase the efficiency to a certain extent. The desorption of Zn^{2+} was even raised to 108%³.

The effects of citric and tartaric acid on the Cd^{2+} and Cu^{2+} desorption were similar, i.e. around 50%, when using sea water as solution. Again the release of Zn^{2+} from slag by tartaric acid reached high levels – in this case, 97% in 24 hours.

Citric acid has strong chelating ability with Cu^{2+} , Cd^{2+} , and Zn^{2+} (Qin *et al.*, 2004; Ottosen *et al.*, 2005). The difference of metallic desorption tendency may be caused by the differences between the complexing ability of citric acid.

It can be concluded that desorption capacity of organic acids can be reinforced with the presence of an inorganic salt. The desorption behaviour of metallic ions was influenced by electrolytes and organic ligands in desorption solution. Desorption of metals can be dominated by the electrolytes K^+ , Na^+ and Ca^{2+} , etc, in sea water, which can release metallic ions from used slag by ionic exchange, at no or low levels of citric or tartaric acids in the solution.

³ Desorption efficiency should be no more than 100% since there is no zinc contained in the original slag sample. Such result could be caused by the error of the measuring method and the low concentration of the analyte.

The increase of organic acids (citric or tartaric) raises the competitive ability of organic ligands in the solution for binding Cd^{2+} , Cu^{2+} and Zn^{2+} , and as a result leads to enhanced desorption capacity of the agent. (Gao *et al.*, 2003).

The assessment of each desorbing agent can also be carried out from the cost perspective⁴.

4.3 Column tests with stormwater sample

Stormwater samples are different from working solutions used in the batch tests in terms of the presence of suspended solids. The surfaces of suspended solids can sometimes acquire an electrical charge, much as dissolved species do. This surface charge can enhance or impede sorption of metallic ions from solution (Benjamin, 2002).

The study on road sediment (Ng, 2004) indicated that the removal of particles over 100 μm would ensure average removal of 75% to 90% of heavy metals and phosphorus in stormwater. However the porous slag, which had been shown to have adsorption capacity to remove metallic ions from solution in the previous experiments, was expected to be used in this study more than as a filter to physically separate solids from solution. The adsorption of soluble metallic ions from the feeding stormwater sample was assumed to be occurred during the process.

4.3.1 Chemical analysis of the stormwater samples

Chemical analysis of the actual stormwater sample was carried out with and without digestion. Dry ashing and nitric acid digestion procedures were applied to evaluate recovery efficiency due to its utility (Hseu, 2004).

⁴ The cost analysis of the desorption tests is presented in Appendix D.

The analysis of the samples (Table 3.12) indicated that the concentrations of each parameter (SS, Cd^{2+} , Zn^{2+} and Cu^{2+}) varied significantly among the sampling sites. Although the Sites 1 and 2 of Oakley Creek were about 300 meters apart, the characteristics of the catchments (well paved residential zone of Site 1 versus mostly unpaved construction field of Site 2) resulted in the elevated levels of all the parameters on Site 2. Hobson Street stands as one of the main accesses to *State Highway 1* from *Auckland CBD*. The further increase of the pollutant concentrations (except for Cd^{2+} which was not detected) in the Hobson St. sample was believed to be contributed by heavy traffic, roof runoff and ambient dust precipitations of the area.

The distribution of metallic ions between the aqueous and solid phase in the samples differs according to the different elements. Cu^{2+} and Cd^{2+} were not detected in the filtrate, i.e. they were mostly attached to suspended solids. Zn^{2+} existed as both soluble and extractable in the samples. The extractable content of Zn^{2+} made up 55~78% of the whole lots in the samples. The wide variance of the mobility was due to the affinity of the element to different targets as well as the nature of samples in terms of the turbidity, carbonates, metallic oxides, organic and inorganic residues (Stead-Dexter *et al.*, 2004).

The comparison of the results with and without digestion of the samples showed that the measurement of the sample directly by AAS without digestion was between the concentration of soluble ions and the total (the sum of soluble and extractable ions). Such differences indicated that most of the mobile ions and a part of the element attached to solid in the samples could be atomized and detected by AAS. The ratios of non-digested concentration over digested (assumed to be the “real” concentration of the sample) of Cd^{2+} , Zn^{2+} and Cu^{2+} were 0%, 33~49% and 0~76% respectively.

The chemical analysis of the synthetic stormwater samples (Table 3.19) indicated that a large proportion of metallic ions (66%~80% of Cd^{2+} , 71%~77% of Zn^{2+} and 75%

~87% of Cu^{2+}) were immobilized by clay. This is the result of the ion exchange as explained in Section 3.6.4.

The measurements of Cd^{2+} , Zn^{2+} and Cu^{2+} in the synthetic stormwater samples by AAS without digestion are 66%~83%, 80%~90% and 50%~87% of the actual concentrations respectively.

Even though the method of direct measuring without digestion could underestimate the metallic ion concentrations, it was applied, as explained in Section 3.6.3, in the column experiments to measure the metallic ions level.

4.3.2 Pollutants removal efficiency in columns

The results of the column experiments were shown in Table 3.14 ~ 3.22.

(1) Cadmium

The amounts of Cd^{2+} in all the samples and the SS and Cu^{2+} in Oakley Creek Site 1 were so low that they could not be determined by the methods in this study.

The concentration of Cd^{2+} in the synthetic stormwater sample was elevated to around $100 \mu\text{g L}^{-1}$.

Different removal efficiencies had been recorded under different conditions. It reached 89% by fine slag at low flow rate. On the contrary, only 16% was removed by coarse slag at high flow rate.

The above analysis could be doubtful considering the large relative error of measuring Cd^{2+} at low concentration (see Table 3.20). The measured concentration of Cd^{2+} is about 50% lower than the actual value when it is as low as $100 \mu\text{g L}^{-1}$. Therefore it is

still hard to draw any definite conclusion on the removal efficiency of Cd^{2+} in the column test with these results.

(2) Copper

The Cu^{2+} removal efficiency by fine and medium slag from Oakley Creek Site 2 sample reached 100% during the 4-hour-cycle at both flow rates (3.9 and 8.9 cm/min). No conclusion could be drawn from other experiments. Erratic removal efficiencies of Cu^{2+} in solution were observed. The very low levels of Cu^{2+} versus the sensitivity of the analysis methods resulted in this uncertainty.

The readings from AAS to measure the Cu^{2+} concentration in Oakley Creek Site 2 and Hobson St. samples were 0.01 and 0.02 absorption unit respectively. These readings convert to concentration of 32 and 67 $\mu\text{g L}^{-1}$ by using the calibration curve. However the fluctuation of the reading was ± 0.03 which means that the actual Cu^{2+} concentrations could be within 0 ~ 160 $\mu\text{g L}^{-1}$ range. The margin of error thus makes drawing any definitive conclusion unwise.

Similarly to the case of Cd^{2+} , the concentration of Cu^{2+} in the synthetic stormwater samples were raised to around 200 $\mu\text{g L}^{-1}$. Although it is safe to say that a portion of Cu^{2+} in the influent could be removed by the slag when passing through the column and the finer aggregate presents likely the better performance than the coarse one, the unambiguous Cu^{2+} removal efficiency by the slag can not be given because of the significant error of the method.

(3) Zinc

Zn^{2+} removal efficiency varied with the size of slag and flow rates of the feeding solution.

The fine slag performed with the highest efficiency to remove zinc at all occasions, followed in sequence by medium and coarse sizes. This is consistent with the results from batch tests.

The tests on Oakley Creek Site 2 and Hobson St. samples were carried out at two flow rates. The slag removed Zn^{2+} more efficiently at the lower rate.

There was no decline of removal efficiency in the 4-hour-cycle except for the test with Hobson St. sample at high flow rate (3.9 cm/min). The high SS content in that sample resulted in the rapid accumulation of residues in the column and blocked the flow path. Pressure was introduced to the column to keep a stable flow rate over the last 2 hours. The effluent became cloudy due to the presumed channelling effect and greater fluid velocity and contained more SS and Zn^{2+} which was attached to the solids.

Similar conclusion can be drawn from the tests with synthetic stormwater sample. The removal efficiency of Zn^{2+} is in reverse proportion to the grain size of the aggregate and the flow rate of the feeding solution, regardless of the initial ionic concentration of the sample.

Zn^{2+} concentrations in the samples are higher ($400 \sim 800 \mu\text{g L}^{-1}$) and AAS is more sensitive to this element, the relative error of measuring Zn is within 10%. Therefore the above conclusions are solid.

(4) Suspended solids

The suspended solids in the sample formed as floc through precipitation or aggregation once the sample was kept stable for a while. The sample was stirred during the test to be homogeneous.

The slag exhibited a similar tendency to remove SS as Zn^{2+} , i.e. the removal efficiency of SS follows inverse proportion to the size of slag as well as the flow rate of the feeding solution. However the removal efficiency of SS is much lower than that of metallic ions. It is assumed that the very small particle size of the suspended solids in the samples results in the low removal efficiency. The removal effect of the aggregate on the actual stormwater runoff, which contains more large particles, would be elevated.

(5) Removal mechanism

A certain portion of metallic ions were associated with the suspended solids. Therefore the removal of suspended solids, as a result of precipitation, led to the removal of metallic ions attached to them.

The amount of Zn^{2+} removed by SS precipitation was significantly lower than the total removal of each element. Thus it is concluded that the remainder of the ions removal was a result of adhesion to the slag.

(6) Control column

A control column, which was blank and used as a quality control measure, was set for each test. The U-shape design of the column and slow flow rate resulted in precipitation of residues at the bottom of the column (as shown in Figure 2.5). The SS removal efficiencies in the control column were around 30%. Unlike the columns filled with slag, the removal efficiency of Cd^{2+} , Zn^{2+} and Cu^{2+} is usually lower than or similar to that of SS in the control column. This reinforces the above proposal that the removal mechanisms for slag were both precipitation and adsorption (Pitcher, 2004).

4.3.3 Perspective of the application

In New Zealand there is no standard for heavy metals in stormwater runoff. The following standards, either for drinking water quality or receiving water bodies, are quoted here as reference.

Table 4.1 Water Quality Standards (unit: mg L^{-1})

<i>Standards</i>	<i>Cadmium</i>	<i>Copper</i>	<i>Zinc</i>
Drinking Water Standard (NZ) MAVs	0.003	2.0	N/A
Drinking Water Standard (US) (MCLs)	0.005	1.3	N/A
National Secondary Drinking Water Regulations (US) (MCLs)	N/A	1.0	5.0
Universal Treatment Standard (US)	0.69	N/A	2.61
Surface Water Standard (CN)	0.005	1.0	2.0

In which: MAVs - Maximum Acceptable Values

MCLs - Maximum Contaminant Levels. The highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards

The concentration of Zn^{2+} in the Hobson St. sample can be reduced from 0.4 mg L^{-1} to $0.1 \sim 0.2 \text{ mg L}^{-1}$ after passing through the slag column. It is hard to decide the efficiency of cadmium and copper removal from stormwater by the slag due to the very low level of these elements in the samples. However the tests using synthetic stormwater samples and the results of the batch tests would likely support the deduction that the slag will have similar (Cd^{2+}) or even better (Cu^{2+}) effect on removing these elements.

The concentration of tested heavy metals in the effluent is lower than the above standards. It makes the melter slag an attractive material to process stormwater runoff.

However attention needs to be paid to the disposal of the used slag. The metallic ions adsorbed by the aggregate can be mobilized by a variety of agents. Therefore the inappropriate disposal may cause a serious problem because of the elevated level of contaminants attached to the used slag.

Chapter 5 Conclusions

1. The melter slag tested in this study is a rather porous material. Previous leaching trials (New Zealand Steel, 1992) indicated that the heavy metals were bound in the aggregate and the mobilization of these elements into aqueous phase can be ignored, especially when it is mixed with neutral or basic solution.
2. Copper, zinc and cadmium were selected in this study for testing. The batch tests showed that the melter slag had the ability to remove these elements from working solutions. The removal efficiency of each ion by the slag is evaluated by two indices, i.e. the decreasing rate of the ion concentration in solution over time and the amount that it can be removed by unit mass of slag. It follows the descending order of $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+}$.
3. Ion exchange is the dominant mechanism when metallic ions are removed by the slag. The decrease of metallic ions was accompanied by the increase of Ca^{2+} concentration and pH in the working solutions. The finest grain size slag, which had the largest specific surface area, was the most effective in removing heavy metals.
4. Different elements have varied binding energy to the aggregate. Competitive adsorption was observed when the slag was mixed with solutions containing several kinds of metallic ions. The affinity of the three tested elements to the slag follows the descending order of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.
5. Author intended to establish an isotherm model to evaluate the equilibrium status of the treatment system and to compare the capacity of the slag in different sizes to remove different elements from solutions. However only Cu^{2+} adsorption by

the melter slag in fine size obeys the Freundlich isotherm model. It is hard to draw any definite conclusion from the data in other experiments. Further studies are needed on this issue in the future.

6. Used slag which is saturated by heavy metals can be recovered and treated for reuse. Desorption of ions from the slag may be achieved by applying inorganic salts (ion exchange), inorganic acids (metallic complexes) and organic acids (chelating). A mixture of inorganic salt and organic acid present the best solution for desorption of heavy metals from slag, e.g. citric acid in sea water can mobilize about 50% of each metallic ion in 24 hours. However tartaric acid has a different effect on each ion. The slag contaminated by Zn^{2+} could almost be completely recovered by tartaric acid in sea water or KCl solution. Tartaric acid and citric acid have similar effect on the desorption of Cd^{2+} and Cu^{2+} (around 50% in 24 hours).

7. The slag can be reused after saturation, given that it is recoverable by a range of desorbing agents. A mixture of citric acid and sea water is recommended considering the best desorption efficiency and the lowest costs.

8. Relatively high levels of Zn^{2+} were found in all the stormwater samples. The SS and Cu^{2+} varied significantly among different samples. Cd^{2+} was present only at trace levels, i.e. 1 or 2 $\mu\text{g L}^{-1}$. A large portion of Zn^{2+} (55 ~ 78%) was attached to suspended solids. All the Cu^{2+} present was extracted in the samples, i.e. Cu^{2+} is firmly bound with organic and/or inorganic suspended solids. The affinity of metallic ions to suspended solids ensures that the removal of solids from stormwater runoff can result in a reduction of metallic ions in the effluent.

9. The melter slag effectively removes pollutants, i.e. suspended solids and heavy metals, from stormwater samples based on the mechanisms of physical filtration and chemical adsorption.

10. The pollutant removal efficiency of the slag column is in inverse proportion to the grain size of the melter slag and the influent flow rate.

The melter slag has the potential to act as an adsorbent to process stormwater runoff. Its capacity for removing suspended solids and heavy metals significantly assist meeting targets for water purification standards.

References

- Adams, B. J., Papa, F. (2000) *Urban Stormwater Management Planning with Analytical Probabilistic Models*. New York, John Wiley & Sons, Inc., p. 358.
- Ahn, J.S.; Chon, C.M.; Moon, H.S.; Kim, K.W. (2003) Arsenic removal using steel manufacturing by-products as permeable reactive materials in mine tailing containment systems. *Water Research* 37: 2478-2488.
- Arias, M.; Perez-Novo, C.; Osorio, F.; Lopez, E.; Soto, B. (2005) Adsorption and desorption of copper and zinc in the surface layer of acid soils. *Journal of Colloid and Interface Science* 288: 21–29.
- Asaf, L.; Nativ, R.; Shain, D.; Hassan, M.; Geyer, S. (2004) Controls on the chemical and isotopic compositions of urban stormwater in a semiarid zone. *Journal of Hydrology* 294: 270–293.
- Auckland City Council (2002) *On-site stormwater management manual*, Auckland, p. 119.
- Auckland City Council (2005) *Solving stormwater problems*, Available online: <http://www.aucklandcity.govt.nz/council/services/stormwater/problems.asp#top> [3/3/2005]
- Auckland Healthcare Services Ltd. (2000) *Environmental Health Risks and Needs in the Auckland Region*, Auckland
- Auckland Regional Council (2004) *Blueprint for monitoring urban receiving environments*, Technical Publication No. 168 revised edition, Auckland, p.66.
- Auckland Regional Council Stormwater Liaison Group (1998) *Auckland Region Urban Stormwater Management Project*, Auckland, p. 51.
- Benjamin, M. M. (2002) *Water Chemistry*. New York, McGraw-Hill, p. 668.
- Binnie, C., Kimber, M.; Smethurst, G. (2002) *Basic Water Treatment*. Cambridge, Thomas Telford Limited, p. 291.
- Bramming, M.; Wikstram, J.O. (2002) A blast furnace view on slags. *Scandinavian Journal of Metallurgy* 31: 88–99.

- Cameron, K.; Madramootoo, C.; Crolla, A.; Kinsley, C. (2003) Pollutant removal from municipal sewage lagoon effluents with a free-surface wetland. *Water Research* 37: 2803–2812.
- Clair, C., Ed. (1964) *The things we need and where they come from: iron & steel*. Watford, Bruce & Gawthorn Ltd, p. 64.
- Davies, D.J.; Oelmann, L.A. (1985) *Metallurgical processes and production technology*. London, Pitman Publishing Ltd, p. 230.
- Dennis, W. H. (1963) *Metallurgy of the ferrous metals*. London, Sir Isaac Pitman & Sons Ltd, p. 393.
- Dimitrova, S. V. (2002) Use of granular slag columns for lead removal. *Water Research* 36: 4001-4008.
- Dimitrova, S. V.; Mehanjiev, D. R. (1998) Lead removal from aqueous solutions by granulated blast-furnace slag. *Water Research* 32(11): 3289-3292.
- Dimitrova, S. V.; Mehanjiev, D. R. (2000) Interaction of blast-furnace slag with heavy metal ions in water solutions. *Water Research* 34(6): 1957-1961.
- Eaton, A.D.; Clesceri, L.S.; Greenberg, A.E. Ed. (1995) *Standard methods for the examination of water and wastewater*. Washington, DC, American Public Health Association.
- Emi, T.; Seetharaman, S. (2000) Future steelmaking plant with minimized energy consumption and waste evolution. *Scandinavian Journal of Metallurgy* 29: 185–193.
- Essington, M. E. (2004). *Soil and water chemistry: an integrative approach*. Boca Raton, CRC Press, p. 534.
- Feng, D.; van Deventer, J.S.J.; Aldrich, C. (2004) Removal of pollutants from acid mine wastewater using metallurgical by-product slags. *Separation and Purification Technology*.
- Feng, M.H.; Shan, X.Q.; Zhang, S.Z.; Wen, B. (2005) A comparison of the rhizosphere-based method with DTPA, EDTA, CaCl_2 , and NaNO_3 extraction methods for prediction of bioavailability of metals in soil to barley. *Environmental Pollution* 137: 231-240.

- Gao, Y.Z.; He, J.Z.; Ling, W.T.; Hu, H.Q.; Liu, F. (2003) Effects of organic acids on copper and cadmium desorption from contaminated soils. *Environment International* 29: 613-618.
- Greenwood, N.N.; Earnshaw, A. (1997) *Chemistry of the Elements*. Oxford, Butterworth-Heinemann, p. 1341.
- Gribbin, J. E. (1997) *Introduction to Hydraulics and Hydrology with Application for Stormwater Management*. New York, Thomson Learning, p. 484.
- Gupta, V.K.; Ali, I.; Suhas; Mohan D. (2003) Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *Journal of Colloid and Interface Science* 265: 257-264.
- Haswell, S.J. (1991) *Atomic absorption spectrometry: theory, design and applications*. Amsterdam, Elsevier Science Publishers B.V, p.529.
- Henze, M.; Harremoës, P.; Jansen, J.I.C.; Arvin, E. (2001) *Wastewater treatment : biological and chemical processes*. New York, Springer, p. 430.
- Hseu, Z. Y. (2004) Evaluating heavy metal contents in nine composts using four digestion methods. *Bioresource Technology* 95: 53–59.
- Jeon, C.; Yoo, Y.J.; Hoell, W.H. (2005) Environmental effects and desorption characteristics on heavy metal removal using carboxylated alginic acid. *Bioresource Technology* 96: 15–19.
- Kang, H.J.; An, K.G.; Kim, D.S. (2004) Utilization of Steel Slag as an Adsorbent of Ionic Lead in Wastewater. *Journal of Environmental Science and Health A39*(11–12): 3015–3028.
- Kingett Mitchell Limited (2003) *A study of roof runoff quality in Auckland New Zealand implications for stormwater management*, Auckland, p. 133.
- Kingsley, D. (2005) *Perth water crisis looms*, ABC Online, Available online: http://www.abc.net.au/science/news/enviro/EnviroRepublish_659064.htm [4/3/2005]
- Knepper, T. P. (2003) Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment. *Trends in Analytical Chemistry* 22(10): 708-724.
- Konduru, R.; Ramakrishna; Viraraghavan, T. (1997) Dye removal using low cost adsorbents. *Water Science and Technology* 36(2-3): 189-196.

- Kozanoglou C.; Catsiki V. A. (1997) Impact of products of a ferronickel smelting plant to the marine benthic life. *Chemosphere* 34(12): 2673-2682.
- Lajunen L.H.J. (1992) *Spectrochemical analysis by atomic absorption and emission*. Cambridge, The Royal Society of Chemistry, p.241.
- Lee, J.H.; Bang, K.W.; Ketchum, L.H.; Choe, J.S.; Yu, M.J. (2002) First flush analysis of urban storm runoff. *The Science of the Total Environment* 293: 163–175.
- Mara, D., Horan, N., Ed. (2003) *The Handbook of Water and Wastewater Microbiology*. Surface waters. San Diego, Academic Press, p. 819.
- McFarlane, A.; Bremmell, K.; Addai-Mensah, J. (2005) Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interactions optimization. *Journal of Colloid and Interface Science* 293: 116-127.
- Menzlin D. (2005) Investigation into the use of steel industry slag aggregate to assist the removal of zinc from stormwater. *Unpublished practicum report*. Auckland, Auckland University of Technology.
- Nathanson, J. A. (2000) *Basic Environmental Technology*. Upper Saddle River, Prentice-Hall, Inc, p. 513.
- New Zealand Steel (1992) *Results of Leaching Trials Conducted on Melter Slag*, Auckland
- Ng, W. H. W. (2004) Identification, transport and treatment of adhered deleterious substances of stormwater in an urban catchment. *Earth & Oceanic Sciences Research Institute*. Auckland, AUT: 142.
- Ng, W.H.W.; Buckeridge, J. (2000) *Review of systems utilized in the Auckland region to contain silt generated in current land development process*. Proceedings of the 7th annual New Zealand Engineering and Technology Postgraduate Conference, Palmerston North, pp 383-389.
- Ng, W.H.W.; Buckeridge, J. (2002) *Heavy metal contamination from stormwater-born sediments: A New Zealand Case Study*. Proceedings of the 2nd World Engineering Congress. Malaysia, pp 79-82.
- Oguz, E. (2005) Thermodynamic and kinetic investigations of PO_4^{3+} adsorption on blast furnace slag. *Journal of Colloid and Interface Science* 281: 62-67.

- Ortiz, N.; Pires, M.A.F.; Bressiani, J.C. (2001) Use of steel converter slag as nickel adsorber to wastewater treatment. *Waste Management* 21: 631-635.
- Ottosen, L.M; Pedersen, A.J.; Ribeiro, A.B.; Hansen, H.K. (2005) Case study on the strategy and application of enhancement solutions to improve remediation of soils contaminated with Cu, Pb and Zn by means of electrodialysis. *Engineering Geology* 77: 317–329.
- Pan, S.C.; Lin, C.C.; Tseng, D.H. (2003) Reusing sewage sludge ash as adsorbent for copper removal from wastewater. *Resources, Conservation and Recycling* 39: 79-90.
- Pitcher, S.K.; Slade, R.C.T.; Ward, N.I. (2004) Heavy metal removal from motorway stormwater using zeolites. *Science of the Total Environment* 334– 335: 161–166.
- Pushpaletha, P.; Rugmini, S.; Lalithambika, M. (2005) Correlation between surface properties and catalytic activity of clay catalysts. *Applied Clay Science* 30: 141-153.
- Qin, F.; Shan, X.Q.; Wei, B. (2004) Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. *Chemosphere* 57: 253–263.
- Ricou, P.; Hequet, V.; Lecuyer, I.; Cloirec P.Le (1999) *Influence of operating conditions on heavy metal cation removal by fly ash in aqueous solutions*. International Ash Utilization Symposium, University of Kentucky, pp. 6.
- Rouessac, F. Rouessac, A. (2000). *Chemical analysis: modern instrumentation methods and techniques*. Chichester, John Wiley & Sons, Ltd., p. 445.
- Salvato, J.A.; Nemerow, N.; Agardy, F. (2003). *Environmental engineering*. New York, John Wiley & Sons, Ltd.,
- Sansalone, J. J. (1999) Adsorptive infiltration of metals in urban drainage -- media characteristics. *The Science of the Total Environment* 235: 179-188.
- Shaw, D. J. (1980) *Introduction to Colloid and Surface Chemistry*. London, Butterworth,. p. 273.
- Sorme, L., Lagerkvist, R. (2002) Sources of heavy metals in urban wastewater in Stockholm. *The Science of the Total Environment* 298: 131–145.

- Stead-Dexter, K. Ward, N.I. (2004) "Mobility of heavy metals within freshwater sediments affected by motorway stormwater." *Science of the Total Environment* 334– 335: 271–277.
- U.S. Geological Survey (2005) *Commodity Statistics and Information*, Available online: http://minerals.usgs.gov/minerals/pubs/commodity/iron_&_steel_slag/feslamcs05.pdf [12/08/2005]
- USEPA (1993). *Storm water management and technology*. Park Ridge, Noyes Data Corporation, p. 487.
- Vandecasteele, C.; Block C.B. (1993) *Modern methods for trace element determination*. Chichester, John Wiley & Sons Ltd., p. 330.
- Williamson, R. B. Kelly, S. (2003) *Regional Discharges Project: Marine Receiving Environment Status Report 2003*, Technical Publication No. 203, p.57.
- Zanders, J. M. (2005) Road sediment: characterization and implications for the performance of vegetated strips for treating road run-off. *Science of the Total Environment* 339: 41– 47.

Abbreviations

<i>AAS</i>	Atomic Absorption Spectrometer
<i>ACC</i>	Auckland City Council
<i>ARC</i>	Auckland Regional Council
C_q	Concentration of material remaining in solution once equilibrium has been reached
<i>ERC</i>	Environmental Response Criteria
<i>ICP-AES</i>	Inductively Coupled Plasma – Atomic Emission Spectrometer
m	Weight of adsorbent
R^2	Correlation coefficient
<i>SS</i>	Suspended Solid
x	Weight of metallic ion adsorbed by aggregate
<i>USEPA</i>	United States Environmental Protection Agency

Glossary

Adsorption: Accumulation of a substance at or near an interface relative to its concentration in the bulk solution.

Apparent adsorption isotherm: The amount of solute adsorbed at a given temperature per unit mass of adsorbent is plotted against the equilibrium concentration.

Complex: An ion formed by an ion combining with an atom or molecule.

Control experiment: An experiment that isolates the effect of one variable on a system by holding constant all variables but the one under observation.

Desorption: The reverse process of adsorption, i.e., it is the release of an adsorbed substance to the bulk solution.

Heavy metal: Metallic elements with high atomic weights, e.g., mercury, chromium, cadmium, arsenic, and lead. They can damage living things at low concentration and tend to accumulate in the food chain.

First flush: The initial period of stormwater runoff during which the concentration of pollutants is substantially higher than during later periods.

Slag: A by-product of smelting process. Slag is a glassy, sand-like material containing small amounts of lead, zinc, copper and other materials.

Stock standard solution: A solution of known concentration for use in volumetric analysis.

Working solution: A synthetic solution prepared with certain amount of metallic ion or mixture of different ions. It is used as adsorbate in the batch tests of this study.

Appendix A

Adsorption Batch Tests Results

Table A.1 Cadmium adsorption by slag (fine size)

Time (h)	Dup.	Items	A			B			C		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.07	19.16	0.15	4.07	19.16	0.15	4.07	19.16	0.15
24	1	C (mg L ⁻¹)	6.19	17.78	0.59	6.28	16.32	1.25	6.45	15.64	1.60
		m (g)	1.0026			2.0047			3.0023		
		x/m (mg/g)	0.22			0.22			0.18		
	2	C (mg L ⁻¹)	6.25	17.67	0.63	6.33	17.22	1.11	6.5	15.87	1.53
		m (g)	1.0033			2.0035			3.0029		
		x/m (mg/g)	0.24			0.15			0.17		
	3	C (mg L ⁻¹)	6.28	18.46	0.73	6.36	17.11	1.22	6.44	14.86	2.08
		m (g)	1.0056			2.0034			3.0088		
		x/m (mg/g)	0.12			0.16			0.22		
Ave.	C (mg L ⁻¹)	6.24	17.97	0.65	6.3233	16.88	1.19	6.46333	15.46	1.74	
	x/m (mg/g)	0.19			0.18			0.19			
Time (h)	Dup.	Items	D			E			Control		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.07	19.16	0.15	4.07	19.16	0.15	4.07	19.16	0.15
24	1	C (mg L ⁻¹)	6.58	14.63	2.26	6.59	12.15	2.81	4.54	19.24	0.03
		m (g)	4.0066			5.0070					
		x/m (mg/g)	0.17			0.21					
	2	C (mg L ⁻¹)	6.55	14.29	2.43	6.52	12.04	2.78			
		m (g)	4.007			5.0029					
		x/m (mg/g)	0.19			0.22					
	3	C (mg L ⁻¹)	6.48	14.18	2.15	6.61	12.83	2.81			
		m (g)	4.0085			5.0059					
		x/m (mg/g)	0.19			0.19					
Ave.	C (mg L ⁻¹)	6.53667	14.37	2.28	6.5733	12.34	2.80				
	x/m (mg/g)	0.18			0.21						

Note: m – mass of slag (adsorbent)
x/m -- mass of metallic ion (adsorbate) taken up by unit slag

Table A.2 Cadmium adsorption by slag (medium size)

Time (h)	Dup.	Items	A			B			C		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.07	23.07	0.00	4.07	23.07	0.00	4.07	23.07	0.00
24	1	C (mg L ⁻¹)	5.53	22.51	0.67	5.77	20.71	1.03	6.11	19.32	1.81
		m (g)	1.0015			2.0023			3.0033		
		x/m (mg/g)	0.08			0.18			0.19		
	2	C (mg L ⁻¹)	5.74	21.82	0.59	5.96	21.40	0.99	6.09	20.01	1.62
		m (g)	1.0033			2.0019			3.0026		
		x/m (mg/g)	0.19			0.12			0.15		
	3	C (mg L ⁻¹)	5.81	21.82	0.71	5.86	20.84	1.10	6.11	20.98	1.70
		m (g)	1.0062			2.0036			3.0054		
		x/m (mg/g)	0.19			0.17			0.10		
	Ave.	C (mg L ⁻¹)	5.69	22.05	0.66	5.86	20.98	1.04	6.10	20.10	1.71
x/m (mg/g)		0.15			0.16			0.15			
Time (h)	Dup.	Element	D			E			Control		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.07	23.07	0.00	4.07	23.07	0.00	4.07	23.07	0.00
24	1	C (mg L ⁻¹)	6.07	18.62	1.85	6.19	17.51	2.60	4.07	23.07	0.04
		m (g)	4.0006			5.0041					
		x/m (mg/g)	0.17			0.17					
	2	C (mg L ⁻¹)	6.15	20.57	1.85	6.19	19.04	2.37			
		m (g)	4.0012			5.0061					
		x/m (mg/g)	0.09			0.12					
	3	C (mg L ⁻¹)	6.29	19.45	2.29	6.18	18.90	2.37			
		m (g)	4.0035			5.0044					
		x/m (mg/g)	0.14			0.13					
	Ave.	C (mg L ⁻¹)	6.17	19.55	2.00	6.19	18.48	2.45			
		x/m (mg/g)	0.13			0.14					

Note: m – mass of slag (adsorbent)
x/m -- mass of metal (adsorbate) taken up by slag

Table A.3 Cadmium adsorption by slag (coarse size)

Time (h)	Dup.	Items	A			B			C		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.03	20.15	0.00	4.03	20.15	0.00	4.03	20.15	0.00
24	1	C (mg L ⁻¹)	5.30	20.15	0.43	5.44	20.40	0.77	5.79	19.00	1.24
		m (g)	1.0011			2.0022			3.0065		
		x/m (mg/g)	0.15			0.06			0.11		
	2	C (mg L ⁻¹)	5.22	20.40	0.43	5.70	19.76	0.67	5.88	19.00	1.05
		m (g)	1.0082			2.0018			3.0092		
		x/m (mg/g)	0.11			0.11			0.11		
	3	C (mg L ⁻¹)	5.09	20.40	0.48	5.70	19.76	0.72	5.78	19.51	1.05
		m (g)	1.0017			2.0080			3.0017		
		x/m (mg/g)	0.11			0.10			0.08		
	Ave.	C (mg L ⁻¹)	5.20	20.32	0.45	5.61	19.98	0.72	5.82	19.17	1.12
x/m (mg/g)		0.13			0.09			0.10			
Time (h)	Dup.	Element	D			E			Control		
			pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺	pH	Cd ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.03	20.15	0.00	4.03	20.15	0.00	4.03	20.15	0.00
24	1	C (mg L ⁻¹)	5.89	19.64	1.29	6.05	18.62	1.68	4.06	21.17	0.05
		m (g)	4.0018			5.0064					
		x/m (mg/g)	0.06			0.08					
	2	C (mg L ⁻¹)	5.98	19.76	1.29	5.97	18.62	1.68			
		m (g)	4.0073			5.0029					
		x/m (mg/g)	0.05			0.08					
	3	C (mg L ⁻¹)	5.89	19.00	1.29	6.03	18.87	1.63			
		m (g)	4.0012			5.0006					
		x/m (mg/g)	0.08			0.07					
	Ave.	C (mg L ⁻¹)	5.92	19.47	1.29	6.02	18.70	1.66			
x/m (mg/g)		0.06			0.07						

Note: m – mass of slag (adsorbent)
x/m -- mass of metal (adsorbate) taken up by slag

Table A.4 Zinc adsorption by slag (fine size)

Time (h)	Dup.	Items	A			B			C		
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.13	21.68	0.00	4.13	21.68	0.00	4.13	21.68	0.00
24	1	C (mg L ⁻¹)	5.84	19.86	0.91	5.92	18.44	1.37	6.17	16.85	1.78
		m (g)	1.0029			2.0027			3.0005		
		x/m (mg/g)	0.37			0.29			0.27		
	2	C (mg L ⁻¹)	5.81	20.39	0.76	5.97	18.97	1.23	6.14	17.55	1.99
		m (g)	1.0039			2.0042			3.0009		
		x/m (mg/g)	0.29			0.25			0.24		
	3	C (mg L ⁻¹)	5.82	19.33	0.61	5.98	18.44	1.14	6.12	16.49	1.72
		m (g)	1.0026			2.0034			3.0018		
		x/m (mg/g)	0.45			0.29			0.29		
	Ave.	C (mg L ⁻¹)	5.82	19.86	0.76	5.96	18.62	1.25	6.14	16.96	1.83
x/m (mg/g)		0.37			0.28			0.27			
Time (h)	Dup.	Element	D			E			Control		
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.13	21.68	0.00	4.13	21.68	0.00	4.13	21.68	0.00
24	1	C (mg L ⁻¹)	6.24	15.25	2.34	6.27	12.77	3.22	4.26	22.34	0.06
		m (g)	4.0008			5.0053					
		x/m (mg/g)	0.27			0.29					
	2	C (mg L ⁻¹)	6.23	15.96	2.28	6.27	13.30	2.63			
		m (g)	4.0017			5.0044					
		x/m (mg/g)	0.21			0.25					
	3	C (mg L ⁻¹)	6.20	15.78	2.10	6.29		14.54			
		m (g)	4.0025			5.0025					
		x/m (mg/g)	0.25			0.23					
	Ave.	C (mg L ⁻¹)	6.22	15.66	2.24	6.28	13.54	3.07			
x/m (mg/g)		0.24			0.26						

Note: m – mass of slag (adsorbent)
x/m -- mass of metal (adsorbate) taken up by slag

Table A.5 Zinc adsorption by slag (medium size)

Time (h)	Dup.	Items	A			B			C		
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.06	20.57	0.09	4.06	20.57	0.09	4.06	20.57	0.09
24	1	C (mg L ⁻¹)	5.53	19.17	0.67	5.83	19.36	1.13	5.92	18.81	1.53
		m (g)	1.0073			2.0024			3.0029		
		x/m (mg/g)	0.30			0.14			0.12		
	2	C (mg L ⁻¹)	5.39	19.36	0.70	5.88	18.44	1.28	6.05		18.08
		m (g)	1.0029			2.006			3.0047		
		x/m (mg/g)	0.27			0.20			0.16		
	3	C (mg L ⁻¹)	5.47	20.63	0.89	5.83	20.45	1.38	5.94		18.99
		m (g)	1.0049			2.0034			3.0051		
		x/m (mg/g)	0.08			0.05			0.11		
	Ave.	C (mg L ⁻¹)	5.46	19.72	0.75	5.85	19.42		5.97	18.63	1.70
x/m (mg/g)		0.22			0.13			0.13			
Time (h)	Dup.	Element	D			E			Control		
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.06	20.57	0.09	4.06	20.57	0.09	4.06	20.57	0.09
24	1	C (mg L ⁻¹)	6.09	18.81	2.05	6.20	16.43	2.66	3.98	21.18	0.09
		m (g)	4.0078			5.0060					
		x/m (mg/g)	0.09			0.14					
	2	C (mg L ⁻¹)	6.11	18.08	2.14	6.22	16.62	2.42			
		m (g)	4.0027			5.0072					
		x/m (mg/g)	0.12			0.14					
	3	C (mg L ⁻¹)	5.98	17.71	2.08	6.05	17.16	2.54			
		m (g)	4.005			5.0056					
		x/m (mg/g)	0.13			0.12					
	Ave.	C (mg L ⁻¹)	6.06	18.20	2.09	6.16	16.74	2.54			
x/m (mg/g)		0.11			0.13						

Table A.6 Zinc adsorption by slag (coarse size)

Time (h)	Dup.	Items	A			B			C		
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.11	21.36	0.09	4.11	21.36	0.09	4.11	21.36	0.09
24	1	C (mg L ⁻¹)	5.47	20.11	0.52	5.8	20.29	0.89	5.92	19.05	1.23
		m (g)	1.0020			2.0056			3.0398		
		x/m (mg/g)	0.13			0.05			0.10		
	2	C (mg L ⁻¹)	5.38	20.11	0.54	5.82	19.05	0.95	5.92	18.52	1.17
		m (g)	1.0178			2.0142			3.0179		
		x/m (mg/g)	0.13			0.14			0.12		
	3	C (mg L ⁻¹)	5.32	20.64	0.49	5.72	20.46	0.97	5.9	19.23	1.26
		m (g)	1.0112			2.0051			3.0021		
		x/m (mg/g)	0.05			0.04			0.09		
Ave.	C (mg L ⁻¹)	5.39	20.29	0.52	5.78	19.93	0.94	5.91	18.93	1.22	
	x/m (mg/g)	0.10			0.08			0.10			

Time (h)	Dup.	Items	D			E			Control			
			pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	pH	Zn ²⁺	Ca ²⁺	
0		C (mg L ⁻¹)	4.11	21.36	0.09	4.11	21.36	0.09	4.11	21.36	0.09	
24	1	C (mg L ⁻¹)	5.95	19.41	1.58	6.04	17.99	1.92	4.32	20.99	0.06	
		m (g)	4.0182			5.0083						
		x/m (mg/g)	0.06			0.09						
	2	C (mg L ⁻¹)	6.06	19.23	1.49	6.04	16.23	2.03				
		m (g)	4.0188			5.0135						
		x/m (mg/g)	0.07			0.14						
	3	C (mg L ⁻¹)	6.07	18.52	1.92	6.09	18.88	1.92				
		m (g)	4.0025			5.0071						
		x/m (mg/g)	0.09			0.06						
Ave.	C (mg L ⁻¹)	6.03	19.05	1.66	6.06	17.70	1.96					
	x/m (mg/g)	0.07			0.10							

Table A.7 Copper adsorption by slag (fine size)

Time (h)	Dup.	Items	A			B			C			
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	
0		C (mg L ⁻¹)	4.07	17.78	0.14	4.07	17.78	0.14	4.07	17.78	0.14	
24	1	C (mg L ⁻¹)	4.75	13.64	0.81	4.72	4.21	1.75	4.79	4.75	2.53	
		m (g)	1.0048			2.0074			3.0075			
		x/m (mg/g)	0.62			1.01			0.65			
	2	C (mg L ⁻¹)	4.92	12.80	1.16	4.77	8.49	1.43	4.90	6.45	2.50	
		m (g)	1.0055			2.0010			3.0060			
		x/m (mg/g)	0.74			0.70			0.57			
	3	C (mg L ⁻¹)	4.80	11.43	0.84	4.82	7.92	1.57	4.84	2.81	2.21	
		m (g)	1.0031			2.0029			3.0039			
		x/m (mg/g)	0.95			0.74			0.75			
	Ave.	C (mg L ⁻¹)	4.82	12.63	0.94	4.77	6.88	1.58	4.84	4.67	2.42	
x/m (mg/g)		0.77			0.82			0.65				
Time (h)	Dup.	Items	D			E			Control			
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	
0		C (mg L ⁻¹)	4.07	17.78	0.14	4.07	17.78	0.14	4.07	17.78	0.14	
24	1	C (mg L ⁻¹)	4.97	3.38	2.82	5.14	1.47	3.93	4.03	17.99	0.20	
		m (g)	4.0041			5.0029						
		x/m (mg/g)	0.54			0.49						
	2	C (mg L ⁻¹)	4.99	2.01	3.58	4.95	0.80	3.26				
		m (g)	4.0018			5.0037						
		x/m (mg/g)	0.59			0.51						
	3	C (mg L ⁻¹)	4.89	2.07	2.94	4.99	1.00	3.08				
		m (g)	4.0072			5.0016						
		x/m (mg/g)	0.59			0.50						
	Ave.	C (mg L ⁻¹)	4.95	2.49	3.11	5.03	1.09	3.42				
x/m (mg/g)		0.57			0.50							

Table A.8 Copper adsorption by slag (medium size)

Time (h)	Dup.	Items	A			B			C			
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	
0		C (mg L ⁻¹)	4.04	19.37	0.10	4.04	19.37	0.10	4.04	19.37	0.10	
24	1	C (mg L ⁻¹)	4.43	8.80	1.45	4.73	3.46	2.34	4.70	3.04	3.01	
		m (g)	1.0049			2.0087			3.0032			
		x/m (mg/g)	1.58			1.19			0.82			
	2	C (mg L ⁻¹)	4.61	14.95	1.20	4.70	11.22	2.03	4.61	5.15	3.01	
		m (g)	1.0058			2.0092			3.0030			
		x/m (mg/g)	0.66			0.61			0.71			
	3	C (mg L ⁻¹)	4.57	9.38	1.30	4.76	8.03	1.82	4.57	5.96	2.91	
		m (g)	1.0077			2.0069			3.0029			
		x/m (mg/g)	1.49			0.85			0.67			
	Ave.	C (mg L ⁻¹)	4.54	11.04	1.32	4.73	7.57	2.06	4.63	4.71	2.98	
x/m (mg/g)		1.24			0.88			0.73				
Time (h)	Dup.	Items	D			E			Control			
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	
0		C (mg L ⁻¹)	4.04	19.37	0.10	4.04	19.37	0.10	4.04	19.37	0.10	
24	1	C (mg L ⁻¹)	4.61	3.88	4.00	4.87	2.04	4.78	3.88	19.37	0.10	
		m (g)	4.0054			5.0061						
		x/m (mg/g)	0.58			0.52						
	2	C (mg L ⁻¹)	4.73	1.96	5.14	4.77	1.11	4.62				
		m (g)	4.0062			5.0072						
		x/m (mg/g)	0.65			0.55						
	3	C (mg L ⁻¹)	4.76	7.22	3.59	4.78	1.42	4.57				
		m (g)	4.0077			5.009						
		x/m (mg/g)	0.45			0.54						
	Ave.	C (mg L ⁻¹)	4.70	4.35	4.24	4.81	1.52	4.66				
x/m (mg/g)		0.56			0.53							

Table A.9 Copper adsorption by slag (coarse size)

Time (h)	Dup.	Items	A			B			C		
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.05	19.31	0.00	4.05	19.31	0.00	4.05	19.31	0.00
24	1	C (mg L ⁻¹)	4.65	16.20	1.25	4.60	13.42	1.54	4.71	12.65	2.44
		m (g)	1.0064			2.0074			3.0054		
		x/m (mg/g)	0.46			0.44			0.33		
	2	C (mg L ⁻¹)	4.67	14.25	0.85	4.91	16.38	1.42	4.79	12.02	2.10
		m (g)	1.0037			2.0024			3.0117		
		x/m (mg/g)	0.76			0.22			0.36		
	3	C (mg L ⁻¹)	4.77	16.00	0.63	4.70	9.93	1.59	4.82	9.03	1.99
		m (g)	1.0072			2.0051			3.0011		
		x/m (mg/g)	0.49			0.70			0.51		
Ave.	C (mg L ⁻¹)	4.70	15.48	0.91	4.74	13.24	1.52	4.77	11.23	2.18	
	x/m (mg/g)	0.57			0.45			0.40			
Time (h)	Dup.	Items	D			E			Control		
			pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺	pH	Cu ²⁺	Ca ²⁺
0		C (mg L ⁻¹)	4.05	19.31	0.00	4.05	19.31	0.00	4.05	19.31	0.00
24	1	C (mg L ⁻¹)	4.75	8.22	2.96	4.82	4.67	4.66	4.20	19.31	0.00
		m (g)	4.0158			5.0177					
		x/m (mg/g)	0.41			0.44					
	2	C (mg L ⁻¹)	4.86	11.08	2.79	4.78	1.81	3.53			
		m (g)	4.0102			5.0129					
		x/m (mg/g)	0.31			0.52					
	3	C (mg L ⁻¹)	4.69	5.30	3.01	4.70	6.87	3.13			
		m (g)	4.0103			5.0094					
		x/m (mg/g)	0.52			0.37					
Ave.	C (mg L ⁻¹)	4.77	8.20	2.92	4.77	4.45	3.77				
	x/m (mg/g)	0.42			0.44						

Table A.10 Cd-Zn-Cu adsorption by slag from multi-ion solution (fine size)

Time (h)	Dup.	Element	A		B		C	
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0		Cd ²⁺	4.04	20.54	4.04	20.54	4.04	20.54
		Zn ²⁺		22.48		22.48		22.48
		Cu ²⁺		20.35		20.35		20.35
		Ca ²⁺		0.30		0.30		0.30
24	1	Cd ²⁺	4.79	20.02	4.73	19.48	5.00	19.75
		Zn ²⁺		21.45		16.30		19.62
		Cu ²⁺		11.92		4.06		6.97
		Ca ²⁺		1.71		2.60		3.55
		m (g)	1.0040		2.0026		3.0022	
		x/m (mg/g) Cd	0.04		0.06		0.03	
		x/m (mg/g) Zn	0.12		0.45		0.13	
		x/m (mg/g) Cu	1.26		1.22		0.67	
	2	Cd ²⁺	4.81	18.94	4.82	19.48	4.85	18.67
		Zn ²⁺		20.12		18.13		19.46
		Cu ²⁺		5.80		2.63		4.95
		Ca ²⁺		1.54		2.96		3.78
		m (g)	1.0061		2.0055		3.0050	
		x/m (mg/g) Cd	0.20		0.06		0.08	
		x/m (mg/g) Zn	0.32		0.31		0.14	
		x/m (mg/g) Cu	2.17		1.33		0.77	
	3	Cd ²⁺	4.73	19.75	4.80	19.75	4.88	18.40
		Zn ²⁺		19.96		20.45		15.96
		Cu ²⁺		7.79		5.73		1.53
		Ca ²⁺		1.48		2.96		4.61
		m (g)	1.0069		2.0058		3.0029	
		x/m (mg/g) Cd	0.08		0.04		0.09	
		x/m (mg/g) Zn	0.35		0.14		0.32	
		x/m (mg/g) Cu	1.87		1.09		0.94	
	Ave.	Cd ²⁺	4.78	19.57	4.78	19.57	4.91	18.94
		Zn ²⁺		20.51		18.29		18.35
		Cu ²⁺		8.50		4.14		4.48
		Ca ²⁺		1.58		2.84		3.98
		x/m (mg/g) Cd	0.11		0.05		0.07	
		x/m (mg/g) Zn	0.26		0.30		0.20	
		x/m (mg/g) Cu	1.77		1.21		0.79	

Table A.10 Cd-Zn-Cu adsorption by slag from multi-ion solution (fine size)

(Continued)

Time (h)	Dup.	Element	D		E		Control		
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	
0		Cd ²⁺	4.04	20.54	4.04	20.54	4.04	20.54	
		Zn ²⁺		22.48		22.48		22.48	
		Cu ²⁺		20.35		20.35		20.35	
		Ca ²⁺		0.30		0.30		0.30	
24	1	Cd ²⁺	4.87	18.94	5.02	18.13	3.99	20.29	
		Zn ²⁺		16.63		15.30		22.28	
		Cu ²⁺		1.99		2.06		20.35	
		Ca ²⁺		5.32		6.15		0.06	
		M (g)	4.0062		5.0016				
		x/m (mg/g) Cd	0.05		0.06				
		x/m (mg/g) Zn	0.21		0.21				
		x/m (mg/g) Cu	0.69		0.55				
	2	Cd ²⁺	4.88	18.94	5.02	18.67			
		Zn ²⁺		16.13		15.63			
		Cu ²⁺		1.07		1.57			
		Ca ²⁺		4.91		6.21			
		m (g)	4.0010		5.0051				
		x/m (mg/g) Cd	0.05		0.05				
		x/m (mg/g) Zn	0.16		0.14				
		x/m (mg/g) Cu	0.72		0.56				
	3	Cd ²⁺	4.89	18.67	5.14	18.94			
		Zn ²⁺		17.63		17.29			
		Cu ²⁺		3.49		2.46			
		Ca ²⁺		5.02		5.73			
		m (g)	4.0054		5.0007				
		x/m (mg/g) Cd	0.06		0.04				
		x/m (mg/g) Zn	0.17		0.15				
		x/m (mg/g) Cu	0.63		0.54				
	Ave.	Cd ²⁺	4.88	18.85	5.06	18.58			
		Zn ²⁺		16.80		16.08			
		Cu ²⁺		2.18		2.03			
		Ca ²⁺		5.08		6.03			
		x/m (mg/g) Cd	0.05		0.05				
		x/m (mg/g) Zn	0.18		0.17				
		x/m (mg/g) Cu	0.68		0.55				

Table A.11 Cd-Zn-Cu adsorption by slag from multi-ion solution (medium size)

Time (h)	Dup.	Element	A		B		C	
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0		Cd ²⁺	3.96	21.34	3.96	21.34	3.96	21.34
		Zn ²⁺		22.79		22.79		22.79
		Cu ²⁺		20.22		20.22		20.22
		Ca ²⁺		0.21		0.21		0.21
24	1	Cd ²⁺	4.80	20.50	4.92	20.38	4.96	19.77
		Zn ²⁺		22.02		22.10		21.01
		Cu ²⁺		8.56		11.05		1.85
		Ca ²⁺		1.72		2.07		3.24
		m (g)	1.0007		2.0045		3.0002	
		x/m (mg/g) Cd	0.13		0.07		0.08	
		x/m (mg/g) Zn	0.12		0.05		0.09	
		x/m (mg/g) Cu	1.75		0.69		0.92	
	2	Cd ²⁺	4.90	20.62	4.87	20.13	4.98	20.25
		Zn ²⁺		21.63		20.47		21.48
		Cu ²⁺		11.75		8.13		2.12
		Ca ²⁺		1.38		2.00		2.89
		m (g)	1.0055		2.0012		3.0045	
		x/m (mg/g) Cd	0.11		0.09		0.05	
		x/m (mg/g) Zn	0.17		0.17		0.07	
		x/m (mg/g) Cu	1.26		0.91		0.90	
	3	Cd ²⁺	4.88	20.62	4.89	20.50	4.94	20.50
		Zn ²⁺		21.32		19.77		18.45
		Cu ²⁺		11.18		5.64		2.35
		Ca ²⁺		1.24		2.34		3.31
		m (g)	1.0050		2.0031		3.0017	
		x/m (mg/g) Cd	0.11		0.06		0.04	
		x/m (mg/g) Zn	0.22		0.23		0.22	
		x/m (mg/g) Cu	1.35		1.09		0.89	
	Ave.	Cd ²⁺	4.86	20.58	4.89	20.34	4.96	20.17
		Zn ²⁺		21.66		20.78		20.31
		Cu ²⁺		10.50		8.27		2.10
		Ca ²⁺		1.45		2.14		3.15
		x/m (mg/g) Cd	0.11		0.08		0.06	
		x/m (mg/g) Zn	0.17		0.15		0.12	
		x/m (mg/g) Cu	1.45		0.89		0.90	

Table A.11 Cd-Zn-Cu adsorption by slag from multi-ion solution (medium size)

(Continued)

Time (h)	Dup.	Element	D		E		Control	
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0		Cd ²⁺	3.96	21.34	3.96	21.34	3.96	21.34
		Zn ²⁺		22.79		22.79		22.79
		Cu ²⁺		20.22		20.22		20.22
		Ca ²⁺		0.21		0.21		0.21
24	1	Cd ²⁺	5.00	19.17	5.02	19.29	4.06	21.34
		Zn ²⁺		17.99		18.06		22.79
		Cu ²⁺		1.54		2.42		20.22
		Ca ²⁺		3.86		4.75		0.14
		m (g)	4.0052		5.0012			
		x/m (mg/g) Cd	0.08		0.06			
		x/m (mg/g) Zn	0.18		0.14			
		x/m (mg/g) Cu	0.70		0.53			
	2	Cd ²⁺	5.09	19.77	5.12	19.77		
		Zn ²⁺		20.00		15.89		
		Cu ²⁺		1.68		0.77		
		Ca ²⁺		3.86		7.09		
		m (g)	4.0056		5.0034			
		x/m (mg/g) Cd	0.06		0.05			
		x/m (mg/g) Zn	0.10		0.13			
		x/m (mg/g) Cu	0.69		0.58			
	3	Cd ²⁺	4.99	20.25	5.06	20.13		
		Zn ²⁺		20.24		19.54		
		Cu ²⁺		1.58		1.85		
		Ca ²⁺		4.48		5.72		
		m (g)	4.0025		5.0037			
		x/m (mg/g) Cd	0.04		0.04			
		x/m (mg/g) Zn	0.10		0.10			
		x/m (mg/g) Cu	0.70		0.55			
	Ave.	Cd ²⁺	5.03	19.73	5.07	19.73		
		Zn ²⁺		19.41		17.83		
		Cu ²⁺		1.60		1.68		
		Ca ²⁺		4.06		5.85		
		x/m (mg/g) Cd	0.06		0.05			
		x/m (mg/g) Zn	0.13		0.12			
		x/m (mg/g) Cu	0.70		0.56			

Table A.12 Cd-Zn-Cu adsorption by slag from multi-ion solution (coarse size)

Time (h)	Dup.	Element	A		B		C	
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0		Cd ²⁺	4.00	20.23	4.00	20.23	4.00	20.23
		Zn ²⁺		21.68		21.68		21.68
		Cu ²⁺		20.13		20.13		20.13
		Ca ²⁺		0.00		0.00		0.00
24	1	Cd ²⁺	4.99	19.44	5.02	19.56	5.20	19.33
		Zn ²⁺		21.17		21.17		20.74
		Cu ²⁺		15.78		11.98		8.08
		Ca ²⁺		0.98		1.55		5.69
		m (g)	1.0076		2.0026		3.0095	
		x/m (mg/g) Cd	0.05		0.02		0.02	
		x/m (mg/g) Zn	0.11		0.05		0.06	
		x/m (mg/g) Cu	0.65		0.61		0.60	
	2	Cd ²⁺	4.18	19.22	5.10	19.22	4.87	18.66
		Zn ²⁺		21.17		20.88		14.77
		Cu ²⁺		16.39		12.40		3.31
		Ca ²⁺		2.53		1.49		1.90
		m (g)	1.0055		2.0062		3.0094	
		x/m (mg/g) Cd	0.08		0.04		0.06	
		x/m (mg/g) Zn	0.11		0.08		0.36	
		x/m (mg/g) Cu	0.56		0.58		0.84	
	3	Cd ²⁺	5.00	19.44	5.01	19.44	5.11	19.11
		Zn ²⁺		21.75		21.10		20.52
		Cu ²⁺		14.15		9.61		5.13
		Ca ²⁺		0.80		2.01		2.70
		m (g)	1.0092		2.0075		3.0026	
		x/m (mg/g) Cd	0.05		0.03		0.03	
		x/m (mg/g) Zn	0.02		0.06		0.07	
		x/m (mg/g) Cu	0.89		0.79		0.75	
	Ave.	Cd ²⁺	4.72	19.37	5.04	19.41	5.06	19.03
		Zn ²⁺		21.37		21.05		18.67
		Cu ²⁺		15.44		11.33		5.51
		Ca ²⁺		1.44		1.69		3.43
		x/m (mg/g) Cd	0.06		0.03		0.04	
		x/m (mg/g) Zn	0.08		0.06		0.16	
		x/m (mg/g) Cu	0.70		0.66		0.73	

Table A.12 Cd-Zn-Cu adsorption by slag from multi-ion solution (coarse size)

(Continued)

(Continued)

Time (h)	Dup.	Element	D		E		Control	
			pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0		Cd ²⁺	4.00	20.23	4.00	20.23	4.00	20.23
		Zn ²⁺		21.68		21.68		21.68
		Cu ²⁺		20.13		20.13		20.13
		Ca ²⁺		0.00		0.00		0.00
24	1	Cd ²⁺	5.09	19.11	5.15	19.11	4.12	19.78
		Zn ²⁺		20.74		20.01		21.90
		Cu ²⁺		2.79		6.17		20.13
		Ca ²⁺		3.16		2.93		0.00
		m (g)	4.0045		5.0002			
		x/m (mg/g) Cd	0.03		0.02			
		x/m (mg/g) Zn	0.04		0.06			
		x/m (mg/g) Cu	0.65		0.42			
	2	Cd ²⁺	5.09	19.11	5.27	18.99		
		Zn ²⁺		19.64		20.95		
		Cu ²⁺		0.52		5.75		
		Ca ²⁺		2.76		5.06		
		m (g)	4.0030		5.0039			
		x/m (mg/g) Cd	0.03		0.02			
		x/m (mg/g) Zn	0.08		0.03			
		x/m (mg/g) Cu	0.73		0.43			
	3	Cd ²⁺	5.05	18.88	5.15	18.21		
		Zn ²⁺		18.84		19.72		
		Cu ²⁺		5.26		2.92		
		Ca ²⁺		3.05		3.45		
		m (g)	4.0094		5.0071			
		x/m (mg/g) Cd	0.03		0.05			
		x/m (mg/g) Zn	0.11		0.07			
		x/m (mg/g) Cu	0.56		0.52			
	Ave.	Cd ²⁺	5.08	19.03	5.19	18.77		
		Zn ²⁺		19.74		20.23		
		Cu ²⁺		2.86		4.95		
		Ca ²⁺		2.99		3.81		
		x/m (mg/g) Cd	0.03		0.03			
		x/m (mg/g) Zn	0.08		0.05			
		x/m (mg/g) Cu	0.65		0.46			

Table A.13 Change of Zn^{2+} in working solution mixed with marble

Time (min)		Fine		Medium		Coarse	
		pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	Ca ²⁺	2.88	23.12	2.88	23.12	2.88	23.12
			0.04		0.04		0.04
15		6.95	10.91	7.00	13.75	7.00	16.48
30		7.15	9.84	7.19	12.80	7.20	14.82
45		7.36	8.65	7.39	10.55	7.38	12.45
60		7.30	7.59	7.35	8.42	7.37	9.72
75		7.38	6.76	7.43	6.64	7.45	7.35
90		7.34	5.81	7.41	5.69	7.44	6.05
105		7.47	4.98	7.51	4.50	7.53	5.33
120	Ca ²⁺	7.49	3.47	7.56	2.97	7.60	3.12
			1.58*		1.58*		2.26*
			148.45		144.29		139.67
			8.62*		8.38*		8.40*

Note: mass of marble – 50 g

C – concentration of the elements in the solution

* -- concentration of the elements in solutions filtered by filter paper (Whatman, No.42)

Table A.14 Change of Cu^{2+} in working solution mixed with marble (ditto)

Time (min)		Fine		Medium		Coarse	
		pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	Ca ²⁺	3.19	17.18	3.19	17.18	3.19	17.18
			1.02		1.02		1.02
15		7.11	4.75	7.08	4.54	6.97	7.11
30		7.29	3.69	7.28	3.26	7.20	4.82
45		7.44	2.72	7.45	2.29	7.43	3.31
60		7.51	2.25	7.54	1.89	7.56	2.29
75		7.56	2.06	7.61	1.54	7.63	1.70
90		7.58	1.63	7.63	1.39	7.66	1.44
			0.61*		0.69*		0.71*
	Ca ²⁺		81.40*		75.85*		72.61*

Table A.15 Change of Zn^{2+} in working solution mixed with slag

Time (min)	Fine		Medium		Coarse	
	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	3.14	22.63	3.14	22.63	3.14	22.63
Ca ²⁺		0.34		0.34		0.34
15		20.91		22.63		22.51
30	4.18	20.33	3.86	23.20	3.15	23.32
45	4.42	19.07	4.2	21.94	3.57	21.94
60	4.64	17.46	4.34	21.37	3.78	21.25
75	4.77	17.00	4.45	21.02	4.03	21.37
90	4.91	16.31	4.48	20.10	4.15	21.14
105	5.08	15.97	4.55	20.68	4.26	21.14
120	5.38	15.16	4.68	19.99	4.38	21.02
135	5.8	14.47	4.73	20.33	4.44	21.02
Ca ²⁺		25.48		17.64		8.17
240	5.98	9.89	4.91	17.74	4.45	20.24
Ca ²⁺		25.61		19.74		8.95
24 hours	5.55	0.19	5.35	9.18	5.17	17.31
Ca ²⁺		43.20		36.06		24.15

Note: mass of slag – 50 g

C – concentration of the elements in the solution

Table A.16 Change of Cu^{2+} in working solution mixed with slag

Time (min)	Fine		Medium		Coarse	
	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	3.03	17.35	3.03	17.35	3.03	17.35
15	4.22	8.82	3.55	14.45	3.26	13.74
30	4.53	4.56	4.07	10.62	3.82	10.55
45	4.95	2.10	4.4	7.65	4.2	7.70
60	5.26	1.02	4.57	5.82	4.35	5.51
75	5.51	0.41	4.73	4.31	4.46	4.12
90	5.56	0.17	4.9	3.09	4.56	2.87
105	5.68	0.15	5.1	2.10	4.66	2.02
120	5.7	0.10	5.26	1.34	4.75	1.32
135	5.72	0.07	5.44	0.78	4.85	0.85
150	5.76	0.02	5.49	0.44	4.95	0.54
180	5.76	0.07	5.52	0.22	5.22	0.07
210	5.87	0.07	5.63	0.29	5.35	0.07
Ca ²⁺		11.13		9.46		6.82

Note: mass of slag – 50 g

C – concentration of the elements in the solution

Table A.17 Change of Cu^{2+} in working solution mixed with slag saturated by Zn^{2+}

Time (min)	Fine		Medium		Coarse	
	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	3.04	17.32	3.04	17.32	3.04	17.32
Ca ²⁺		0.07		0.07		0.07
Zn ²⁺		0.00		0.00		0.00
15	3.43	14.83	3.16	16.25	3.11	16.29
30	3.97	11.79	3.50	14.54	3.25	14.78
45	4.20	9.33	3.80	12.96	3.42	12.84
60	4.27	7.60	3.99	11.64	3.55	11.55
75	4.37	5.24	4.13	9.72	3.75	9.67
90	4.43	3.97	4.20	8.40	3.90	8.43
105	4.50	3.31	4.28	7.40	4.02	7.19
120	4.55	2.48	4.34	6.26	4.13	6.02
135	4.63	1.80	4.40	5.09	4.22	4.92
150	4.66	1.36	4.44	4.12	4.30	3.92
165	4.72	1.17	4.47	3.39	4.35	3.07
Ca ²⁺		1.04		0.36		0.27
Zn ²⁺		1.91		1.73		1.12
Initial Zn content in slag (mg)	3.37		2.02		0.8	
adsorbed Cu ²⁺ (mg)	2.42		2.09		2.14	
released Zn ²⁺ (mg)	0.29		0.26		0.17	

Note: mass of slag – 50 g

C – concentration of the elements in the solution

Table A.18 Change of Zn^{2+} in working solution mixed with slag saturated by Cu^{2+}

Time (hour)	Fine		Medium		Coarse	
	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)	pH	C (mg L ⁻¹)
0	4.15	18.65	4.15	18.65	4.15	18.65
Cu ²⁺		0.00		0.00		0.00
Ca ²⁺		0.00		0.00		0.00
24	6.53	1.41	6.43	1.75	5.99	4.16
Cu ²⁺		0.00		0.00		0.00
Ca ²⁺		13.07		12.78		7.90
Initial Cu content in slag (mg)	3.06		3.06		3.05	
adsorbed Zn ²⁺ (mg)	2.59		2.54		2.17	
released Cu ²⁺ (mg)	0		0		0	

Note: mass of slag – 50 g

C – concentration of the elements in the solution

Appendix B

Desorption Batch Tests Results

Table B.1 Desorption of Cadmium by 0.01M KCl

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.71	0.00	0.00	5.71	0.00	0.00	5.71	0.00	0.00
m (g)	0.9993			2.0024			2.9969		
adsorbed Cd (mg)	0.21			0.43			0.53		
Overnight									
24 h	5.95	0.60	0.10	6.01	1.16	0.43	6.08	1.64	0.43
Recovery (%)	43.86			41.00			46.81		
96 h	5.85	0.07	0.09	6.06	0.09	0.20	6.18	0.10	0.44
Recovery (%)	5.04			3.25			2.96		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.71	0.00	0.00	5.71	0.00	0.00	5.71	0.00	0.00
m (g)	3.9966			5.0008					
adsorbed Cd (mg)	0.68			1.05					
Overnight									
24 h	6.17	1.92	0.62	6.20	2.18	0.96	5.73	0.02	0.19
Recovery (%)	42.47			31.21					
96 h	6.21	0.12	0.43	6.34	0.12	0.72	5.43	0.00	0.24
recovery (%)	2.71			1.75					

Table B.2 Desorption of Cadmium by 0.01M NaCl

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.48	0.00	0.00	5.48	0.00	0.00	5.48	0.000	0.00
m (g)	0.9983			1.9990			3.0004		
adsorbed Cd (mg)	0.22			0.29			0.49		
Overnight									
24 h	5.75	0.57	0.24	5.86	1.03	0.38	5.98	1.46	0.43
Recovery (%)	38.57			53.25			44.38		
96 h	5.89	0.05	0.23	6.06	0.09	0.20	6.05	0.08	0.17
Recovery (%)	3.11			4.77			2.46		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.48	0.00	0.00	5.48	0.00	0.00	5.48	0.00	0.00
m (g)	3.9976			4.9913					
adsorbed Cd (mg)	0.73			1.06					
Overnight									
24 h	6.13	1.67	0.77	6.10	2.02	0.67	5.50	0.02	0.10
Recovery (%)	34.46			28.47					
96 h	6.26	0.11	0.57	6.24	0.14	0.53	5.43	0.00	0.00
recovery (%)	2.31			2.01					

Table B.3 Desorption of Cadmium by 0.01M NaNO₃

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.63	0.00	0.00	5.63	0.00	0.00	5.63	0.00	0.00
m (g)	0.9996			2.0002			3.0046		
adsorbed Cd (mg)	0.22			0.29			0.49		
Overnight									
24 h	5.84	0.57	0.24	5.91	1.06	0.29	6.03	1.51	0.57
Recovery (%)	81.94			51.80			35.14		
96 h	5.86	0.01	0.15	6.01	0.06	0.12	6.19	0.09	0.23
Recovery (%)	3.11			4.77			2.46		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	5.63	0.00	0.00	5.63	0.00	0.00	5.63	0.00	0.00
m (g)	4.0032			4.999					
adsorbed Cd (mg)	0.75			0.95					
Overnight									
24 h	6.05	1.50	0.38	6.05	1.90	0.62	5.53	0.02	0.05
Recovery (%)	30.16			30.03					
96 h	6.14	0.09	0.15	6.30	0.12	0.23	5.37	0.00	0.00
recovery (%)	1.86			1.82					

Table B.4 Desorption of Zinc by 0.01M KCl

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.81	0.00	0.00	5.81	0.00	0.00	5.81	0.00	0.00
m (g)	1.0014			1.9988			2.9954		
adsorbed Zn (mg)	0.27			0.49			0.24		
Overnight									
24 h	6.15	0.14	0.52	6.04	0.27	0.49	6.10	0.30	0.58
Recovery (%)	7.93			8.47			18.82		
96 h	6.69	0.01	0.76	6.73	0.02	0.73	6.69	0.02	0.87
Recovery (%)	0.79			0.67			1.34		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.81	0.00	0.00	5.81	0.00	0.00	5.81	0.00	0.00
m (g)	3.9937			4.9956					
Adsorbed Zn (mg)	0.96			1.34					
Overnight									
24 h	6.20	0.47	0.87	6.22	0.58	1.13	5.54	0.01	0.23
Recovery (%)	7.29			6.48					
96 h	6.86	0.03	1.08	6.91	0.03	1.57	5.57	0.00	0.12
Recovery (%)	0.45			0.32					

Table B.5 Desorption of Zinc by 0.01M NaCl

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.80	0.00	0.00	5.80	0.00	0.00	5.80	0.00	0.00
m (g)	1.0020			1.9998			2.9943		
adsorbed Zn (mg)	0.19			0.41			0.62		
Overnight									
24 h	6.09	0.16	0.41	6.11	0.25	0.70	6.18	0.34	0.70
Recovery (%)	12.34			9.33			8.22		
96 h	6.56	0.04	0.52	6.71	0.04	0.58	6.89	0.04	0.93
Recovery (%)	2.80			1.33			1.05		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.80	0.00	0.00	5.80	0.00	0.00	5.80	0.00	0.00
m (g)	3.9960			4.9969					
Adsorbed Zn (mg)	0.86			1.26					
Overnight									
24 h	6.16	0.40	0.81	6.11	0.47	0.79	5.56	0.00	0.12
Recovery (%)	7.06			5.60					
96 h	6.96	0.04	0.96	6.98	0.06	0.93	5.52	0.00	0.09
Recovery (%)	0.63			0.69					

Table B.6 Desorption of Zinc by 0.01M NaNO₃

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.66	0.00	0.00	5.66	0.00	0.00	5.66	0.00	0.00
m (g)	1.0010			2.0006			2.9983		
adsorbed Zn (mg)	0.35			0.49			0.78		
Overnight									
24 h	5.97	0.14	0.35	5.96	0.25	0.49	6.78	0.38	0.61
Recovery (%)	5.83			7.58			7.23		
96 h	6.55	0.02	0.38	6.64	0.05	0.41	6.78	0.04	0.79
Recovery (%)	0.92			1.56			0.83		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	5.66	0.00	0.00	5.66	0.00	0.00	5.66	0.00	0.00
m (g)	3.9948			4.9948					
Adsorbed Zn (mg)	0.88			1.07					
Overnight									
24 h	6.05	0.43	0.64	6.22	0.58	1.16	5.43	0.00	0.17
Recovery (%)	7.22			8.09					
96 h	6.81	0.06	0.73	6.97	0.04	1.63	5.57	0.00	0.12
Recovery (%)	0.98			0.61					

Table B.7 Desorption of Copper by 0.01M KCl

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	5.29	0.00	0.00	5.29	0.00	0.00	5.29	0.00	0.00
m (g)	1.0018			2.0004			2.9997		
adsorbed Cu (mg)	0.62			2.03			1.95		
Overnight									
24 h	5.71	0.00	0.18	5.78	0.00	0.31	5.86	0.00	0.60
Recovery (%)	0.00			0.00			0.00		
96 h	5.80	0.00	0.21	6.01	0.00	0.32	6.18	0.00	0.74
Recovery (%)	0.00			0.00			0.00		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	5.29	0.00	0.00	5.29	0.00	0.00	5.29	0.00	0.00
m (g)	3.9940			4.9962					
Adsorbed Cu (mg)	2.16			2.45					
Overnight									
24 h	5.76	0.00	0.57	5.91	0.00	0.83	5.54	0.00	0.00
Recovery (%)	0.00			0.00					
96 h	5.99	0.00	0.62	6.26	0.00	1.06	5.63	0.00	0.00
Recovery (%)	0.00			0.00					

Table B.8 Desorption of Copper by 0.01M NaCl

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	5.51	0.00	0.00	5.51	0.00	0.00	5.51	0.00	0.00
m (g)	1.0025			1.9981			2.9982		
adsorbed Cu (mg)	0.75			1.39			1.70		
Overnight									
24 h	5.71	0.00	0.29	5.71	0.00	0.26	5.60	0.00	0.52
Recovery (%)	0.00			0.00			0.00		
96 h	5.90	0.00	0.29	5.89	0.00	0.21	5.86	0.00	0.65
Recovery (%)	0.00			0.00			0.00		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	5.51	0.00	0.00	5.51	0.00	0.00	5.51	0.00	0.00
m (g)	3.9965			4.9994					
Adsorbed Cu (mg)	2.37			2.55					
Overnight									
24 h	5.93	0.00	0.86	5.67	0.00	0.65	5.39	0.00	0.00
Recovery (%)	0.00			0.00					
96 h	6.20	0.00	0.79	5.91	0.00	0.71	5.18	0.00	0.00
Recovery (%)	0.00			0.00					

Table B.9 Desorption of Copper by 0.01M NaNO₃

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	6.01	0.00	0.00	6.01	0.00	0.00	6.01	0.00	0.00
m (g)	1.0016			1.9989			3.0006		
adsorbed Cu (mg)	0.95			1.48			2.25		
Overnight									
24 h	5.70	0.00	0.18	5.80	0.00	0.39	5.94	0.00	0.42
Recovery (%)	0.00			0.00			0.00		
96 h	5.75	0.00	0.12	6.04	0.00	0.41	6.10	0.00	0.44
Recovery (%)	0.00			0.00			0.00		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	6.01	0.00	0.00	6.01	0.00	0.00	6.01	0.00	0.00
m (g)	4.0024			5.0016					
Adsorbed Cu (mg)	2.36			2.52					
Overnight									
24 h	5.74	0.00	0.65	5.96	0.00	0.62	5.52	0.00	0.00
Recovery (%)	0.00			0.00					
96 h	6.03	0.00	0.74	6.18	0.00	0.53	5.28	0.00	0.00
Recovery (%)	0.00			0.00					

Table B.10 Desorption of Cadmium by 0.02M Citric Acid

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.48	0.00	0.00	2.48	0.00	0.00	2.48	0.00	0.00
m (g)	0.9999			1.9990			2.9987		
adsorbed Cd (mg)	0.19			0.25			0.46		
Overnight									
24 h	2.58	0.41	0.11	2.61	0.73	0.14	2.67	1.25	0.23
Recovery (%)	32.40			43.88			40.87		
96 h	2.49	0.10	0.25	2.50	0.16	0.33	2.56	0.12	1.10
Recovery (%)	8.15			9.51			4.07		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.48	0.00	0.00	2.48	0.00	0.00	2.48	0.00	0.00
m (g)	4.0032			4.999					
adsorbed Cd (mg)	0.75			0.95					
Overnight									
24 h	2.70	1.68	0.17	2.80	1.86	0.29	2.53	0.00	0.00
Recovery (%)	67.05			46.09					
96 h	2.65	0.09	0.38	2.72	0.12	1.12	2.46	0.00	0.00
recovery (%)	3.62			3.09					

Table B.11 Desorption of Cadmium by 0.02M Citric Acid + 0.01M KCl

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.40	0.00	0.00	2.40	0.00	0.00	2.40	0.00	0.00
m (g)	1.0050			2.0019			3.0023		
adsorbed Cd (mg)	0.19			0.33			0.31		
Overnight									
24 h	2.54	0.57	0.40	2.63	0.95	0.52	2.68	1.14	0.77
Recovery (%)	45.90			42.53			54.53		
96 h	2.45	0.11	1.15	2.58	0.22	1.83	2.60	0.09	3.50
Recovery (%)	9.05			9.68			4.35		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.40	0.00	0.00	2.40	0.00	0.00	2.40	0.00	0.00
m (g)	3.9976			4.9983					
adsorbed Cd (mg)	0.54			0.63					
Overnight									
24 h	2.73	1.61	0.66	2.78	1.72	0.40	2.47	0.00	0.00
Recovery (%)	44.55			41.31			/		
96 h	2.68	0.12	3.75	2.73	0.18	1.23	2.41	0.00	0.00
recovery (%)	3.45			4.35			/		

Table B.12 Desorption of Zinc by 0.02M Citric Acid

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.48	0.00	0.00	2.48	0.00	0.00	2.48	0.00	0.00
m (g)	1.0014			2.0028			2.9988		
adsorbed Zn (mg)	0.27			0.41			0.47		
Overnight									
24 h	2.57	0.54	0.06	2.62	1.27	0.29	2.69	2.53	0.23
Recovery (%)	29.58			46.19			81.52		
96 h	2.46	0.02	0.19	2.52	0.05	1.92	2.60	0.16	0.88
Recovery (%)	1.22			1.90			5.03		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.48	0.00	0.00	2.48	0.00	0.00	2.48	0.00	0.00
m (g)	3.9958			4.9976					
Adsorbed Zn (mg)	0.47			0.68					
Overnight									
24 h	2.73	2.87	0.17	2.75	3.34	0.14	2.53	0.00	0.00
Recovery (%)	92.51			73.17					
96 h	2.68	0.27	0.55	2.72	0.33	0.36	2.46	0.00	0.00
Recovery (%)	8.63			7.33					

Table B.13 Desorption of Zinc by 0.02M Citric Acid + 0.01M KCl

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.40	0.00	0.00	2.40	0.00	0.00	2.40	0.00	0.00
m (g)	1.0038			2.0008			3.0011		
adsorbed Zn (mg)	0.08			0.11			0.33		
Overnight									
24 h	2.52	0.69	0.47	2.59	0.81	1.31	2.65	2.34	0.52
Recovery (%)	126.40			110.60			106.68		
96 h	2.45	0.03	1.18	2.48	0.09	6.65	2.58	0.20	1.89
Recovery (%)	5.43			12.22			9.17		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.40	0.00	0.00	2.40	0.00	0.00	2.40	0.00	0.00
m (g)	3.9958			4.9976					
Adsorbed Zn (mg)	0.47			0.69					
Overnight									
24 h	2.72	3.61	0.35	2.78	3.78	0.41	2.47	0.00	0.00
Recovery (%)	104.20			94.12					
96 h	2.72	0.40	0.79	2.76	0.39	0.88	2.41	0.00	0.00
Recovery (%)	11.58			9.63					

Table B.14 Desorption of Copper by 0.02M Citric Acid

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.50	0.00	0.00	2.50	0.00	0.00	2.50	0.00	0.00
m (g)	1.0018			2.0004			2.9997		
adsorbed Cu (mg)	0.62			2.03			1.95		
Overnight									
24 h	2.61	1.83	0.24	2.65	2.47	0.21	2.70	2.71	0.37
Recovery (%)	44.28			18.18			20.82		
96 h	2.45	0.79	0.57	2.48	3.02	0.84	2.58	0.96	2.80
Recovery (%)	19.06			22.24			7.37		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.50	0.00	0.00	2.50	0.00	0.00	2.50	0.00	0.00
m (g)	3.9940			4.9962					
Adsorbed Cu (mg)	2.16			2.45					
Overnight									
24 h	2.72	2.82	0.37	2.76	2.01	0.26	2.54	0.00	0.00
Recovery (%)	19.57			12.31					
96 h	2.61	0.86	0.92	2.71	0.45	1.28		0.00	0.00
Recovery (%)	5.95			2.73					

Table B.15 Desorption of Copper by 0.01M KCl + 0.02M Citric Acid

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.41	0.00	0.00	2.41	0.00	0.00	2.41	0.00	0.00
m (g)	1.0025			1.9981			2.9982		
adsorbed Cu (mg)	0.75			1.39			1.70		
Overnight									
24 h	2.54	2.01	1.52	2.62	2.32	0.39	2.67	3.10	0.58
Recovery (%)	40.38			25.04			27.38		
96 h	2.41	0.62	3.99	2.48	1.34	2.91	2.56	0.72	2.74
Recovery (%)	12.41			14.40			6.36		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.41	0.00	0.00	2.41	0.00	0.00	2.41	0.00	0.00
m (g)	3.9965			4.9994					
Adsorbed Cu (mg)	2.37			2.55					
Overnight									
24 h	2.75	3.10	0.53	2.76	1.51	0.45	2.45	0.00	0.00
Recovery (%)	40.38			25.04					
96 h	2.64	0.69	3.10	2.74	0.27	1.30	2.35	0.00	0.00
Recovery (%)	4.35			1.62					

Table B.16 Desorption of Copper by 0.01M KCl + 0.02M Tartaric Acid

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.37	0.00	0.00	2.37	0.00	0.00	2.37	0.00	0.00
m (g)	1.0016			1.9989			3.0006		
adsorbed Cu (mg)	0.95			1.48			2.25		
Overnight									
24 h	2.52	2.68	0.13	2.59	2.78	0.11	2.65	3.73	0.18
Recovery (%)	42.21			28.24			24.95		
96 h	2.36	1.27	0.68	2.49	1.37	0.57	2.56	2.06	0.84
Recovery (%)	19.99			13.91			13.74		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.37	0.00	0.00	2.37	0.00	0.00	2.37	0.00	0.00
m (g)	3.9965			4.9994					
Adsorbed Cu (mg)	2.37			2.55					
Overnight									
24 h	2.70	3.84	0.21	2.74	2.47	0.21	2.41	0.00	0.13
Recovery (%)	24.35			14.53					
96 h	2.69	0.86	1.09	2.74	1.03	0.68	2.30	0.00	0.00
Recovery (%)	5.43			6.06					

Table B.17 Desorption of Copper by Sea Water

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	7.97	0.00	597.59	7.97	0.00	597.59	7.97	0.00	597.59
m (g)	1.0049			2.0071			3.0031		
adsorbed Cu (mg)	0.49			0.94			1.09		
Overnight									
24 h	8.02	0.19	192.27	8.00	0.23	724.90	7.99	0.23	688.52
Recovery (%)	5.89			3.71			3.21		
96 h	8.03	0.18		8.05	0.22		8.05	0.22	
Recovery (%)	3.31			2.31			2.00		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	7.97	0.00	597.59	7.97	0.00	597.59	7.97	0.00	597.59
m (g)	3.9981			5.0008					
Adsorbed Cu (mg)	1.57			1.74					
Overnight									
24 h	7.97	0.43	795.05	7.98	0.39	698.92	7.96	0.00	828.83
Recovery (%)	4.08			3.36					
96 h	8.06	0.29		8.06	0.29		7.98	0.07	
Recovery (%)	2.08			1.88					

Table B.18 Desorption of Copper by 0.01M Citric Acid in Sea Water

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.49	0.14	722.10	2.49	0.14	722.10	2.49	0.14	722.10
m (g)	1.0036			2.0058			2.9963		
adsorbed Cu (mg)	1.58			2.38			2.44		
Overnight									
24 h	2.55	3.21		2.58	2.20		2.6	3.31	
Recovery (%)	29.06			12.94			19.46		
96 h	2.52	1.56	827.90	2.65	1.13	755.04	2.69	0.33	748.42
Recovery (%)	13.78			6.41			1.34		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.49	0.14	722.10	2.49	0.14	722.10	2.49	0.14	722.10
m (g)	3.9995			4.9927					
Adsorbed Cu (mg)	2.32			2.59					
Overnight									
24 h	2.63	3.90		2.66	3.52		2.43	0.14	
Recovery (%)	24.34			19.56					
96 h	2.72	0.29	682.19	2.80	0.33	708.68	2.38	0.11	798.10
Recovery (%)	1.18			1.26					

Table B.19 Desorption of Copper by 0.02M Citric Acid in Sea Water

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.13	0.00	722.30	2.13	0.00	722.30	2.13	0.00	722.30
m (g)	1.0055			2.0037			3.002		
adsorbed Cu (mg)	0.33			0.83			1.19		
Overnight									
24 h	2.23	1.44	761.27	2.29	2.95	769.07	2.33	3.85	753.48
Recovery (%)	64.64			53.28			48.65		
96 h	2.09	0.18		2.16	0.25		2.19	0.22	
Recovery (%)	4.90			4.59			2.76		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.13	0.00	722.30	2.13	0.00	722.30	2.13	0.00	722.30
m (g)	4.0052			4.9958					
Adsorbed Cu (mg)	1.31			1.50					
Overnight									
24 h	2.35	3.96	792.45	2.37	3.96	594.99	2.16	0.00	937.95
Recovery (%)	45.27			39.73					
96 h	2.23	0.18		2.28	0.22		2.02	0.07	
Recovery (%)	2.08			2.19					

Table B.20 Desorption of Copper by 0.03M Citric Acid in Sea Water

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.14	0.17	739.15	2.14	0.17	739.15	2.14	0.17	739.15
m (g)	1.0062			2.0018			2.9988		
adsorbed Cu (mg)	1.50			1.70			2.01		
Overnight									
24 h	2.19	3.76		2.22	3.31		2.26	3.38	
Recovery (%)	37.73			29.28			25.24		
96 h	2.10	0.44	798.10	2.14	0.33	771.60	2.19	0.47	758.36
Recovery (%)	2.92			1.61			2.44		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.14	0.17	739.15	2.14	0.17	739.15	2.14	0.17	739.15
m (g)	4.0022			5.0020					
Adsorbed Cu (mg)	1.82			2.69					
Overnight									
24 h	2.30	3.62		2.33	3.73		2.08	0.00	
Recovery (%)	29.89			20.81					
96 h	2.23	0.25	725.24	2.30	0.36	708.68	2.03	0.15	771.60
Recovery (%)	0.90			1.22					

Table B.21 Desorption of Copper by 0.02M Tartaric Acid in Sea Water

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.07	0.00	815.83	2.07	0.00	815.83	2.13	0.00	815.83
m (g)	1.0076			2.0051			3.0016		
adsorbed Cu (mg)	0.42			0.96			1.23		
Overnight									
24 h	2.08	1.90	670.34	2.14	3.46	506.65	2.22	3.93	659.94
Recovery (%)	67.40			54.11			47.71		
96 h	1.82	0.11		1.88	0.22		1.92	0.33	
Recovery (%)	2.57			3.41			3.98		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.07	0.00	815.83	2.07	0.00	815.83	2.13	0.00	815.83
m (g)	3.9978			5.0010					
Adsorbed Cu (mg)	1.35			1.64					
Overnight									
24 h	2.27	3.77	527.43	2.26	3.50	678.13	1.99	0.00	639.16
Recovery (%)	41.78			31.97					
96 h	1.96	0.29		2.00	0.29		1.81	0.04	
Recovery (%)	3.22			2.66					

Table B.22 Desorption of Copper by 0.02M Tartaric Acid

Items	1			2			3		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.36	0.00	0.17	2.36	0.00	0.17	2.36	0.00	0.17
m (g)	1.005			2.006			3.0016		
adsorbed Cu (mg)	0.40			0.68			1.17		
Overnight									
24 h	2.57	1.55	0.08	2.62	2.06	0.11	2.65	3.07	0.14
Recovery (%)	58.71			45.57			39.32		
96 h	2.42	0.11		2.47	0.18		2.50	0.22	
Recovery (%)	4.12			4.02			2.79		
Items	4			5			Blank		
	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)	pH	Cu (ppm)	Ca (ppm)
Feeding solution	2.36	0.00	0.17	2.36	0.00	0.17	2.36	0.00	0.17
m (g)	4.0025			5.004					
Adsorbed Cu (mg)	1.30			1.73					
Overnight									
24 h	2.70	2.45	0.17	2.71	2.60	0.19	2.50	0.00	0.22
Recovery (%)	28.30			22.55					
96 h	2.57	0.18		2.6	0.44		2.42	0.00	
Recovery (%)	2.10			3.78					

Table B.23 Desorption of Cadmium by Sea Water

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	7.93	0.00	688.98	7.93	0.00	688.98	7.93	0.00	688.98
m (g)	1.0002			1.9985			3.0024		
adsorbed Cd (mg)	0.15			0.11			0.32		
Overnight									
24 h	7.93	0.18		7.99	0.35		7.97	1.00	
Recovery (%)	16.04			42.76			45.25		
96 h	8.06	0.07		8.05	0.08		8.06	0.20	
Recovery (%)	6.43			10.01			9.08		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	7.93	0.00	688.98	7.93	0.00	688.98	7.93	0.00	688.98
m (g)	3.9972			4.9998					
adsorbed Cd (mg)	0.24			0.45					
Overnight									
24 h	8.00	0.99		7.99	1.25		7.99	0.02	
Recovery (%)	61.07			41.06					
96 h	8.09	0.17		8.06	0.25		8.02	0.00	
recovery (%)	11.02			8.38					

Table B.24 Desorption of Cadmium by 0.02M Citric Acid in Sea Water

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.13	0.00	770.35	2.13	0.00	770.35	2.13	0.00	770.35
m (g)	1.0067			1.9998			3.0058		
adsorbed Cd (mg)	0.11			0.11			0.32		
Overnight									
24 h	2.29	0.25		2.32	0.48		2.36	0.83	
Recovery (%)	32.75			68.40			38.19		
96 h	2.33	0.07		2.34	0.08		2.36	0.10	
Recovery (%)	4.57			6.55			3.13		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.13	0.00	770.35	2.13	0.00	770.35	2.13	0.00	770.35
m (g)	4.0019			4.9969					
adsorbed Cd (mg)	0.21			0.38					
Overnight									
24 h	2.40	0.85		2.43	1.32		2.24	0.00	
Recovery (%)	60.59			51.70					
96 h	2.34	0.08		2.38	0.13		2.19	0.03	
recovery (%)	3.27			3.94					

Table B.25 Desorption of Cadmium by 0.02M Tartaric Acid in Sea Water

Items	1			2			3		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.09	0.00	656.43	2.09	0.00	656.43	2.09	0.00	656.43
m (g)	1.0002			2.0052			2.9963		
adsorbed Cd (mg)	0.11			0.21			0.25		
Overnight									
24 h	2.12	0.18		2.17	0.75		2.22	0.78	
Recovery (%)	24.21			53.61			47.36		
96 h	2.06	0.03		2.08	0.06		2.11	0.06	
Recovery (%)	1.67			2.56			2.16		
Items	4			5			Blank		
	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)	pH	Cd (ppm)	Ca (ppm)
Feeding solution	2.09	0.00	656.43	2.09	0.00	656.43	2.09	0.00	656.43
m (g)	3.9975			4.9955					
adsorbed Cd (mg)	0.32			0.34					
Overnight									
24 h	2.24	1.40		2.29	1.31		2.08	0.00	
Recovery (%)	60.59			51.70					
96 h	2.14	0.13		2.16	0.12		2.05	0.02	
recovery (%)	5.04			4.29					

Table B.26 Desorption of Zinc by Sea Water

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	7.93	0.08	688.98	7.93	0.08	688.98	7.93	0.08	688.98
m (g)	1.0016			2.0041			3.0374		
adsorbed Zn (mg)	0.13			0.11			0.29		
Overnight									
24 h	7.96	0.04		7.97	0.04		7.96	0.07	
Recovery (%)	2.44			3.06			2.59		
96 h	8.00	0.03		8.05	0.04		8.04	0.04	
Recovery (%)	2.41			4.02			1.83		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	7.93	0.08	688.98	7.93	0.08	688.98	7.93	0.08	688.98
m (g)	4.0146			4.9517					
Adsorbed Zn (mg)	0.24			0.44					
Overnight									
24 h	7.95	0.09		7.93	0.09		7.99	0.02	
Recovery (%)	4.07			2.42					
96 h	8.03	0.05		8.04	0.04		8.02	0.01	
Recovery (%)	2.68			1.20					

Table B.27 Desorption of Zinc by 0.02M Citric Acid in Sea Water

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.13	0.02	770.35	2.13	0.02	770.35	2.13	0.02	770.35
m (g)	0.9911			1.947			3.0151		
adsorbed Zn (mg)	0.13			0.28			0.37		
Overnight									
24 h	2.32	0.24		2.37	0.89		2.44	1.66	
Recovery (%)	25.91			46.30			66.32		
96 h	2.37	0.07		2.41	0.10		2.47	0.20	
Recovery (%)	4.13			3.40			6.61		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.13	0.02	770.35	2.13	0.02	770.35	2.13	0.02	770.35
m (g)	4.0156			5.0093					
Adsorbed Zn (mg)	0.26			0.71					
Overnight									
24 h	2.43	1.46		2.49	2.86		7.99	0.02	
Recovery (%)	81.86			59.73					
96 h	2.46	0.15		2.57	0.34		2.19	0.04	
Recovery (%)	6.44			6.41					

Table B.28 Desorption of Zinc by 0.02M Tartaric Acid in Sea Water

Items	1			2			3		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.09	0.03	656.43	2.09	0.03	656.43	2.09	0.03	656.43
m (g)	1.0109			2.0029			2.9998		
adsorbed Zn (mg)	0.05			0.08			0.26		
Overnight									
24 h	2.14	0.32		2.19	0.70		2.3	1.50	
Recovery (%)	83.48			126.25			83.48		
96 h	2.09	0.05		2.11	0.09		2.14	0.18	
Recovery (%)	6.03			10.73			8.45		
Items	4			5			Blank		
	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)	pH	Zn (ppm)	Ca (ppm)
Feeding solution	2.09	0.03	656.43	2.09	0.03	656.43	2.09	0.03	656.43
m (g)	3.9982			5.0013					
Adsorbed Zn (mg)	0.37			0.32					
Overnight									
24 h	2.30	1.97		2.34	2.37		2.08	0.03	
Recovery (%)	79.71			112.04					
96 h	2.15	0.25		2.18	0.30		2.05	0.03	
Recovery (%)	8.91			12.74					

Table B.29 Desorption of metallic ions by carbonic acid in DI water

Items		1*		2		3		4		5	
		pH	Conc. (ppm)	pH	Conc. (ppm)	pH	Conc. (ppm)	pH	Conc. (ppm)	pH	Conc. (ppm)
Initial Concen. (mg L ⁻¹)	Cd	6.18	0.00	6.18	0.00	6.18	0.00	6.18	0.00	6.18	0.00
	Zn		0.00		0.00		0.00		0.00		
	Cu		0.00		0.00		0.00		0.00		
m (g)		1.0040		1.9995		3.0009		4.0023		5.0000	
adsorbed Cd (mg)		0.11		0.18		0.16		0.24		0.24	
adsorbed Zn (mg)		0.17		0.35		0.20		0.42		0.65	
adsorbed Cu (mg)		1.27		1.81		2.72		2.78		2.92	
1 hour											
Concen. (mg L ⁻¹)	Cd	4.65	0.01	3.61	0.05	3.62	0.10	3.66	0.23	3.77	0.35
	Zn		0.01		0.34		0.37		0.59		1.05
	Cu		0.07		0.92		0.96		1.37		1.44
desorbed Cd (mg)		0.00		0.01		0.02		0.03		0.05	
desorbed Zn (mg)		0.00		0.05		0.06		0.09		0.16	
desorbed Cu (mg)		0.01		0.14		0.14		0.21		0.22	
recovery (%)	Cd	1.42		4.27		9.48		14.44		22.32	
	Zn	1.05		14.48		28.34		21.28		24.37	
	Cu	0.81		7.64		5.30		7.39		7.39	
4 hours											
Concen. (mg L ⁻¹)	Cd	4.86	0.00	3.83	0.01	3.86	0.04	3.86	0.05	4.03	0.13
	Zn		0.01		0.42		0.26		0.25		0.77
	Cu		0.03		1.10		0.82		0.96		0.89
desorbed Cd (mg)		0.00		0.00		0.01		0.01		0.02	
desorbed Zn (mg)		0.00		0.06		0.04		0.04		0.11	
desorbed Cu (mg)		0.01		0.16		0.12		0.14		0.13	
recovery (%)	Cd	0.00		0.85		3.79		3.28		8.53	
	Zn	1.05		18.16		19.98		8.99		17.71	
	Cu	0.40		9.06		4.54		5.17		4.58	
24 hours											
Concen. (mg L ⁻¹)	Cd	4.90	0.00	4.19	0.03	4.20	0.08	4.3	0.14	4.53	0.20
	Zn		0.01		0.54		0.31		0.39		0.99
	Cu		0.21		0.48		0.27		0.41		0.55
desorbed Cd (mg)		0.00		0.00		0.01		0.02		0.03	
desorbed Zn (mg)		0.00		0.08		0.05		0.06		0.15	
desorbed Cu (mg)		0.03		0.07		0.04		0.06		0.08	
recovery (%)	Cd	0.00		2.56		7.58		9.19		12.47	
	Zn	0.53		23.16		23.69		13.82		22.81	
	Cu	2.43		3.96		1.51		2.22		2.82	
Accumulated	recovery (%) - Cd	1.42		7.68		20.85		26.91		43.32	
	recovery (%) - Zn	2.63		55.81		72.01		44.09		64.88	
	recovery (%) - Cu	3.64		20.67		11.35		14.77		14.79	

Note: * -- control sample mixed with DI water without CO₂ inflow.

Table B.30 Desorption of metallic ions by carbonic acid in sea water

Items		1*		2		3**		4		5	
		pH	Conc.	pH	Conc.	pH	Conc.)	pH	Conc.	pH	Conc.
Initial Concen. (mg L ⁻¹)	Cd	7.94	0.01	7.94	0.01	7.94	0.01	7.94	0.01	7.94	0.01
	Zn		0.01		0.01		0.01		0.01		0.01
	Cu		0.00		0.00		0.00		0.00		0.00
m(g)		1.0033		2.0000		/		3.9976		4.9983	
adsorbed Cd (mg)		0.11		0.13		/		0.16		0.18	
adsorbed Zn (mg)		0.22		0.45		/		0.38		0.49	
adsorbed Cu (mg)		1.36		2.19		/		2.80		2.76	
1 hour											
Concen. (mg L ⁻¹)	Cd	7.85	0.06	4.64	0.20	4.61	0.01	4.63	0.27	4.63	0.34
	Zn		0.02		0.51		0.11		0.50		0.70
	Cu		0.14		2.09		0.00		2.26		2.70
desorbed Cd (mg)		0.01		0.03		0.00		0.04		0.05	
desorbed Zn (mg)		0.00		0.08		0.01		0.07		0.10	
desorbed Cu (mg)		0.02		0.31		0.00		0.34		0.41	
recovery (%)	Cd	7.11		21.94		/		23.70		27.31	
	Zn	0.42		16.60		/		18.90		21.06	
	Cu	1.52		14.33		/		12.12		14.72	
4 hours											
Concen. (mg L ⁻¹)	Cd	7.88	0.06	4.72	0.11	4.69	0.01	4.71	0.13	4.72	0.17
	Zn		0.03		0.26		0.05		0.29		0.42
	Cu		0.14		0.38		0.00		0.48		0.68
desorbed Cd (mg)		0.01		0.02		0.00		0.02		0.02	
desorbed Zn (mg)		0.00		0.04		0.01		0.04		0.06	
desorbed Cu (mg)		0.02		0.06		0.00		0.07		0.10	
recovery (%)	Cd	7.11		12.19		/		11.37		13.66	
	Zn	1.25		8.30		/		10.77		12.41	
	Cu	1.52		2.58		/		2.57		3.73	
24 hours											
Concen. (mg L ⁻¹)	Cd	7.16	0.04	4.80	0.09	4.73	0.03	4.80	0.07	4.82	0.09
	Zn		0.04		0.23		0.22		0.42		0.95
	Cu		0.41		0.65		0.00		0.10		0.89
desorbed Cd (mg)		0.00		0.01		0.00		0.01		0.01	
desorbed Zn (mg)		0.00		0.03		0.03		0.06		0.14	
desorbed Cu (mg)		0.06		0.10		0.00		0.02		0.13	
recovery (%)	Cd	4.27		9.75		/		5.69		6.83	
	Zn	1.66		7.29		/		16.03		28.77	
	Cu	4.55		4.46		/		0.55		4.84	
Accumulated recovery (%)	Cd	18.49		43.88		/		40.76		47.79	
	Zn	3.32		32.19		/		45.71		62.24	
	Cu	7.58		21.37		/		15.24		23.29	

Note: * -- Control sample mixed with DI water without CO₂ inflow.

** -- Blank test, no sample was placed in the flask.

Table B.31 Desorption of metallic ions by 5% nitric acid

Items		1	2	3	4	5
Initial Concentration (mg L ⁻¹)	Cd	0.00	0.00	0.00	0.00	0.00
	Zn	0.00	0.00	0.00	0.00	0.00
	Cu	0.00	0.00	0.00	0.00	0.00
	Ca	0.00	0.00	0.00	0.00	0.00
m (g)		1.0044	2.0036	3.0055	4.0015	5.0016
adsorbed Cd (mg)		0.08	0.08	0.17	0.10	0.12
adsorbed Zn (mg)		0.11	0.15	1.07	0.34	0.14
adsorbed Cu (mg)		0.56	0.58	0.84	2.94	2.16
24 hours						
Final Concentration (mg L ⁻¹)	Cd	0.13	0.16	0.51	0.54	0.56
	Zn	0.23	0.74	1.98	1.83	0.95
	Cu	1.81	4.16	7.84	13.03	8.87
	Ca	20.89	1.70	1.82	3.08	16.67
desorbed Cd (mg)		0.02	0.02	0.08	0.08	0.08
desorbed Zn (mg)		0.03	0.11	0.30	0.27	0.14
desorbed Cu (mg)		0.27	0.62	1.18	1.95	1.33
recovery (%)	Cd	22.77	29.27	45.53	79.92	70.87
	Zn	31.56	72.34	27.70	81.15	100.88
	Cu	48.37	108.00	140.22	66.44	61.66

Table B.32 Desorption of metallic ions by 10% nitric acid

Items		1	2	3	4	5
Initial Concentration (mg L ⁻¹)	Cd	0.00	0.00	0.00	0.00	0.00
	Zn	0.00	0.00	0.00	0.00	0.00
	Cu	0.00	0.00	0.00	0.00	0.00
	Ca	0.00	0.00	0.00	0.00	0.00
m (g)		1.0064	2.0020	3.0076	4.0036	4.9977
adsorbed Cd (mg)		0.0506	0.0337	0.0674	0.1012	0.1012
adsorbed Zn (mg)		0.1091	0.1091	0.1746	0.1746	0.2837
adsorbed Cu (mg)		0.6525	1.2222	1.8066	2.6003	2.0939
24 hours						
Final Concentration (mg L ⁻¹)	Cd	0.09	0.17	0.36	0.43	0.54
	Zn	0.16	0.34	0.66	0.86	1.34
	Cu	2.58	4.42	7.84	10.38	8.47
	Ca	1.38	2.45	2.89	4.28	3.71
desorbed Cd (mg)		0.01	0.03	0.05	0.06	.08
desorbed Zn (mg)		0.02	0.05	0.10	0.13	0.20
desorbed Cu (mg)		0.39	0.66	1.18	1.56	1.27
recovery (%)	Cd	27.09	77.29	79.32	63.67	79.96
	Zn	22.42	46.50	56.56	73.69	70.78
	Cu	59.30	54.22	65.06	59.89	60.70

Appendix C

Column Tests Results

Table C.1 Properties of the stormwater samples

<i>Items</i>	<i>Oakley Creek (Site 1)</i>	<i>Oakley Creek (Site 2)</i>	<i>Hobson St.</i>
pH	7.14	6.89	7.00
Absorbance	0.011	1.021	5.177
SS (mg kg ⁻¹)	4.98	79.01	431.81
Cd ²⁺ (mg L ⁻¹)	0.000	0.000	0.000
Zn ²⁺ (mg L ⁻¹)	0.053	0.154	0.386
Cu ²⁺ (mg L ⁻¹)	0.000	0.032	0.067
Cd ²⁺ (mg L ⁻¹) *	0.001	0.002	0.000
Zn ²⁺ (mg L ⁻¹) *	0.161	0.314	0.882
Cu ²⁺ (mg L ⁻¹) *	0.004	0.042	0.134

Note: * – Measurement of the ion concentrations by nitric acid digestion

Table C.2 Specifications of the columns

<i>Items</i>	<i>Coarse</i>	<i>Medium</i>	<i>Fine</i>
Mass of slag (g)	5.9711	5.9958	5.9952
Height of column(cm)	22.2	19.6	19.2
Volume of column (mL)	4.15	3.66	3.59
Density of slag (g/mL)	1.44	1.64	1.67

Table C.3 Removal of heavy metals from Oakley Creek (Site 1) stormwater sample

Flow rate: 3.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0057		6.0030		6.0064	
Retention time		/		7'27"		10'21"		10'46"	
1 st h	pH	7.96	7.86	7.87	8.03	0.147	/	0.070	/
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.036	33.33	0.036	33.33	0.012	77.78	0.012	77.78
	Cu ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
2 nd h	pH	7.98	7.93	8.03	8.00	0.003	/	0.048	/
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.053	0.00	0.024	55.56	0.000	100.00	0.012	77.78
	Cu ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
3 rd h	pH	8.11	8.09	8.09	8.13	0.155	/	0.128	/
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.030	44.44	0.018	66.67	0.006	88.89	0.012	77.78
	Cu ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
4 th h	pH	8.23	8.21	8.19	8.23	0.029	/	0.083	/
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.030	44.44	0.018	66.67	0.006	88.89	0.012	77.78
	Cu ²⁺	0.000	/	0.000	/	0.000	/	0.000	/

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.4 Removal of heavy metals from Oakley Creek (Site 2) stormwater sample

Flow rate: 3.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0050		6.0073		5.9997	
Retention time		/		11'40"		11'25"		11'08"	
1 st h	pH	7.09	7.21	7.26	7.29				
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.107	30.77	0.042	73.08	0.036	76.92	0.024	84.62
	Cu ²⁺	0.032	0.00	0.032	0.00	0.000	100.00	0.000	100.00
2 nd h	pH	7.11	7.17	7.34	7.33	0.696	36.50	0.471	57.03
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.077	50.00	0.059	61.54	0.053	65.38	0.036	76.92
	Cu ²⁺	0.032	79.21	0.032	0.00	0.000	100.00	0.000	100.00
3 rd h	pH	7.26	7.31	7.42	7.38	0.482	54.70	0.459	56.86
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.077	50.00	0.047	69.23	0.042	73.08	0.036	76.92
	Cu ²⁺	0.032	0.00	0.032	0.00	0.000	100.00	0.000	100.00
4 th h	pH	7.25	7.25	7.36	7.39				
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.083	46.15	0.059	61.54	0.042	73.08	0.036	76.92
	Cu ²⁺	0.032	0.00	0.032	0.00	0.000	100.00	0.000	100.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.5 Removal of heavy metals from Oakley Creek (Site 2) stormwater sample

Flow rate: 8.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		5.9982		5.9987		5.9272	
Retention time		/		5'37"		3'27"		6'30"	
1 st h	pH	7.09	7.18	7.18	7.15	0.666	38.22	0.512	52.50
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.125	19.23	0.119	23.08	0.077	50.00	0.053	65.38
	Cu ²⁺	0.032	50.00	0.000	100.00	0.000	100.00	0.000	100.00
2 nd h	pH	7.32	7.29	7.33	7.33	0.703	34.79	0.448	58.44
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.131	15.38	0.095	38.46	0.083	46.15	0.036	76.92
	Cu ²⁺	0.000	100.00	0.000	100.00	0.000	100.00	0.000	100.00
3 rd h	pH	7.38	7.39	7.43	7.41	0.566	47.50	0.498	53.80
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.113	26.92	0.107	30.77	0.071	53.85	0.036	76.92
	Cu ²⁺	0.032	50.00	0.000	100.00	0.000	100.00	0.000	100.00
4 th h	pH	7.42	7.38	7.44	7.37	0.518	51.95	0.553	48.70
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.119	23.08	0.101	34.62	0.077	50.00	0.042	73.08
	Cu ²⁺	0.000	100.00	0.000	100.00	0.000	100.00	0.000	100.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.6 Removal of heavy metals from Hobson St. stormwater sample

Flow rate: 1.96 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0033		6.0065		6.0024	
Retention time		21'30"		20'55"		20'0"		20'23"	
1 st h	pH	7.11	7.18	7.27	7.41	2.208	47.95	1.671	60.61
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.346	10.29	0.250	35.29	0.136	64.71	0.091	76.47
	Cu ²⁺	0.034	50.00	0.034	50.00	0.000	100.00	0.000	100.00
2 nd h	pH	7.18	7.27	7.30	7.43	2.237	46.86	1.980	52.97
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.341	10.29	0.250	35.29	0.170	55.88	0.131	66.18
	Cu ²⁺	0.034	50.00	0.034	50.00	0.034	50.00	0.034	50.00
3 rd h	pH	7.22	7.26	7.28	7.43	2.483	44.18	2.345	47.28
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.352	10.29	0.244	36.76	0.199	48.53	0.136	64.71
	Cu ²⁺	0.034	50.00	0.034	50.00	0.034	50.00	0.000	100.00
4 th h	pH	7.20	7.24	7.31	7.43	2.295	50.53	1.896	59.13
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.307	10.29	0.250	35.29	0.170	55.88	0.108	72.06
	Cu ²⁺	0.034	50.00	0.034	50.00	0.000	100.00	0.000	100.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.7 Removal of heavy metals from Hobson St. stormwater sample

Flow rate: 3.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0031		6.0044		6.0054	
Retention time		12'55"		7'43"		11'12"		10'48"	
1 st h	pH	7.30	7.31	7.37	7.46	3.179	38.59	2.465	52.39
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.346	10.29	0.267	30.88	0.182	52.94	0.125	67.65
	Cu ²⁺	0.067	0.00	0.067	0.00	0.067	0.00	0.034	50.00
2 nd h	pH	7.24	7.28	7.38	7.41	2.899	43.25	3.614	29.25
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.329	14.71	0.250	35.29	0.199	48.53	0.170	55.88
	Cu ²⁺	0.034	50.00	0.034	50.00	0.000	100.00	0.000	100.00
3 rd h	pH	7.27	7.29	7.34	7.39	3.228	32.30	3.868	18.88
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.318	17.65	0.273	29.41	0.221	42.65	0.210	45.59
	Cu ²⁺	0.067	0.00	0.034	50.00	0.067	0.00	0.067	0.00
4 th h	pH	7.31	7.32	7.34	7.36	3.460	29.76	3.788	23.10
	Cd ²⁺	0.000	/	0.000	/	0.000	/	0.000	/
	Zn ²⁺	0.346	10.29	0.329	14.71	0.267	30.88	0.210	45.59
	Cu ²⁺	0.034	50.00	0.067	0.00	0.000	100.00	0.034	50.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.8 Removal of SS and heavy metals from synthetic stormwater sample 1

Flow rate: 3.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0033		6.0037		6.0007	
Retention time		/		11'27"		11'33"		11'08"	
1 st h	pH	6.33		5.91		5.92		5.99	
	Absorbance	0.135	27.42	0.162	12.90	0.146	21.51	0.133	28.49
	Cd ²⁺	0.063	20.00	0.056	30.00	0.032	60.00	0.016	80.00
	Zn ²⁺	0.235	19.18	0.179	38.36	0.099	65.75	0.028	90.41
	Cu ²⁺	0.143	0.00	0.041	71.43	0.041	71.43	0.020	85.71
2 nd h	pH	6.50		6.31		6.38		6.52	
	Absorbance	0.146	21.93	0.142	24.06	0.159	14.97	0.147	21.39
	Cd ²⁺	0.079	0.00	0.063	20.00	0.040	50.00	0.032	60.00
	Zn ²⁺	0.247	15.07	0.203	30.14	0.115	60.27	0.036	87.67
	Cu ²⁺	0.123	14.29	0.020	85.71	0.041	71.43	0.020	85.71
3 rd h	pH	6.37		6.42		6.56		6.57	
	Absorbance	0.161	15.26	0.174	8.42	0.145	23.68	0.150	21.05
	Cd ²⁺	0.079	0.00	0.063	20.00	0.040	50.00	0.024	70.00
	Zn ²⁺	0.231	20.55	0.143	50.68	0.088	69.86	0.036	87.67
	Cu ²⁺	0.123	14.29	0.020	85.71	0.020	85.71	0.000	100.00
4 th h	pH	6.44		6.37		6.48		6.62	
	Absorbance	0.178	7.29	0.162	15.63	0.146	23.96	0.169	11.98
	Cd ²⁺	0.079	0.00	0.063	20.00	0.040	50.00	0.024	70.00
	Zn ²⁺	0.239	17.81	0.183	36.99	0.119	58.90	0.056	80.82
	Cu ²⁺	0.082	42.86	0.020	85.71	0.020	85.71	0.020	85.71

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.9 Removal of SS and heavy metals from synthetic stormwater sample 2

Flow rate: 3.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0017		5.9994		6.0031	
Retention time		/		10'57"		11'20"		10'49"	
1 st h	pH	6.31		5.95		5.84		5.91	
	Absorbance	0.280	16.91	0.284	15.73	0.258	23.44	0.211	37.39
	Cd ²⁺	0.061	0.000	0.053	12.500	0.030	50.000	0.030	50.000
	Zn ²⁺	0.465	8.602	0.394	22.581	0.312	38.710	0.197	61.290
	Cu ²⁺	0.041	50.000	0.020	75.000	0.020	75.000	0.020	75.000
2 nd h	pH	6.40		6.13		6.18		6.32	
	Absorbance	0.278	16.27	0.274	17.47	0.274	17.47	0.275	17.17
	Cd ²⁺	0.061	0.000	0.053	12.500	0.053	12.500	0.030	50.000
	Zn ²⁺	0.470	7.527	0.399	21.505	0.290	43.011	0.148	70.968
	Cu ²⁺	0.061	25.000	0.020	75.000	0.020	75.000	0.020	75.000
3 rd h	pH	6.39		6.22		6.31		6.43	
	Absorbance	0.304	8.98	0.293	12.28	0.280	16.17	0.284	14.97
	Cd ²⁺	0.061	0.000	0.061	0.000	0.053	12.500	0.038	37.500
	Zn ²⁺	0.459	9.677	0.416	18.280	0.323	36.559	0.208	59.140
	Cu ²⁺	0.061	25.000	0.041	50.000	0.020	75.000	0.020	75.000
4 th h	pH	6.35		6.23		6.33		6.45	
	Absorbance	0.297	12.13	0.304	10.06	0.285	15.68	0.301	10.95
	Cd ²⁺	0.061	0.000	0.061	0.000	0.053	12.500	0.030	50.000
	Zn ²⁺	0.476	6.452	0.405	20.430	0.328	35.484	0.213	58.065
	Cu ²⁺	0.082	0.000	0.041	50.000	0.020	75.000	0.020	75.000

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.10 Removal of SS and heavy metals from synthetic stormwater sample 3

Flow rate: 1.96 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0002		5.9992		5.9996	
Retention time		/		23'27"		23'53"		27'33"	
1 st h	pH	6.26		5.66		5.97		6.01	
	Absorbance	0.548	30.46	0.516	34.52	0.422	46.45	0.249	68.40
	Cd ²⁺	0.068	18.18	0.046	45.45	0.038	54.55	0.008	90.91
	Zn ²⁺	0.585	13.82	0.485	28.46	0.248	63.41	0.088	86.99
	Cu ²⁺	0.188	0.00	0.094	50.00	0.075	60.00	0.019	90.00
2 nd h	pH	6.35		6.05		6.11		6.31	
	Absorbance	0.551	29.72	0.527	32.78	0.484	38.27	0.429	45.28
	Cd ²⁺	0.061	27.27	0.038	54.55	0.015	81.82	0.008	90.91
	Zn ²⁺	0.574	15.45	0.436	35.77	0.248	63.41	0.099	85.37
	Cu ²⁺	0.169	10.00	0.075	60.00	0.056	70.00	0.038	80.00
3 rd h	pH	6.31		6.13		6.24		6.45	
	Absorbance	0.540	31.73	0.528	33.25	0.513	35.15	0.458	42.10
	Cd ²⁺	0.061	27.27	0.038	54.55	0.023	72.73	0.008	90.91
	Zn ²⁺	0.590	13.01	0.425	37.40	0.276	59.35	0.127	81.30
	Cu ²⁺	0.188	0.00	0.094	50.00	0.075	60.00	0.075	60.00
4 th h	pH	6.24		6.14		6.27		6.50	
	Absorbance	0.561	29.26	0.553	30.26	0.538	32.16	0.501	36.82
	Cd ²⁺	0.084	0.00	0.046	45.45	0.046	45.45	0.015	81.82
	Zn ²⁺	0.623	8.13	0.474	30.08	0.303	55.28	0.121	82.11
	Cu ²⁺	0.169	10.00	0.094	50.00	0.075	60.00	0.038	80.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.11 Removal of SS and heavy metals from synthetic stormwater sample 3

Flow rate: 2.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6.0033		6.0065		6.0024	
Retention time		/		11'0"		10'25"		9'35"	
1 st h	pH	6.34		5.63		5.64		5.53	
	Absorbance	0.641	14.42	0.577	22.96	0.513	31.51	0.473	36.85
	Cd ²⁺	0.073	10.00	0.033	60.00	0.008	90.00	0.008	90.00
	Zn ²⁺	0.427	38.10	0.427	38.10	0.367	46.83	0.181	73.81
	Cu ²⁺	0.018	75.00	0.018	75.00	0.018	75.00	0.000	100.00
2 nd h	pH	6.12		5.86		6.01		6.09	
	Absorbance	0.579	22.90	0.567	24.50	0.573	23.70	0.488	35.02
	Cd ²⁺	0.073	10.00	0.024	70.00	0.016	80.00	0.008	90.00
	Zn ²⁺	0.580	15.87	0.476	30.95	0.416	39.68	0.186	73.02
	Cu ²⁺	0.018	75.00	0.018	75.00	0.018	75.00	0.018	75.00
3 rd h	pH	6.00		5.99		6.12		6.23	
	Absorbance	0.669	11.16	0.606	19.52	0.655	13.01	0.607	19.39
	Cd ²⁺	0.081	0.00	0.041	50.00	0.041	50.00	0.008	90.00
	Zn ²⁺	0.651	5.56	0.520	24.60	0.471	31.75	0.285	58.73
	Cu ²⁺	0.070	0.00	0.018	75.00	0.018	75.00	0.018	75.00
4 th h	pH	6.01		5.94		6.12		6.26	
	Absorbance	0.662	12.08	0.668	11.29	0.677	10.09	0.668	11.29
	Cd ²⁺	0.081	0.00	0.041	50.00	0.033	60.00	0.024	70.00
	Zn ²⁺	0.668	3.17	0.542	21.43	0.504	26.98	0.367	46.83
	Cu ²⁺	0.035	50.00	0.035	50.00	0.018	75.00	0.018	75.00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Table C.12 Removal of SS and heavy metals from synthetic stormwater sample 3

Flow rate: 8.92 cm/min

Items		Control column		Coarse slag		Medium slag		Fine slag	
		C	η	C	η	C	η	C	η
Mass of slag (g)		/		6. 0059		5. 9993		6. 0022	
Retention time		/		4' 35"		4' 30"		4' 40"	
1 st h	pH	6. 76		6. 16		5. 95		5. 99	
	Absorbance	0. 682	6. 45	0. 644	11. 66	0. 637	12. 62	0. 581	20. 30
	Cd ²⁺	0. 078	9. 09	0. 063	27. 27	0. 063	27. 27	0. 039	54. 55
	Zn ²⁺	0. 609	4. 27	0. 587	7. 69	0. 489	23. 08	0. 380	40. 17
	Cu ²⁺	0. 124	40. 00	0. 041	80. 00	0. 062	70. 00	0. 021	90. 00
2 nd h	pH	6. 72		6. 43		6. 48		6. 49	
	Absorbance	0. 678	7. 63	0. 652	11. 17	0. 681	7. 22	0. 656	10. 63
	Cd ²⁺	0. 078	9. 09	0. 070	18. 18	0. 063	27. 27	0. 039	54. 55
	Zn ²⁺	0. 587	7. 69	0. 560	11. 97	0. 489	23. 08	0. 380	40. 17
	Cu ²⁺	0. 145	30. 00	0. 041	80. 00	0. 062	70. 00	0. 021	90. 00
3 rd h	pH	6. 59		6. 45		6. 53		6. 57	
	Absorbance	0. 691	5. 86	0. 672	8. 45	0. 692	5. 72	0. 676	7. 90
	Cd ²⁺	0. 086	0. 00	0. 078	9. 09	0. 063	27. 27	0. 047	45. 45
	Zn ²⁺	0. 614	3. 42	0. 576	9. 40	0. 565	11. 11	0. 446	29. 91
	Cu ²⁺	0. 165	20. 00	0. 083	60. 00	0. 083	60. 00	0. 062	70. 00
4 th h	pH	6. 49		6. 37		6. 47		6. 56	
	Absorbance	0. 691	6. 62	0. 731	1. 22	0. 703	5. 00	0. 676	8. 65
	Cd ²⁺	0. 078	9. 09	0. 078	9. 09	0. 078	9. 09	0. 055	36. 36
	Zn ²⁺	0. 614	3. 42	0. 587	7. 69	0. 544	14. 53	0. 457	28. 21
	Cu ²⁺	0. 165	20. 00	0. 124	40. 00	0. 103	50. 00	0. 062	70. 00

Note: C – Concentration of the ions (mg L⁻¹)

H –Removal efficiency of the pollutants from the stormwater sample (%)

Appendix D

Cost analysis of desorption tests

The price of the chemicals used as desorbing agent in the tests is shown in the following table.

Table D.1 Price of the chemicals used in the desorption test

<i>Chemical</i>	<i>Citric acid*</i>	<i>Tartaric acid*</i>	<i>KCl*</i>	<i>CO₂**</i>	<i>Sea Water</i>
Price (\$/kg)	51.00	145.60	40.85	40.00	/

Note: * -- Reagent grade

** -- 30 kg CO₂ cylinder (Food Grade)

The costs for preparing 1 L of 0.02M citric and tartaric acid solution are \$0.21 and \$0.44 respectively. Considering the similar effect of citric and tartaric acids on the desorption of heavy metals from slag, citric acid with sea water is recommended because it is more cost-effective.