USE OF BAUXITE REFINING RESIDUE TO REDUCE THE MOBILITY OF
HEAVY METALS IN MUNICIPAL WASTE COMPOST

by

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I, Henricus Theodorus Hofstede, declare that this thesis contains original research by the undersigned which has not previously been submitted for a degree at any other university.

Signed,

Henricus Theodorus Hofstede

The following papers of the presented research have been published to date:


Toegewijd aan

mijn ouders en Lucas
Abstract

Use of bauxite refining residue to reduce the mobility of heavy metals in municipal waste compost.

PhD thesis by

Harrie Hofstede

Due to the adverse environmental impact of landfills and the lack of space for nearby population centres an unprecedented interest has developed in waste recycling with the objective to reduce the volume of waste disposed. Generally organic matter represents the largest fraction in the domestic waste stream including food, garden and paper waste.

In the past efforts have been made to process this organic fraction into municipal compost. However contamination of the compost with heavy metals has in many cases resulted in the lack of suitable markets and subsequent closure of compost facilities. A study was undertaken and aimed at reducing the concentration and mobility of heavy metals in municipal compost.

Bauxite refining residue has a high capacity to immobilise metals in soils through precipitation, cation exchange and chemisorption (Fe- and Al-oxides).

The first step in the study was to assess the metal adsorption capacity of red mud by equilibrating red mud with metal solutions. Metal removal from solution proved very high.

Subsequently, the effect of red mud addition to municipal compost was studied in relation to metal mobility. In particular the interaction of metals with the mobile soluble organic fraction, the humic and fulvic acids, was investigated. It was found that most metals remained in the insoluble humin fraction and the metals in solution remained complexed to the soluble organic fraction. Red mud appeared to be able to adsorp fulvic and humic acids and thus indirectly immobilise the metals in solution. Red mud did not appear to be able to transfer metals from the organic fraction to the mineral red mud fraction.
It was hypothesised that, in order for the metals to be adsorbed to red mud, the red mud needed to be present in the organic waste prior to composting. Metal adsorption to red mud is a rapid chemical reaction while metal complexation to the organic fraction takes a number of weeks, since it must be sufficiently oxidised to contain functional groups.

In order to verify this hypothesis, an installation with seven incubators was developed which allowed composting to be undertaken under computer controlled conditions and monitored for temperature, airflow and carbon dioxide respiration. The incubators were filled with 10 kg of a mixture of grass clippings and sawdust. The first incubator functioned as a control. The contents of the rest of the incubators were spiked with the following metals: Cd, Cr, Cu, Ni, Pb and Zn. In addition the contents of the 3rd - 7th incubators were amended with an increasing percentage of red mud, respectively 10, 20, 25, 30 and 40 % by weight. After the mixture was composted, the metal mobility was reduced by approx. 80 - 99 %, depending on the metal. The mobility was assessed as leachable and plant available in relation to the total metal content. Red mud did not affect the composting process if < 40 % red mud was added.

The next step was to compost municipal organic waste in a pilot plant (capacity 5 m³) using batches with and without red mud. Mixed waste was collected from 150 households and the glass, metal and plastic fractions were removed by manual sorting. The rest was composted.

The red mud - compost had a relatively lower metal content and a reduced metal mobility compared to compost without red mud. The red mud - compost also had a 300 times higher pH buffer capacity and 90 % less soluble organic matter.

The addition of red mud prior to composting was found to reduce the concentration and mobility of metals in compost, improve the quality of compost as a soil conditioner, increased the resistance of the organic fraction against further breakdown and this process thus adds value to both red mud and organic waste.
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Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statement</td>
<td>ii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vi</td>
</tr>
<tr>
<td>Table of contents</td>
<td>vii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xv</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xxii</td>
</tr>
<tr>
<td>List of Plates</td>
<td>xxv</td>
</tr>
</tbody>
</table>

Chapter 1  Introduction and objectives.  1

1.1 Introduction  1

1.2 Current strategies to minimise metal contamination  6
   1.2.1 Traditional methods  7
   1.2.2 Two bin system  8
   1.2.3 Separate collection of hazardous waste  8

1.3 Hypothesis  9

1.4 Objectives of the study  10

1.5 Layout of thesis  10

Chapter 2  Literature review.  12

2.1 Introduction  12

2.2 Organic waste composting  12
   2.2.1 Introduction  12
   2.2.2 Principles of composting  13
      2.2.2.1 Definition  13
      2.2.2.2 Composting process  13
      2.2.2.3 Requirements for the composting process  16
   2.2.3 Properties of compost  18
   2.2.4 Municipal compost quality  19
2.2.5 Conclusion

2.3 Soluble organic matter fraction and its interaction with heavy metals
2.3.1 Fractionation of organic matter
2.3.2 Nature and properties of humic and fulvic acids
2.3.2.1 Basic structure and functional groups
2.3.3 Metal - Humic matter interaction
2.3.3.1 Metal-humic matter complexation
2.3.3.2 Stability constants
2.3.3.3 Valency change of metal ions by humic matter
2.3.4 Transportation of metal - humic matter complexes through soil
2.3.5 Humic matter interaction with the soil mineral fraction
2.3.6 Photo physical characteristics of humic materials
2.3.6.1 Introduction
2.3.6.2 Absorption laws
2.3.6.3 $E_4/E_6$ Ratio
2.3.6.4 $\Delta \log K$
2.3.7 Conclusion

2.4 Bauxite refining residue
2.4.1 Bauxite refining residue production
2.4.2 Metal binding ability of fine bauxite residue
2.4.2.1 Ion exchange
2.4.2.2 Precipitation
2.4.2.3 Chemisorption
2.4.2.4 Adsorption isotherms
2.4.2.5 Metal mobility
2.4.3 Gypsum as an amendment of bauxite residue
2.4.3.1 Effect of gypsum on red mud amended organic matter
2.4.3.2 Effect of gypsum on metal adsorption capacity of red mud

2.5 Conclusion
Chapter 3  Interaction of heavy metals with bauxite refining residue.  

3.1 Introduction  

3.2 Materials and methods  

3.2.1 Experiment I  

3.2.1.1 Red mud preparation  

3.2.1.2 Time dependence of heavy metal adsorption  

3.2.1.3 Adsorption isotherms  

3.2.2 Experiment II  

3.2.2.1 Red mud preparation  

3.2.2.2 Adsorption isotherms  

3.2.3 Experiment III  

3.3 Results  

3.3.1 Experiment I  

3.3.1.1 Equilibrium time  

3.3.1.2 Adsorption isotherms  

3.3.2 Experiment II  

3.3.2.1 Metal adsorption isotherms of gypsum neutralised red mud  

3.3.2.2 Adsorption isotherms of acid neutralised red mud  

3.3.2.3 Preferential adsorption of metals onto red mud - gypsum  

3.3.2.4 Preferential adsorption onto acid neutralised red mud  

3.3.3 Experiment III  

3.3.3.1 Solid : Solution Ratio of 5  

3.3.3.2 Solid : solution ratio of 100  

3.4 Discussion  

3.4.1 Adsorption isotherms  

3.4.2 Correlation of the isotherms with the Langmuir and Freundlich models  

3.4.3 Effect of red mud neutralisation method  

3.4.4 Solid concentration  

3.4.5 Preferential metal adsorption  

3.4.6 Effect of metal adsorption on red mud  

3.4.7 Metal removal mechanism  

3.5 Conclusions
Chapter 4  The effect of bauxite refining residue (red mud) on the solubility of heavy metals in municipal compost.

4.1 Introduction

4.2 Methodology

4.2.1 Introduction

4.2.2 Analysis of Auckland municipal compost

4.2.3 Effect of red mud on metal speciation in compost

4.2.4 Effect of red mud on the fractionation of organo - metallic complexes

4.2.5 Effect of red mud on the leachable metals and soluble organic matter

4.2.6 Effect of red mud on metal leaching from percolation columns

4.3 Results

4.3.1 Auckland municipal compost analysis

4.3.2 Effect of red mud on metal speciation in compost

4.3.2.1 Exchangeable and weak-acid extractable cations

4.3.2.2 Plant available and soil solution soluble metals

4.3.3 Effect of red mud on the fractionation of organo - metallic complexes

4.3.3.1 Characterisation of humic and fulvic acids

4.3.3.2 Fractionation of soluble organic acids

4.3.3.2.1 Fulvic acids

4.3.3.2.2 Humic acids

4.3.4 Effect of red mud on the leachable metals, the soluble organic matter and its optical characteristics

4.3.4.1 Effect of red mud on the leachable heavy metals in municipal compost

4.3.4.2 The effect of gypsum on metal solubilisation

4.3.4.3 Adsorption of soluble heavy metals and organic acids onto red mud

4.3.4.4 Role of humic acids in soluble metal retention

4.3.4.5 Effect of red mud on the optical properties of compost extracts

4.3.4.6 Role of humic acids

4.3.4.7 The effect of gypsum addition

4.3.4.8 Adsorption of soluble organic acids to red mud

4.3.5 Effect of gypsum on metal leaching from red mud - compost
Chapter 5  A laboratory facility to study the composting process.

5.1 Introduction  120
5.2 Composting incubators  121
5.3 Monitoring system  122
5.4 Process control and data acquisition system  125
5.5 Materials and methods  126
5.6 Results  127
  5.6.1 Temperature  127
  5.6.2 pH  129
  5.6.3 Respiration  130
  5.6.4 Soluble organic matter  132
  5.6.5 Carbon to nitrogen ratio  133
  5.6.6 Carbon and nitrogen balance  134
  5.6.7 Overall mass balance  134
5.7 Discussion  136
  5.7.1 Process simulation and control  136
  5.7.2 Process monitoring  137
5.8 Conclusion  138

Chapter 6  Laboratory study on the effect of red mud on mobility of heavy metals and rate of biodegradation during composting.

6.1 Introduction  140
6.2 Materials and Methods  142
  6.2.1 Process  142
  6.2.2 Analysis  144
6.3 Results  147
6.3.1 Introduction

6.3.2 Heavy metal mobility

6.3.2.1 Quality of data

6.3.2.2 Metal mobility as a function of time

6.3.2.3 Effect of red mud addition on the mobility of heavy metals

6.3.2.3.1 Leachable metals

6.3.2.3.2 Plant available metals

6.3.2.3.3 Acid extractable metals

6.3.2.3.4 Effect of red mud on the metal extraction ratios

6.3.4 Composting process parameters

6.3.4.1 pH

6.3.4.2 Gas respiration balance

6.3.4.3 Temperature

6.3.5 Compost maturity

6.3.5.1 Soluble organic matter

6.3.5.2 E4/E6 ratio

6.3.6 Compost quality

6.3.6.1 Buffer capacity

6.3.6.2 Carbon to nitrogen ratio

6.3.6.3 Salinity

6.3.6.4 Macro elements

6.3.7 Mass balances

6.4 Discussion

6.4.1 Effect of metal spiking on the composting process.

6.4.2 Effect of time on the mobility of heavy metals.

6.4.3 Effect of red mud on the mobility of heavy metals.

6.4.4 Compost maturity

6.4.5 Compost quality

6.5 Conclusions

Chapter 7 Municipal refuse composting.

7.1 Introduction
7.2 Materials and methods

7.2.1 Pilot plant

7.2.2 Pilot plant operation

7.2.2.1 Waste preparation

7.2.2.2 Composting runs

7.2.2.3 Process monitoring

7.3 Results

7.3.1 General pilot plant operation

7.3.2 Operational matters for each run

7.3.2.1 Run 1

7.3.2.2 Run 2

7.3.2.3 Run 3

7.3.3 Waste fractionation

7.3.4 Composting process

7.3.4.1 Red mud amended municipal waste composting I (run 1)

7.3.4.1.1 Process parameters

7.3.4.1.2 Heavy metal content and mobility

7.3.4.1.3 Particle size distribution

7.3.4.2 Plain municipal waste composting (run 2)

7.3.4.2.1 Process parameters

7.3.4.2.2 Heavy metal content and mobility

7.3.4.2.3 Particle size distribution

7.3.4.3 Red mud amended municipal waste composting II (run 3)

7.3.4.3.1 Process parameters

7.3.4.3.2 Heavy metal content and mobility

7.3.4.3.3 Particle size distribution

7.3.5 Mass balances

7.4 Discussion

7.4.1 Waste composition

7.4.2 Compost process and the effect of red mud addition

7.4.3 Effect of red mud addition on heavy metal mobility

7.4.4 Compost quality

7.5 Conclusions
Chapter 8  General discussion, conclusions and recommendations. 239

8.1 General discussion 239
8.2 Conclusions 243
8.3 Recommendations for further research 244

References

Appendix  On Apple Macintosh compatible floppy disc
(Microsoft Excel 3.0 and Word 5)
List of Figures

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The changes in temperature and pH during the four stages of the composting process</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Fractionation of humus based on extraction of soil organic matter and further subdivision of the extracted material</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Some of the typical compounds found among the products of chemically decomposed humic acids</td>
<td>24</td>
</tr>
<tr>
<td>2.4</td>
<td>Typical type of compound composing fulvic acid</td>
<td>24</td>
</tr>
<tr>
<td>2.5</td>
<td>Different types of metal - ligand complexation</td>
<td>27</td>
</tr>
<tr>
<td>2.6</td>
<td>Effect of ionic strength on log K values of metal - fulvic acid complexes at pH 3</td>
<td>31</td>
</tr>
<tr>
<td>2.7</td>
<td>Representative examples of the 4 curves of the different classes of adsorption</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>The time dependence of the change in pH of red mud as a function of increasing HCl addition</td>
<td>58</td>
</tr>
<tr>
<td>3.2</td>
<td>The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for cadmium with red mud gypsum, including the pH of the equilibrium solution</td>
<td>62</td>
</tr>
<tr>
<td>3.3</td>
<td>The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for nickel with red mud gypsum, including the pH of the equilibrium solution</td>
<td>62</td>
</tr>
<tr>
<td>3.4</td>
<td>The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for zinc with red mud gypsum, including the pH of the equilibrium solution</td>
<td>63</td>
</tr>
<tr>
<td>3.5</td>
<td>The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with acid neutralised red mud, including the pH of the equilibrium solution</td>
<td>64</td>
</tr>
<tr>
<td>3.6</td>
<td>The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with acid neutralised red mud, including the pH of the equilibrium solution</td>
<td>65</td>
</tr>
</tbody>
</table>
3.7 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with acid neutralised red mud, including the pH of the equilibrium solution

3.8 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with acid neutralised red mud, including the pH of the equilibrium solution

3.9 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with acid neutralised red mud, including the pH of the equilibrium solution

3.10 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions

3.11 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions

3.12 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions

3.13 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions

3.14 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions

3.15 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions
3.16 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.17 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.18 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.19 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for lead with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.20 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.21 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution

3.22 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution

3.23 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution

3.24 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>The measured and calculated adsorption isotherms, according to the</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>Langmuir and Freundlich equations, for lead with red mud gypsum with</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a solution/solid ratio of 100, including the pH of the equilibrium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td></td>
</tr>
<tr>
<td>3.26</td>
<td>The measured and calculated adsorption isotherms, according to the</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Langmuir and Freundlich equations, for nickel with red mud gypsum with a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution/solid ratio of 100, including the pH of the equilibrium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td></td>
</tr>
<tr>
<td>3.27</td>
<td>The measured and calculated adsorption isotherms, according to the</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Langmuir and Freundlich equations, for zinc with red mud gypsum with</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a solution/solid ratio of 100, including the pH of the equilibrium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>The UV and visible spectra of fulvic and humic acids in compost</td>
<td>99</td>
</tr>
<tr>
<td>4.2</td>
<td>The effect of red mud on the distribution of zinc over the different</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>molecular fractions of a compost fulvic acid extract</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>The effect of red mud on the distribution of copper over the different</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>molecular fractions of a compost fulvic acid extract</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Effect of red mud addition on metal levels in a compost extract before</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>and after humic acid removal</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Effect of red mud-gypsum addition on metal levels in a compost extract</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>before and after humic acid removal</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>Effect of RM and RMG amendment to compost and RM to a compost extract</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>on the pH in water extracts</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>The effect of red mud addition to a compost - water extract and removal</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>of humic acids on the metal levels in solution</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>The effect of red mud addition to compost water extracts on the UV/visible light spectra of the extracts</td>
<td>109</td>
</tr>
<tr>
<td>4.9</td>
<td>The effect of red mud addition to compost on the UV/visible light spectra of CaCl₂ extracts</td>
<td>110</td>
</tr>
<tr>
<td>4.10</td>
<td>Nickel leaching from red mud and red mud - gypsum amended compost</td>
<td>114</td>
</tr>
<tr>
<td>4.11</td>
<td>Copper leaching from red mud and red mud - gypsum amended compost</td>
<td>114</td>
</tr>
<tr>
<td>4.12</td>
<td>Zinc leaching from red mud and red mud - gypsum amended compost</td>
<td>115</td>
</tr>
<tr>
<td>5.1</td>
<td>Diagram of one of the composting incubators and the associated</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>monitoring and process control equipment</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Schematic diagram of the laboratory composting facility showing the</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>composting incubators and process control system</td>
<td></td>
</tr>
</tbody>
</table>
The relationship between the level of oxygen and carbon dioxide in the effluent gas and the development of the temperature in the incubator

The development of the pH in the substrate during composting

The chemical oxygen demand of a water extract of the compost during composting

Schematic model of the conversion products during composting

The development of the mass balance during composting

The effect of red mud addition on plant available zinc during composting

The effect of red mud addition on plant available chromium during composting

The effect of red mud addition on plant available copper during composting

The effect of red mud addition on plant available cadmium during composting

The effect of red mud addition on plant available nickel during composting

The effect of red mud addition on plant available lead during composting

The effect of red mud addition on the leachable zinc during composting

The effect of red mud addition on the leachable chromium during composting

The effect of red mud addition on the leachable copper during composting

The effect of red mud addition on the leachable cadmium during composting

The effect of red mud addition on the leachable nickel during composting

The effect of red mud addition on the leachable lead during composting

Effect of time on the acid extractable zinc

Effect of time on the acid extractable chromium

The effect of time on the acid extractable cadmium

The effect of time on the acid extractable copper

The effect of time on the acid extractable nickel

The effect of time on the acid extractable lead

The effect of red mud addition on the leachable chromium, cadmium and lead

The effect of red mud addition on the leachable copper and nickel
6.21 The effect of red mud addition on the leachable zinc 164
6.22 The effect of red mud addition on the plant available chromium, cadmium, nickel and lead 164
6.23 The effect of red mud addition on the plant available copper 165
6.24 The effect of red mud addition on the plant available zinc 165
6.25 The effect of red mud addition on the acid extractable zinc and copper 166
6.26 The effect of red mud addition on the acid extractable chromium, cadmium, nickel and lead 167
6.27 The effect of red mud on the development of the pH during the thermophilic stage of the composting process 170
6.28 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting in the control incubator 174
6.29 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting in the blank incubator 174
6.30 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 10% red mud 175
6.31 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 20% red mud 175
6.32 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 25% red mud 176
6.33 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 30% red mud 176
6.34 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 40% red mud 177
6.35 Solubilisation of organic matter during the thermophilic stage of composting measured as the chemical oxygen demand of a water extract 178
6.36 The mass balance of the composting process in the control incubator 187
6.37 The mass balance of the composting process in the blank incubator 188
6.38 The mass balance of the composting process in the incubator with 10% red mud amendment 188
6.39 The mass balance of the composting process in the incubator with 20% red mud amendment 189
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.40</td>
<td>The mass balance of the composting process in the incubator with 25% red mud amendment</td>
</tr>
<tr>
<td>6.41</td>
<td>The mass balance of the composting process in the incubator with 30% red mud amendment</td>
</tr>
<tr>
<td>6.42</td>
<td>The mass balance of the composting process in the incubator with 40% red mud amendment</td>
</tr>
<tr>
<td>7.1</td>
<td>Diagram of the composting pilot plant</td>
</tr>
<tr>
<td>7.2</td>
<td>Temperature, moisture content, organic matter content, pH and soluble organic matter during composting (run 1)</td>
</tr>
<tr>
<td>7.3</td>
<td>Temperature, moisture content, organic matter content, pH and soluble organic matter during composting (run 2)</td>
</tr>
<tr>
<td>7.4</td>
<td>Temperature, moisture content, organic matter content, pH and soluble organic matter during composting (run 3)</td>
</tr>
</tbody>
</table>
List of tables

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Current and future heavy metal standards in municipal compost</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Heavy metals in municipal solid wastes</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Number of functional groups per molecule of soil humic acids and soil fulvic acids</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Sequence of affinity of divalent metal ions for soil organic matter related to selected properties of metals</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>Particle size distribution of bauxite refining residue</td>
<td>40</td>
</tr>
<tr>
<td>2.4</td>
<td>Negative logarithm of the solubility product of metal precipitates (pK₈)</td>
<td>43</td>
</tr>
<tr>
<td>3.1</td>
<td>Settling velocity of red mud at different initial heavy metal concentrations</td>
<td>60</td>
</tr>
<tr>
<td>3.2</td>
<td>Metals for which experimental adsorption isotherms could be determined</td>
<td>80</td>
</tr>
<tr>
<td>3.3</td>
<td>The correlation coefficients between the isotherms of red mud gypsum (RMG) and red mud acid (RMA) and the Langmuir and Freundlich equations for both single metal and preferential adsorption</td>
<td>80</td>
</tr>
<tr>
<td>3.4</td>
<td>Maximum metal adsorption capacity for RMG and RMA for individual and mixed metal solutions according to the Langmuir equation</td>
<td>82</td>
</tr>
<tr>
<td>4.1</td>
<td>Results of Auckland municipal compost analysis</td>
<td>95</td>
</tr>
<tr>
<td>4.2</td>
<td>Effect of red mud on the exchangeable and acid extractable zinc and lead (mg/kg compost) in municipal compost.</td>
<td>96</td>
</tr>
<tr>
<td>4.3</td>
<td>The effect of red mud on plant available and soil solution soluble cadmium, copper and nickel concentrations</td>
<td>98</td>
</tr>
<tr>
<td>4.4</td>
<td>UV absorbance at four wavelengths and the E₄/E₆ ratios and Δlog K values of fulvic and humic acids in compost</td>
<td>99</td>
</tr>
<tr>
<td>4.5</td>
<td>Kₐ₄₅ values of fulvic acids obtained from compost/red mud mixtures separated on a Sephadex G-10 column</td>
<td>100</td>
</tr>
<tr>
<td>4.6</td>
<td>The distribution of copper and zinc in the soluble organic fraction of compost</td>
<td>103</td>
</tr>
<tr>
<td>4.7</td>
<td>Total organic carbon concentrations in compost extracts with red mud and the effect of humic acid removal</td>
<td>106</td>
</tr>
<tr>
<td>4.8</td>
<td>The effect of red mud on the Δlog K and E₄/E₆ values of compost extracts</td>
<td>111</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.9</td>
<td>The effect of increasing red mud and red mud-gypsum additions to compost and to water extracts of compost on the absorbance of the extracts at their most sensitive wavelength</td>
<td>112</td>
</tr>
<tr>
<td>4.10</td>
<td>Effect of gypsum amendment of red mud on metal leaching from a red mud - compost percolation column</td>
<td>115</td>
</tr>
<tr>
<td>5.1</td>
<td>Compost process and maturity parameters and the analytical methods applied</td>
<td>127</td>
</tr>
<tr>
<td>5.2</td>
<td>Statistical analysis of the sum of the carbon dioxide and oxygen balance during the composting process</td>
<td>131</td>
</tr>
<tr>
<td>5.3</td>
<td>Total organic carbon, total nitrogen and the C/N ratio during composting</td>
<td>133</td>
</tr>
<tr>
<td>5.4</td>
<td>The carbon and nitrogen balance at three time intervals</td>
<td>134</td>
</tr>
<tr>
<td>5.5</td>
<td>The mass balance during composting</td>
<td>136</td>
</tr>
<tr>
<td>6.1</td>
<td>Substrate consistency of the batches in each compost reactor</td>
<td>143</td>
</tr>
<tr>
<td>6.2</td>
<td>Metal concentrations in the spiking solution and compost</td>
<td>143</td>
</tr>
<tr>
<td>6.3</td>
<td>Relevant parameters and frequency of monitoring or analysis</td>
<td>146</td>
</tr>
<tr>
<td>6.4</td>
<td>Test of the significance of the effect of red mud addition on the leachable and plant available heavy metals using analysis of variance</td>
<td>149</td>
</tr>
<tr>
<td>6.5</td>
<td>The reduction in metal mobility for each metal as a function of red mud addition and as a function of time</td>
<td>162</td>
</tr>
<tr>
<td>6.6</td>
<td>Heavy metal content of red mud and the metal recovery from red mud with acid after equilibration with the spiking solution</td>
<td>168</td>
</tr>
<tr>
<td>6.7</td>
<td>Effect of red mud on the relative metal mobility indexed to the blank</td>
<td>169</td>
</tr>
<tr>
<td>6.8</td>
<td>Statistical analysis of sum of the oxygen and carbon dioxide concentration</td>
<td>171</td>
</tr>
<tr>
<td>6.9</td>
<td>The E₄/E₆ ratio in the separate fulvic and humic acid fractions during composting</td>
<td>180</td>
</tr>
<tr>
<td>6.10</td>
<td>Effect of red mud on the pH buffer capacity of the final compost and the relation to loss of carbon as CO₂</td>
<td>181</td>
</tr>
<tr>
<td>6.11</td>
<td>The correlation between the loss of carbon during composting and red mud addition as well as the buffer capacity</td>
<td>182</td>
</tr>
<tr>
<td>6.12</td>
<td>The effect of red mud on the carbon to nitrogen ratio in the substrate during the thermophilic stage of composting</td>
<td>183</td>
</tr>
<tr>
<td>6.13</td>
<td>Electrical conductivity in compost - red mud extracts</td>
<td>184</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>6.14</td>
<td>Macro elements and total nitrogen content of the blank and the 20% red mud amended compost</td>
<td>185</td>
</tr>
<tr>
<td>6.15</td>
<td>The pH levels required to be exceeded before metal hydroxide precipitation takes place</td>
<td>194</td>
</tr>
<tr>
<td>7.1</td>
<td>Composition of the domestic waste</td>
<td>213</td>
</tr>
<tr>
<td>7.2</td>
<td>The total organic carbon, total nitrogen and the C/N ratio of the waste during composting</td>
<td>216</td>
</tr>
<tr>
<td>7.3</td>
<td>Total metal content in municipal red mud-compost and the plant available and leachable fractions (run 1)</td>
<td>218</td>
</tr>
<tr>
<td>7.4</td>
<td>Compost particle size distribution on the basis of weight (run 1)</td>
<td>219</td>
</tr>
<tr>
<td>7.5</td>
<td>The carbon to nitrogen ratio in plain municipal waste during composting</td>
<td>222</td>
</tr>
<tr>
<td>7.6</td>
<td>Heavy metal content in mature plain municipal compost and the plant available and leachable fractions (run 2)</td>
<td>224</td>
</tr>
<tr>
<td>7.7</td>
<td>The particle size distribution in plain municipal compost (run 2)</td>
<td>224</td>
</tr>
<tr>
<td>7.8</td>
<td>Development of the C/N ratio during red mud amended municipal waste composting (run 3)</td>
<td>227</td>
</tr>
<tr>
<td>7.9</td>
<td>Heavy metal content in mature municipal red mud-compost and the plant available and leachable fractions (run 3)</td>
<td>229</td>
</tr>
<tr>
<td>7.10</td>
<td>Compost particle size distribution (run 3)</td>
<td>230</td>
</tr>
<tr>
<td>7.11</td>
<td>A comparison of the mass balances for each run</td>
<td>230</td>
</tr>
<tr>
<td>7.12</td>
<td>The leachable and plant available heavy metals as a percentage of the total metal concentration in the compost</td>
<td>235</td>
</tr>
</tbody>
</table>
List of Plates

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Pilot plant setup with conveyor belt, reactor, motor and gear box and the sorting bins</td>
<td>204</td>
</tr>
<tr>
<td>7.2</td>
<td>Mixed domestic waste on the conveyor belt prior to sorting and discharge of organic fraction into the reactor</td>
<td>205</td>
</tr>
<tr>
<td>7.3</td>
<td>The red mud compost of run I after discharge from the reactor and prior to maturation</td>
<td>237</td>
</tr>
<tr>
<td>7.4</td>
<td>The plain municipal compost of run 2 after discharge from the reactor and prior to maturation</td>
<td>237</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction and objectives

1.1 Introduction

Of all solid municipal domestic waste produced in Australia approximately 55% by mass consists of food and garden waste. Other components are paper (24%), plastics (2.4%), glass (7%), metals (3%) and other inorganics (10 - 15%) (West Australian Department of Commerce and Trade, and WA Municipal Association, 1993). The organic fraction has a strong impact on the environment and can be hazardous. The reasons for this are 1) the large volume, occupying 50-70% of landfill space, 2) its putrescible nature, making it a potential source of pathogenic organisms, 3) the large volume of environmentally harmful gases, e.g. methane, released during its uncontrolled decomposition, and 4) the decomposing organic matter is a major contributor to groundwater pollution through its dissolution and the function of soluble organic matter as a carrier for inorganic pollutants (e.g. heavy metals). Furthermore it creates odour and attracts pests.

The main sources of organic waste besides domestic waste are industry (breweries, abattoirs, food), agriculture, the timber sector and sewage treatment plants. Some of the organic wastes are used on soils (sawdust, sewage sludge), re-used as a basis for other products e.g., brewery waste or used as stockfeed. However, most of the waste is landfilled.

In Western Australia alone combined domestic organic waste production is estimated to be approaching 0.5 million tonnes annually (Department of Commerce and Trade, and WA Municipal Association, 1993). Australia wide the organic waste production can be estimated to be in excess of 10 million tonnes annually, agricultural and industrial waste included.

One of the main challenges in any integrated waste management strategy is to deal appropriately and effectively with organic waste. The current practice of landfilling organic waste is rapidly becoming an inappropriate waste disposal practice and unsustainable in the long term. It consumes large areas of land, results in low land value and is generally strongly objected to by residents, e.g. NIMBYs*, and consequently landfilling is fast...
disappearing in major cities as the sole waste disposal strategy. In cities with low housing densities, transport costs can become prohibitive as suitable landfill space is only available well away from waste generation centres.

This organic waste has, however, considerable potential as a resource when stabilised through composting. It is high in organic matter and contains nutrients such as nitrogen (2%), phosphorus (0.5 - 0.7%), potassium (0.6 - 0.9%) and trace elements (Diaz et al., 1993). Composting has the advantage of reducing the waste volume by 40 - 50% and furthermore all the advantages associated with the production of a soil conditioner.

To be cost effective it is of paramount importance that the end product, compost, has commercial value in a market that is of sufficient size to absorb the quantity produced. Potential markets include local governments, market gardeners, nurseries, viticulture, agriculture and householders. The market for compost is potentially large though correlated to the price and quality of the compost. A consistent and certifiable high quality compost in a carefully developed market should be the basis for composting to be cost-effective, environmentally sustainable and therefore successful (Bertoldi et al., 1990).

The quality of compost made from organic waste relates amongst others to the level of contamination by heavy metals, since metals do not decompose and may concentrate at higher levels in the food chain. It appears that one of the main issues that limits composting of municipal waste in the United States and Europe is limited markets as a result of a combination of contamination by heavy metals and soil protection legislation restricting the application of soil amenders based on their metal content. Most soils require protection from contamination for sustainable land use. For this purpose soil protection guidelines are in place or being developed that limit the application of heavy metals to soils (Council of the European Communities, 1980, 1982; Hansen and Tjell, 1979; USEPA, 1977) and these guidelines become progressively more restrictive (Table 1.1). The level of heavy metals can thus determine the maximum application rate of compost and hence the size of the market for the compost.

The widespread use of heavy metals in consumer products has led to heavy metals being present in significant levels in the mixed domestic waste stream (Table 1.2). Some of the most common sources of heavy metals in domestic waste are dry cell batteries (lead,
mercury, zinc, cadmium), metal coatings (cadmium, chromium, zinc), paints, solvents, cosmetics, dyes, pesticides, lubricants and metals in their pure state (copper, lead, zinc) and in electronic equipment. So the metals appear in their metallic form as well as in metal compounds.

Table 1.1 Current and future heavy metal standards in municipal compost in mg/kg dry matter.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Netherlands* to end 1994</th>
<th>from 1995</th>
<th>CEC#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>2</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>200</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>Copper</td>
<td>300</td>
<td>60</td>
<td>500</td>
</tr>
<tr>
<td>Mercury</td>
<td>2</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>Nickel</td>
<td>50</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>200</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>Zinc</td>
<td>900</td>
<td>200</td>
<td>1500</td>
</tr>
<tr>
<td>Arsenic</td>
<td>25</td>
<td>15</td>
<td>-</td>
</tr>
</tbody>
</table>

# Council of European Communities, 1980.

The contamination, introduced by the above mentioned sources into the mixed waste stream, has serious consequences for the recycling of the organic fractions in the waste through composting. Once mixed, the metals are spread throughout the total waste stream in the form of dust, metal particles and metal compounds. This metal dispersion is very difficult to reverse through mechanical waste separation processes. These processes consist of sieving, magnetic conveyor belts, trommels, air classification, etc. These types of separation are based on distinctive physical properties of the various waste fractions.

Most integrated solid waste management systems are designed to receive mixed domestic waste. This waste is processed by a separation installation which generally recovers the following separate fractions, plastics, metals, glass for recycling and a compostable fraction, which is marked by a high content of organic matter and paper. Some facilities include
recovery of the fraction with a high calorific value, e.g. plastics, rubbers, clothing to be used as fuel in an incinerator with a net energy output (electricity). This fraction is called refuse derived fuel (RDF).

Table 1.2 Heavy metals (mg/kg dry mass) in municipal solid wastes (Ehrig, 1989).

<table>
<thead>
<tr>
<th>Metal</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>3.5</td>
<td>40-50</td>
<td>11</td>
<td>3.5</td>
<td>2-14</td>
<td>3-9</td>
</tr>
<tr>
<td>Copper</td>
<td>238</td>
<td>411-532</td>
<td>400</td>
<td>400</td>
<td>120-210</td>
<td>31-345</td>
</tr>
<tr>
<td>Lead</td>
<td>399</td>
<td>210-370</td>
<td>400</td>
<td>210</td>
<td>110-330</td>
<td>294-545</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.6</td>
<td>0.3-0.4</td>
<td>4</td>
<td>1.1</td>
<td>1-14</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td>521</td>
<td>588-742</td>
<td>1200</td>
<td>1200</td>
<td>300-1000</td>
<td>310-956</td>
</tr>
</tbody>
</table>

(1) Greiner (1983); (2) Fresenius et al. (cited in Ehrig, 1989); (3) Belevi and Baccini (1987); (4) Nielsen (1978); (5) Vogl (1978); (6) Billtewski (1989); concentrations in wastes with 30% moisture; Such wastes also contain about 76-108 mg/kg chromium and 13 mg/kg nickel.

Other systems concentrate more on participation of householders, in source separation recycling schemes. This obviates, in an ideal situation, the need for a waste separation installation which has high capital and operating costs. If a source separation scheme includes separate collection of the organic fraction, the contamination of organic matter with heavy metals is considerably reduced (Oosthoek and Smit, 1987).

Of the domestic waste stream in Perth, Western Australia, the most easily recyclable fractions in terms of separation and economics, are glass (10%), metals (5%), paper (20%) and finally plastics (10%) which still poses difficulties in identification of the various types and stable markets. These fractions account for 45% of the waste stream. The residual fraction (55%) consists mainly of organic matter in the form of garden refuse (20%) and food scraps (30%). This organic fraction can be easily composted. However, contamination as a result of previous mixing with the inorganic fractions has to be monitored and a comparison of the levels of contamination in municipal compost with established standards for environmentally sustainable metal levels in soils, will have to be favourable. This contamination relates to total concentrations as well as to the mobility, i.e. the level of interaction of the contaminants with the environment.
The main cause for heavy metals to occur in domestic organic waste is that domestic refuse is only separated after collection, allowing metal containing wastes to mix with the organic fraction. Since during the composting process a reduction in weight of up to 50% occurs, any metal contaminants will concentrate in the end product (Hammer, 1992).

One way of avoiding such contamination is to separately collect the putrescible, so-called garden, fruit and vegetable (GFV) fraction. This practice has recently been adopted in the Netherlands. Their aim is to separately collect and compost 750,000 tonnes of GFV waste by 1994 and 1,000,000 tonnes by 1995. This represents 70% of the total domestic organic waste produced (Ministerie van volkshuisvesting, ruimtelijke ordening en milieubeheer, 1991). Considering that approximately 50% of the total waste stream is organic, it follows that effectively 35% of total domestic waste produced, is turned into a compost that conforms with the strict metal contamination guidelines, though it still contains xeno-biotic heavy metals such as cadmium and lead (Oosthoek and Smit, 1987). This approach requires extensive public education programs, co-operation of householders and involves increased waste collection costs.

Heavy metals occur throughout the geosphere, many of which are very much part of the biosphere as well. Though most metals can be found in any type of soil, the majority of the metals in the geosphere are not participating in life processes and are locked up in concentrated mineral deposits. The introduction of mining and metal processing industry has started a redistribution of metals in the geosphere and anthroposphere. This redistribution has resulted in increased metal concentrations in air, water and land.

Much research has been done and is continuing into the environmental and human health effects of this redistribution of metals. As the metal-containing materials flow passes through society and turns into waste, two main forms of disposal exist for these metals, either further concentrated or dispersed, since metals are biologically and chemically indestructible. The first option is the currently predominant practice of disposal in landfills, either untreated or more concentrated i.e. in the form of incinerator ashes, which generally require concrete encasing. This form creates a metal pollution point source. Thus it replaces secure metal deposits with landfill type deposits in which the metals are more environmentally mobile. The other option is to recycle the metals back into the environment at an appropriate rate, such that at no time its metal assimilation capacity is
not exceeded. This prevents point source pollution and aims to redistribute the concentrated contamination to reach levels at which they do not pose a threat to environmental health. This could be a more sustainable approach to contaminated waste disposal.

Contamination is defined as either the presence of xenobiotic substances, e.g. cadmium or lead, that have no proven function in life processes, or an excess of biotic substances, e.g. copper or zinc, which function as essential trace elements but are toxic at high levels. In the case of metals, it is the amount of metal at a given time at a certain location that is mobile, e.g. available to plants or for leaching, the so called metal release flux, that causes contamination. In a practical sense it restricts application so as to prevent uptake by vegetables or groundwater contamination. From this, it follows that contamination occurs when a metal adversely affects an ecosystem or gains an entry point into the food chain.

So the presence of metals in soils itself does not constitute pollution until it is available in the environment at levels above acceptable or safe values. The results of research over three years presented by Petruzelli et al., (1991) showed for example that doses of sewage sludge at metal levels declared illegal after 1992 in Europe contributed to increases in crop yield and no significant increase in metal uptake by the crop was observed. This means that removal of the interactive flux of metals through slowing down the rate of release would remove the potentially adverse effects on the environment.

1.2 Current strategies to minimise metal contamination

From experiences in recent years in Europe and the United States it can be learned that increasingly restrictive legislation on the application to soil of metal - contaminated municipal compost resulted in Europe to moving towards composting only the biowaste fraction. The European standards are aiming to limit the content of heavy metals in compost to natural background levels.

In the US, large scale mixed solid waste composting, often involving sewage sludge, is still the predominant approach. The standards in the US are based on research that determined the maximum amount of heavy metals that may be applied to land and still prove safe for plant growth and accidental ingestion of soil. Most compost from plants in the US meets
the standards based on this so-called 'no observed adverse effect level' (NOAE) principle. However, there are at least two reasons to question this approach to metal standards. Firstly, establishment of composting facilities demands high capital investment and long term markets to recover these costs. Repeated applications of heavy metal contaminated municipal compost up to the 'NOAE' level over decades can cause seriously contaminated soils. This contamination is irreversible if future research proves the risks. Secondly, the irregular testing and sampling size of 1 kg per 10 - 300 tonnes is inadequate to screen out batches exceeding the standards (Hammer, 1992). For batches that exceed even these standards, dilution with bulking agents might prove to be an easy way out for the operator. Nevertheless, mixed solid waste composting can be produced cheaper and on a larger scale (Hammer, 1992).

In Perth, the poor sandy soils of the Swan Coastal Plain have very little capacity to reduce mobility of heavy metals from municipal waste compost due to their acidity (low pH) and low ion retention capacity. Thus metals can easily pass through the soil and contaminate the groundwater. This makes these soils particularly sensitive to compost containing high levels of metals.

It is in the interests of the long term success of a composting facility to produce compost with a low content of metals and low metal mobility. A number of approaches and new technologies to achieve this are outlined.

1.2.1 Traditional methods.

The efforts of MSW composting plants to reduce the heavy metal burden in the final compost mainly take the form of utilising mechanical means during waste processing, such as:

1. separation of magnetic materials;
2. separation by sieve fractions; and
3. processing of matured compost (e. g. stoner or air table)
However, evidently producing compost low in heavy metals by strict European standards through mechanical means only has hitherto been unsuccessful. The reduction in landfill requirement with these methods is estimated to be maximum 50% (Krauß, 1987).

1.2.2 Two bin system

Since the compostable fraction occupies the largest volume in the total waste stream, it seems sensible to collect this fraction separately in order to keep the number of household bins to a minimum, since other recyclable materials such as glass and plastics require separation prior to reprocessing. In addition, most of the contamination in recyclable goods is a result of cross contamination between biodegradable and other material e. g. glass and metal in compost; biodegradable matter contaminating glass, metals, plastics and clothing. Waste separation on this basis, can also mean separation of the wet (organics) and dry (inorganic) waste fraction. The mechanical separation of the separately collected dry inorganic fraction only can result in higher recovery of good quality recyclables.

Elimination of the organic fraction from mechanical waste separation processes by separate collection reduces the capital investment and maintenance costs of such an installation considerably. Compost with low metal concentrations can then be produced from the so-called biowaste (Schutte, 1990).

1.2.3 Separate collection of hazardous waste.

Public collection experiments in Germany where a truck visited residential areas for a short period to enable residents to deliver their hazardous waste to the truck were unsuccessful. The recovery was on average only 0.01 g lead and 0.6 g copper and zinc per resident per year. The average heavy metal contribution to municipal waste by residents is 30g lead and 70g copper/zinc per resident per year (Krauß et al., 1987).

Having learnt from this experiment the authority sought closer collection contact with the residents and distributed special plastic bags for the collection of heavy metal containing waste. Aluminium cans were included in this separate collection scheme as a means to stimulate the collecting ambition. A list of products containing the targeted heavy metals was distributed in conjunction with the bags.
The result was very encouraging. This approach resulted in the collection of 87 g of aluminium, 1.5 g lead and 12 g copper/zinc. All the materials collected were small in size and thus particularly important to be prevented from entering the waste stream and thus of relevance to compost quality, since this fraction is difficult to remove from waste. A further recovery improvement by a factor 10 is possible according to the study (Krauß et al., 1987).

1.3 Hypothesis

The hypothesis of this study is that bauxite refining residue addition to metal containing municipal compost reduces the mobility of the metals in the environment where the compost is applied, by reducing the plant availability and groundwater leaching, without adversely affecting the efficiency of the composting process itself.

It is clear that whatever the approach is in organic waste recycling by composting, the soils will receive an increased loading of metals, and the effects can range from improved yield due to compensation for trace element deficiencies, to potential phyto-toxicity in soils. The possible adverse environmental health effects of this increased loading can be limited if the mobility of these metals is reduced and their release extended over a longer period of time to avoid the occurrence of environmentally damaging concentrations. This can be achieved by changing the process by which metals are released from organic matter as a result of decomposition and subsequent metal solubilisation to a dependency on the soil solution to solid equilibrium in combination with high stability constants for the metal-solid complexes. The release of metals will then be regulated as a function of the mobile metal levels in the environment. If these levels are found not to have a detrimental effect on the environment then safe environmental assimilation of metals in conjunction with organic waste recycling can be achieved.

The research described in this thesis explores the concept of using the level of interaction of metal contaminants with the environment, as opposed to their total presence, as a basis to manage environmental pollution and enable reinstatement of a most essential natural process without which life would not be sustainable: organic matter recycling. The research proposes a process for this concept of environmental pollution management.
The hypothesis is that amendment of organic waste with bauxite refining residue will produce a compost with improved soil conditioning properties and reduced mobility of metal that may be present in the organic waste.

1.4 Objectives of the study

It is in this context that the first objective of this study is to reduce the mobility of heavy metals in municipal waste compost by moving the metals from being complexed to the organic fraction to being complexed to an inorganic fraction that can form strong complexes with metals. Bauxite refining residue will be tested for its ability to perform this role.

The second objective is to study the effect of amending organic waste with bauxite refining residue on the quality of the organic waste as a substrate for composting and the effect on the composting process itself.

1.5 Layout of the thesis

The central focus of the thesis is the interaction between organic matter, metals and bauxite refining residue during the aerobic decomposition of organic waste by composting. In Chapter 2 these three components will be described individually and their interaction is discussed with reference to the published literature in so far as it is relevant to the objectives of this study. Each section concludes with a summary of the pertinent aspects.

Chapter three describes the laboratory experiments carried out to assess the ability of bauxite refining residue to remove metals from a solution and to determine the mechanisms involved. After establishing the ability of red mud to adsorb metals, experiments were carried out to determine the mobility of metals in a mature municipal compost and the effect of red mud on the mobility of metals. This is described in Chapter 4.

In order to assess the effect of red mud on the metal mobility during composting, it was necessary to produce metal contaminated compost in a controlled environment and adding red mud to the raw organic matter prior to the composting process. To enable such an experiment to be carried out a computer controlled laboratory composting system was
designed and developed. This composting system and an experiment to demonstrate its suitability is described in Chapter 5.

The experiment to determine the effect of red mud on metal mobility during composting and the effect on the compost process itself is described in Chapter 6. This is an extensive chapter due to the large number of parameters monitored as well as the large amount of data since seven incubators were monitored, each having a different treatment.

Due to the promising results of the experiments described in Chapter 6, it was decided to test the previously stated hypothesis using the organic fraction of actual municipal refuse. For this purpose a small pilot plant was constructed and three batches of municipal refuse compost were produced. The batches included red mud amended compost as well as plain compost in order to assess the effect of red mud on metal mobility in the compost as well as other relevant soil conditioner criteria. This pilot plant study is described in chapter 7.

Chapter 8 consists of an evaluation of the research presented including a general discussion, conclusions and recommendations for further research.
Chapter 2

Literature review

2.1 Introduction

The research described in this thesis revolves in principle around the dynamic three way interaction between heavy metals, red mud (RM) and organic matter, during the aerobic decomposition, known as composting, of the organic waste. Heavy metals are reactive with both red mud and decomposed organic matter through adsorption and precipitation. RM and organic matter interact through red mud adsorption of soluble and insoluble organic matter, chemical reduction of oxides in red mud and dispersion/flocculation of soluble organic matter.

This research is being done in the context of the desire to recycle organic waste through composting. The composting process is described in the first section of this literature review. The review then explores the nature and properties of organic matter and red mud including their interactions with heavy metals. It summarises our current understanding of the complex interactions that take place between these three substances in a soil situation and during the composting process though little information is available on the latter.

The objective of the literature review is to collect research information in the context of the hypothesis and identify the information still required to achieve the stated objective of reducing the mobility and concentration of heavy metals in municipal compost, through research.

The research described in subsequent chapters is designed to fill the hiatus between existing research information and confirmation of the hypothesis.

2.2 Organic waste composting

2.2.1 Introduction

Since 50-70% by mass of the domestic waste stream is compostable, it is the diversion of this fraction with which the highest reduction in waste going to landfill can be achieved. This is
the main reason for the surge in interest in organic waste composting in the last 20 years. Besides waste reduction objectives, the diversion of organic fraction is also desirable as this fraction is responsible for most of the environmental impact of landfills. The decomposing waste in a landfill produces powerful greenhouse gases (methane has many times the potency as carbon dioxide), results in high strength leachates that threaten ground water quality and is also responsible for odours. The interest in composting is thus quite justified.

A part of the hypothesis and a large part of the experimental work relies on the biological and chemical conversion processes that take place during composting. In order to appreciate these sections of the thesis, an understanding of compost and the composting process is required.

2.2.2 Principles of composting

2.2.2.1 Definition

The definition of composting of organic matter includes the following aspects: the process is microbiological, requires oxygen (aerobic) and releases water and carbon dioxide; the process includes a thermophilic period during which the temperature in the substrate rises to above 55°C as a result of heat released during the oxidation of organic compounds; the process produces a biologically stabilised, odourless and humus like material that has beneficial properties for soils and stimulates plant growth (Zucconi and Bertoldi, 1987). Composting is a true natural recycling process as it follows the reverse process of a growing plant, i.e. a growing plant takes up moisture, carbon dioxide and energy (sun) and releases oxygen. Composting is a natural process that takes place as soon as favourable conditions prevail. This definition is elaborated on below.

2.2.2.2 Composting process

Composting is the process whereby organic matter is rapidly decomposed by a range of microorganisms using oxygen. During the process heat is released which speeds up the process and this also sanitisises the material by neutralising pathogens, weed seeds and plant disease when sufficiently high temperatures are reached (Haug, 1980).
Under ideal conditions, the complete composting process consists of four different stages (Figure 2.1). Each stage is carried out by different genera of bacteria, fungi, protozoa and actinomycetes. During each stage the microbes use original organic compounds and the waste and by-products of a previous generation as a nutrient and energy source, thus further decomposing the organic matter until a stable humus has formed (Gray et al., 1971a).

*Incubation or mesophilic phase*

This stage lasts for approximately 24 hours, when the conditions are favourable, during which the organic matter is rapidly invaded by mesophilic composting organisms, including bacteria, actinomycetes and fungi. These organisms thrive in a temperature range of 25° - 45°C. The mesophilics grow in this phase on the more easily assimilated substances eg. sugars, soluble protein, starch, organic acids, etc. The high metabolic activity and the exothermic decomposition processes, and provided the ratio of the volume of compost to its surface area is sufficient to provide insulation to the composting material, cause the temperature to rise. The temperature rise strongly favours thermophilic sporogenous bacteria. The activity of these bacteria takes the process into the thermophilic phase (Finstein and Morris, 1975).

*Thermophilic phase*

This is the "hot" period, during which organic matter is decomposed rapidly. The temperature can go up to 70°C in the hot core. This is undesirable since at this temperature most composting microbes, including some thermophilic ones, are killed. This considerably reduces the decomposition rate. However 55°C is the optimum temperature, during which the decomposition rate is highest. The oxygen demand is very high in this phase and thus aeration is essential to avoid oxygen supply becoming inhibiting. This phase lasts for 2-3 weeks depending on aeration and substrate. Temperatures below 55°C allow the development of eumycetes and actinomycetes which are the main decomposers of long chain polymers, cellulose and lignin (Bertoldi and Zucconi, 1987).
**Cooling Phase**

This phase sets in once the rate of heat generation as a result of microbially mediated decomposition process falls below the rate of heat loss from the region where the decomposition is occurring as a result of diminishing bioavailable organic substrate. The temperature drops as a result of heat loss due to water evaporation and convection. When the temperature drops below 45°C mesophilic bacteria and other organisms will re-invade the fresh compost. This phase lasts for a few days.

**Compost maturation phase**

The fresh compost needs to stabilise (mature) further, since fresh compost can be phytotoxic to plants due to high ammonia content and the presence of metabolic intermediates. The level of activity of fungi, protozoa and actinomycetes is highest during this phase, while bacterial activity slowly declines. At this stage large polymers such as lignin and cellulose are decomposed and the humification process sets in (de Bertoldi et al., 1983). The activity of actinomycetes produces the compound 'geosmine' which gives matured compost its fresh earthy smell. For this phase applies that the longer the maturation period lasts the better the compost, though 3-4 weeks would be a minimum. Earthworms and insects can also play an important role during maturation though they are not considered part of the process.

Figure 2.1  The changes in temperature and pH during the four stages of the composting process; A. mesophilic, B. thermophilic, C. cooling, D. maturing (Gray et al., 1971a).
Composting is a hygienic process that is capable of neutralising pathogens (disease) and weed seeds from organic waste. The high temperature (minimum of 60°C for 24 hours or 55°C for 3 days) kills all pathogens and weed seeds (Golueke, 1982; Kawata et al., 1977). In addition, during the maturation period fungi produce antibiotic compounds that suppress pathogen development. The conditions prevailing during composting also give pathogens a competitive disadvantage with other, benign, micro-organisms. This property of the process gives compost the added bonus of a plant disease suppressant when used on productive soils (Hoitink et al., 1993).

2.2.2.3 Requirements for the composting process.

There are five requirements for composting to take place (Gray et al., 1971b):

1. organic matter;
2. moisture (40-60%);
3. nutrients (C : N : P = 250 : 10 : 1);
4. air (oxygen); and
5. microorganisms

Organic matter

Organic matter is the substrate that naturally occurring microorganisms use as an energy source for their metabolism. Examples of particular compounds that they digest are starches, sugars, waxes, vegetable oils, cellulose, pectin and lignin. The more easily metabolised organic compounds such as soluble sugars and organic acids are decomposed and mineralised early in the process. These compounds are high in energy and the release of this energy during decomposition is responsible for the rise in temperature during the early stages of the process. Later in the process during the maturation phase, the natural long-chain polymers like lignin which are difficult to break down are decomposed. However, it is these polymers that form the basis of the humus in mature compost (Bertoldi and Zucconi, 1987).

Moisture

The moisture content of the substrate is an important process parameter, since composting is a microbial process. The microbes require a minimum moisture content of 40 % to avoid
their activity being halted (Diaz, 1993). The upper limit is approximately 60%. This upper limit is to prevent the occurrence of anaerobic conditions which will change the process from composting to fermentation (e.g. rotting), due to the pores in the substrate being blocked by moisture thus impairing aeration of the substrate.

Nutrients

Apart from energy, microbes require nutrients to form amino acids and proteins for growth and multiplication. The main nutrients are nitrogen and phosphorus, which are essential in the formation of protein, DNA etc., and trace elements. These nutrients occur in various concentrations in organic matter e.g. wood and paper are deficient in nutrients while manures and grass clippings contain excess nutrients for the composting process. In order for all carbonaceous materials to be decomposed a certain nutrient balance is required. This nutrient balance is expressed as the carbon to nitrogen ratio (C/N ratio). The optimal C/N ratio in the raw substrate is 20 - 30. If the C/N ratio is too low the pH may rise to 8.5 - 9 due to excess release of ammonia (NH₃) from the deamination of amino acids. Existing ammonium ions (NH₄⁺) in the matrix also become volatile at this pH according to the reaction:

\[
\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{NH}_3\text{OH(s)} \longrightarrow \text{NH}_3(aq) + \text{H}_2\text{O} \longrightarrow \text{NH}_3(g) + \text{H}_2\text{O}
\]

ammonium ammonia

The release of ammonia causes three problems. First, ammonia is an odorous and irritating gas, secondly nitrogen is lost from the compost thus reducing its nutritional value to plants. If the C/N ratio is too high the composting process is slowed down and complete decomposition may not occur; in addition, the final compost may exercise a nitrogen demand on the receiving soil, thus depriving plants of nitrogen. The C/N ratio is thus also an important quality parameter for the final compost. Finally, the gas is a cause for acid rain symptoms due to formation of ammonium sulphate in humid air. In soils, this is quickly converted into nitric and sulphuric acid. However this is of minor concern in Australia.

During composting carbon is lost as carbon dioxide, thus reducing the C/N ratio to approximately 10 in the final compost. The C/N ratio has been found to be useful as an
indicator of the maturity of the compost. A fully degraded mature compost should have a C/N ratio of 10 - 20 (Gray et al., 1971b).

*Oxygen*

Composting is a strictly aerobic process wherein oxygen is required to act as an electron acceptor for the carbon oxidation process. Sufficient aeration is thus vital for composting. In a static pile oxygen levels can drop to below 1% in the interstitial gas space and carbon dioxide levels can reach 20%, creating anaerobiosis. These levels are clearly restrictive for composting. To avoid interference with microbial metabolism, oxygen levels should be in the range of 10 - 18% with less than 15% carbon dioxide. It must be noted that the prevailing level of carbon dioxide in the composting atmosphere is the result of an equilibrium between the level of air ventilation and the amount of carbon dioxide released as a result of microbial metabolism. The amount of carbon dioxide released can therefore be used as an indication of the intensity of the microbial activity.

*Micro organism*

The composting of organic substrate involves a broad range of micro organisms. These include bacteria, fungi, actinomycetes, euymycetes, basidiomycetes and protozoa. All these organisms are naturally present, though to an extent dormant, in organic matter. They are activated by creating favourable conditions for composting. Microbial activity is usually limited by less than optimum process conditions.

2.2.3 *Properties of compost*

Mature compost can improve the structure of sandy soils as well as that of heavy clay soils, by the formation of soil aggregates. This will improve water retention capacity thus reducing irrigation requirements. Compost also improves water absorption of sandy soils by acting as a wetting agent. In heavy clay soils compost can improve soil aeration, tillage and drainage a, thus remediating waterlogging.

Compost contains considerable amounts of nitrogen (1 - 2%), phosphorus (0.5 - 1%), potassium (0.1 - 0.5%) and trace elements (Ca, Mg, etc.) which are slowly released as the
compost is broken down further. Compost can also adsorb applied fertiliser and release it slowly. This reduces the extent of fertiliser leaching into ground water. During the composting process certain organic compounds are produced that prevent seed germination, giving compost the property of suppressing weed growth. If the composting process is carried out properly the compost will be free of human and plant pathogens, and weed seeds. Compost is found to benefit plant growth and produce healthy vegetables, with more flavour than vegetables grown solely using synthetic fertilisers (Commission Research into Biological Agricultural Methods, 1976).

2.2.4 Municipal compost quality

For composting to be successful as a waste treatment option, it is imperative that the emphasis is on producing a quality product, for which a demand exists, rather than treating it as an alternative waste disposal option. The latter could lead to the production of inferior compost for which no market exists and could result in the compost having to be landfilled. Compost quality can be measured against two main criteria:

1 the quality of the compost in relation to its use as a soil conditioner; and
2 the level of contamination as a legacy of the source of the raw material.

In order to substantiate compost quality as a marketing tool, a set of quality criteria needs to be developed that is relevant to market requirements.

*Physical and chemical properties*

In order to assess the quality of municipal compost, a set of standards for relevant properties is needed for comparison. Important measures for compost quality are (ORCA, 1992):

- organic matter content;
- maturity;
- nutrient content (N,P,K);
- acidity (pH 6.5-7.5);
- smell (odourless);
- texture (fine, coarse);
- moisture content (40-50%); and
- salinity (<2 g/l)

When compost quality meets predetermined standards, there should be a procedure available to obtain certification for the product. Conditions of certification should include an initial review procedure and an on-going quality control system.

Contamination

Quality standards for municipal compost need to include maximum allowable levels of contaminants. The three main groups of potential contaminants that require regulation are:

- the non biodegradable fraction;
- pathogens and weed seeds; and
- heavy metals

Non biodegradable fraction

The contamination by inorganics mainly affects the safety and visual appearance of the product. For example the presence of glass splinters presents a safety risk to home gardeners when handling the product. The visual presence of glass and pieces of plastic in various colours reduces the market value of the product even though they do not interfere with the quality of the compost as a soil conditioner.

Pathogens and weed seeds

The nature of municipal solid waste carries with it the risk of contamination by pathogens and weed seeds. The presence of pathogens and weed seeds can effectively be dealt with by a proper composting process. The high temperature (55 - 70°C) and the formation of natural antibiotics produced by fungi are sufficient to neutralise these contaminants. In fact mature composts are found to be effective in reducing weed growth and plant disease.
Heavy metals

Contamination by heavy metals of the organic matter in the waste stream is one of the main reasons that has prevented composting from being a widely accepted waste treatment process. The reasons for this are public opposition to using the product and regulations restricting the use of heavy metal-containing compost (Bertoldi and Zucconi, 1990).

During the composting process the organic matter is modified in such a way that heavy metals can be adsorbed or incorporated into the humus. When the compost is applied to soils and further decomposes, these metals are released and made available for plant uptake and leaching into ground water. Metals thus are a cause of concern for the environmental health of soils, ground water and crops.

In order to control the level of contamination received by soils, and prevent the disposal of contaminated organic wastes as soil amenders, soil protection legislation that restricts application of heavy metal containing soil amenders has been put in place in most countries (Commission of the European Communities, 1982; USEPA, 1977). Depending on the metal concentrations in the compost, this can restrict the legal application rate and thus market volume. Perhaps an even more important and even harder to tackle consequence is the public perception of metal containing compost as undesirable.

In Western Australia, no specific legislation or standards are in place by either the EPA or the WA Health Department. The EPA takes the stand that each application is to be treated individually and generally the major considerations are existing land use, the benefits of compost application and environmental health.

2.2.5 Conclusion

Recycling of the organic fraction of the waste stream by means of composting is a relatively simple, "low tech" process and has significant potential to reduce the amount of waste going into landfills and the long term environmental impact of landfills. However, for composting to play a successful part in an integrated waste management strategy, the compost has to be of commercial quality and long term stable markets for the compost have to be developed or expanded.
Currently the term 'compost' is not defined or protected in Australia. This allows any product, compost or not, to be sold as compost, only restricted perhaps by the level of acceptance in the market place. It is in the interest of large scale composting and marketing of compost to have the term 'compost' protected in order to prevent the term being tainted by inferior non-compost products on the market.

2.3 Soluble organic matter fraction and its interaction with heavy metals

2.3.1 Fractionation of soil organic matter

Organic matter can be divided into a humic and a non-humic fraction (Figure 2.2). The non-humic matter fraction, referred to as the humin fraction, includes those compounds whose physical and chemical characteristics are still recognisable, such as fats, waxes, oils, resins, water soluble polysaccharides, hemicellulose, cellulose and proteins (Stevenson, 1965). Most of these compounds are readily subject to microbial attack and thus have a relatively short life span. Bonding or adsorption to inorganic soil constituents increases their resistance against biological degradation.

The humic matter on the other hand is a relatively stable by-product of the microbial transformation of a great variety of biochemical compounds, including the intermediate humin fraction, derived from dead cells and extracellular products of various organisms (Jackson, 1975). During the first stages of organic matter humification, high molecular weight humic acids and humins are formed. A number of processes have been put forward that are responsible for further degradation of these intermediates into humic acids and lower molecular weight fulvic acids, though all are of a microbial oxidative nature. The humic matter fraction can be separated into a fraction which is soluble in an alkaline solution and a fraction which is not. The alkaline solution soluble humic matter is defined as the humic and fulvic acid fraction.

At low pH the humic acid molecules are aggregated into colloidal particles with very little or no charge, which causes them to precipitate (Ritchie and Posner, 1982). In this way the fulvic and humic acids can be separated.
Because humic substances can form stable complexes with metal ions, minerals, non-humic compounds and certain anions (Mortensen, 1965), the soluble humic matter fraction can play an important role in the transportation of these products through the soil. The transportation of heavy metals by humic and fulvic acids is discussed in more detail in section 2.3.4.

![Diagram showing the fractionation of humus based on extraction of soil organic matter and further subdivision of the extracted material](Image)

Figure 2.2 Fractionation of humus based on extraction of soil organic matter and further subdivision of the extracted material (Stevenson, 1965).

### 2.3.2 Nature and properties of humic and fulvic acids

It is important to note that no sharp division exists between the three humic matter fractions, humins, fulvic acids and humic acids. They are all part of an extremely heterogeneous polymer system and the differences between the subdivisions are due to variations in elemental composition, acidity, degree of polymerisation and molecular weight (Jackson et al., 1978). Molecular weight ranges from a few hundred for fulvic acids to tens of thousands for the humic acids and the humin fractions.

The principal reason for the chemical differences is probably the difference in source material. Environmental factors may impose additional diversification (Jackson, 1975). But also the degree of maturity of the humic matter causes variations. When humic matter becomes more mature, the aromatic compounds become more highly condensed, oxygen
and nitrogen bearing functional groups are split off, the aromaticity of the humus increases and unsaturated aliphatic chains may condense with each other.

2.3.2.1 Basic structure and functional groups

A brief discussion of the structural nature and functional groups of humic and fulvic acids is given here. Jackson et al. (1978) presented a detailed review on this topic.

*Humic acids*

Basically humic acids all have aromatic nuclei in the form of flat lattices of cyclic polymerised carbon. The basic structure consists largely of condensation products of compounds such as catechol, syringaldehyde and 3,5-dehydroxybenzoic acid (Figure 2.3). Side chains are connected to the aromatic nuclei which carry various functional groups such as carboxyl, phenolic and alcoholic hydroxyl, methoxyl, carbonyl and quinone groups.

![Figure 2.3 Some of the typical compounds found among the products of chemically decomposed humic acids (Manahan, 1979).](image)

It is likely that -O- and -N- linkages are contained in the humic acid structure to bind compounds such as those in Figure 2.3. In addition, hydrogen bonds between functional groups may be involved in binding the aromatic components of the humic acid molecules. The molecular weight of humic acids is thus very high and can be 10,000 - 100,000.

*Fulvic acids*

Fulvic acids contain aromatic rings which form an open structure in a two- or three-dimensional array (Figure 2.4). The open structure is held together at least partly by hydrogen bonds between the functional groups. The functional groups identified in humic acids have also been identified in fulvic acids.
More important than the structural networks of humic and fulvic acids are their functional groups content. It has been concluded that fulvic acids contain more functional groups, particularly carboxyl, per molecule than do humic acids (Table 2.1), despite fulvic acids being of lower molecular weight than humic acids. There are no methoxyl and quinone functional groups to be found in fulvic acid and no alcoholic hydroxyl groups in humic acid. Functional groups are not evenly distributed among the molecular weight fractions (Gamble et al., 1984).

![Chemical structure of functional groups in humic and fulvic acids]

**Figure 2.4** Typical type of compound composing fulvic acid (Manahan, 1979).

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Humic acid</th>
<th>Fulvic acid</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxyl</td>
<td>3 - 4</td>
<td>6 - 8</td>
<td>- COOH</td>
</tr>
<tr>
<td>phenolic hydroxyl</td>
<td>3 - 4</td>
<td>2 - 4</td>
<td>φ - OH</td>
</tr>
<tr>
<td>alcoholic hydroxyl</td>
<td>-</td>
<td>3 - 4</td>
<td>C - OH</td>
</tr>
<tr>
<td>methoxyl</td>
<td>±1 - 2%</td>
<td>-</td>
<td>C - O - C</td>
</tr>
<tr>
<td>carbonyl</td>
<td>-</td>
<td>2 - 3</td>
<td>C = O</td>
</tr>
<tr>
<td>quinones</td>
<td>3 - 4</td>
<td>-</td>
<td>O = φ = O</td>
</tr>
</tbody>
</table>

φ = benzene ring

**2.3.3 Metal - humic matter interaction**

**2.3.3.1 Metal - humic matter complexation**

Humic and fulvic acids behave as negatively charged species due to the ionisation of their acidic carboxyl and hydroxyl groups. That is why they can attach to positively charged...
particles like metal ions and form stable complexes. Shapiro (1964) found that the yellow organic acids in coloured waters can keep considerable quantities of ferric iron in solution even though the pH and redox potential are high. After esterification of the -COOH and -OH groups the iron -binding capacity disappeared. Stevenson (1976) found evidence that -COOH groups play the prominent role in complex formation. Because fulvic acids have more carboxyl and hydroxyl functional groups, they probably can complex more heavy metals than humic acids.

It is suggested that humic compounds of different origins differ in their metal-binding behaviour because of different functional group contents (Jackson, 1975). The lower molecular weight fractions seem to have a greater metal holding capacity than the higher molecular weight fractions because of a relatively higher functional group content.

Several functional groups have a higher attraction for specific metals, for example, hydroxyl and carboxyl for Zn, and carboxyl and phenolic hydroxyl for Cd, Cu, and Zn. As a consequence humic and fulvic acids show a selective preference for metal adsorption which is the result of the accumulated selectivity of the functional groups present.

The way that metal-humic matter complexes are formed or the form in which they exist determines the nomenclature. The ions or molecules that are bonded or co-ordinated with the metal are termed ligands. These ligands are bonded to the metal through two or more different ligand atoms (Figure 2.5). They can form part of heterocyclic rings. Rings formed in this way are termed chelate rings. A metal complex which contains one or more chelate rings is called a metal chelate and the ligands involved are termed chelating ligands. Detailed information about this type of complex formation has been given by Houghton (1979).

Marinsky et al., cited by McBride (1989), found indications for the bonding of metals to one ligand. In the formation, the following complex was found:

\[ M^{2+} + A^- = MA^+ \]

where \( A^- \) is the dissociated organic ligand and \( M^{2+} \) is a divalent metal.

Although metal bonding to organic matter can be viewed as an ion exchange process between \( A^- \) and metal ions on acidic functional groups, the high degree of selectivity
shown by organic matter for certain metals strongly suggests that some metals coordinate directly, i.e. form inner sphere complexes with the functional groups (McBride, 1989). Of particular interest is the fact that selectivity coefficients for metal adsorption are highly dependent on the degree of loading and the presence of competing metals (McBride, 1989).

![Monobasic Acid](image1)

![Dibasic Acid](image2)

![Hydroxyacid](image3)

Figure 2.5 Different types of metal-ligand complexation (Page et al., 1981).

A typical sequence of metal-organic matter affinities is given in Table 2.2, but these sequences are commonly inconsistent, dependent on the nature of the organic matter, the method used to measure metal bonding, and the pH at which bonding is measured. It shows in this instance, however, the high correlation between metal affinity for soil organic matter and electronegativity.

Table 2.2 Sequence of affinity of divalent metal ions for soil organic matter related to selected properties of metals (McBride, 1989).

<table>
<thead>
<tr>
<th>Affinity sequence</th>
<th>Cu &gt;</th>
<th>Ni &gt;</th>
<th>Pb &gt;</th>
<th>Co &gt;</th>
<th>Ca &gt;</th>
<th>Zn &gt;</th>
<th>Mn &gt;</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro negativity</td>
<td>2.0</td>
<td>1.91</td>
<td>1.87</td>
<td>1.88</td>
<td>1.00</td>
<td>1.65</td>
<td>1.55</td>
<td>1.31</td>
</tr>
<tr>
<td>CFSE®</td>
<td>22.2</td>
<td>29.3</td>
<td>0</td>
<td>17.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>pK1*</td>
<td>7.5</td>
<td>9.4</td>
<td>7.8</td>
<td>9.6</td>
<td>12.7</td>
<td>9.6</td>
<td>10.7</td>
<td>11.4</td>
</tr>
</tbody>
</table>


© Crystal field stabilisation energy (kcal/mole) for an octahedral complex.

* Negative logarithm of the first hydrolysis constant.
2.3.3.2 Stability constants

To evaluate the potential hazard of heavy metal - organic matter complexes transported through the soil, the main factors that control the extent of metal-soluble organic matter interactions need to be established. These main factors according to Mantoura et al. (1978) are:

(i) the value of the stability constant for the metal-humic matter complex;
(ii) the pH which provides a measure of the competition for metal adsorption from carbonate and hydroxy ligands; and
(iii) the major ion concentrations, which control the competition between metals for humic matter adsorption sites.

The last two factors can be measured easily. The determination of the stability constant of the humic matter - metal complex is not easy however, due to the complicated nature of the binding of metal ions by humic substances.

Complex formation can be regarded as a competitive reaction between the metal ion and $H^+$ for reactive sites on the ligand. For a two-step process, the reactions are:

$$
\text{k}_1 \\
\text{HA} + M^{2+} \rightarrow MA^+ + H^+ \\
(1)
$$

and

$$
\text{k}_2 \\
\text{HA} + MA^+ \rightarrow MA_2 + H^+ \\
(2)
$$

where the successive constants $k_1$ and $k_2$, called stepwise formation constants (Manahan, 1979) are given by:

$$
k_1 = \frac{(MA^+)(H^+)}{(HA)(M^{2+})} \hspace{1cm} (3)
$$

$$
k_2 = \frac{(MA_2)(H^+)}{(HA)(MA^+)} \hspace{1cm} (4)
$$
The overall formation constant, \( K \), is given by:

\[
K = k_1 \cdot k_2 = \frac{(MA_2)(H^+)^2}{(HA)2(M^{2+})}
\]  

There are different methods to measure this constant such as the use of ion exchange equilibria and the method of continuous variation (Schnitzer and Hansen, 1970), potentiometric titration (Stevenson, 1976), gel filtration (Baham et al., 1978) and paper chromatography (Takamatsu et al., 1983).

In general, the stability of complexes of the various metals seems to follow the Irving-Williams order of stabilities of chelates formed by metal ions with ligands (Mantoura et al., 1978). The order is a function of a combination of the valency of a metal cation (Z), its ionic radius (R) and the ionisation potential (I₂), and is positively correlated to the latter two. The order most accurately applies to the transition metals. According to this order, the stability order is: \( Mg < Ca < Cd = Mn < Co < Zn = Ni < Cu < Hg \). Takamatsu et al. (1983) found with a paper chromatography test with metal - humic acids a slightly different order: \( Mn < Co = Cd < Zn < Ni < Pb < Hg < Cu \). This could be attributed to experimental discrepancies, however other parameters such as ionic radius, electronegativity, and first hydrolysis constants can be used as a measure to indicate metal adsorption affinity (Table 2.2).

Although humic acids have less metal binding capacity, the stability constants are substantially higher than those of fulvic acids. Stability constants data generally indicate that, under the same conditions, the heavy metals cadmium, nickel, and zinc are less strongly complexed to soil humic substances than copper or lead (Bunzl et al., 1976; Page et al., 1981).

The influence of \( pH \) on the stability constant

It has been concluded that the \( pH \) of the soil solution has a significant effect on the stability constant, which increases with increasing \( pH \) (Schnitzer & Skinner, 1966 & 1967; Schnitzer & Hansen, 1970; Mantoura et al., 1978). This is probably caused by two different processes.
Firstly, the pH is important in determining the solubility and the state of hydrolysis of the metal cations and therefore their ability to complex with humic or fulvic acids. Secondly the charge of the humic matter depends on the pH. At low pH values, humic acid molecules for instance are aggregated into colloidal particles with very little or no charge. If the pH is increased the negative charge on the molecule increases as dissociation occurs. At the same time the aggregates disintegrate, as the molecules become more hydrated, until they are all completely dispersed in solution (Ritchie and Posner, 1982).

Kiekens (1983) showed that in fact there are two stability maxima for humic and fulvic acids, one occurring at pH 6 and another at pH 9. This might be attributed to the different dissociation constants of functional carboxyl (-COOH) and hydroxyl (-OH) groups.

The pH also influences the order of stability. Schnitzer and Skinner (1966, 1967) reported an order change from Mg < Mn < Zn < Ca < Co < Pb < Ni < Fe < Cu at pH 3.5 to Mg < Zn < Ca < Co = Mn < Ni < Fe < Pb < Cu at pH 5.0. The change in order of metals relative to the results of Takamatsu et al., 1983 and the theoretical Irving-Williams order show the relevance of experimental conditions and the complexity of making accurate theoretical predictions.

The organo-metallic complex stability increases with increasing pH and the solubilisation of metallic ions increases with a decreasing pH. This effect may result from the competition that exists between the metal and the hydrogen ions for the weakly acidic complexation sites. Freundlich isotherms suggest that cadmium, nickel, and zinc tend to displace one hydrogen ion, while copper displaces two hydrogen ions for each complex formed (Lake, 1987).

The influence of ionic strength on the stability constant

Schnitzer and Hansen (1970) noted a marked effect of ionic strength on the stability constants (log K) of metal - fulvic acid complexes (Figure 2.6).

With increasing ionic strength (I), the stability constants decrease. This is probably due to the increase in competition between the different ions in solution to complex with organic matter when the ionic strength of the solution increases. Because the ionic strength of the soil solution is normally low, log K values obtained at very low ionic strength are more
likely to represent conditions existing in the soil solution than those at high ionic strength (Houghton, 1979).

Figure 2.6 Effect of ionic strength on log-K values of metal-fulvic acid complexes at pH 3 (Schnitzer and Hansen, 1970).

2.3.3.3 Valency change of metal ions by humic matter

Humic matter not only forms complexes with metal ions, it seems to be able to reduce these cations as well. This is unrelated to soil environmental factors and microorganisms which are known to have reducing capacities as well. Organic molecules with the capability to complex with metals can potentially increase concentrations of these metals in soil solutions by dissolution reactions at mineral surfaces. Generally the metal complexing ability of the organics within the range of soil pH is a good indicator of their ability to adsorb to metal oxides and enhance mineral dissolution. In the case of Fe oxides, the general reaction is:

Fe (III) - organic complex ----> Fe (II) + oxidised organic.

This reaction is promoted at low pH and is facilitated for Fe (III) - organic complexes involving phenolic groups. It is relevant that soil fulvic acids reduce Fe (III) by an
apparently similar process. Fulvic acids are known to have the ability to increase metal solubility by forming soluble complexes.

A wide range of organic compounds can be oxidised at Mn oxide surfaces. These include diphenolics, salicylic acid, pyruvic acid, oxalic acid and fulvic acids. Certain monophenols, particularly those that have electron donatory substituents on the aromatic ring, when added to soils containing Fe and Mn oxides are chemically oxidised, releasing Fe$^{2+}$ and Mn$^{2+}$ as soluble products. The extent to which the redox processes described herein can increase the solubility of trace metals, apart from Fe and Mn, is has not yet been established, but it is reasonable to expect that the dissolution of efficient metal scavengers such as Mn and Fe oxides will release significant levels of other metals into soil solution (McBride, 1989).

The appearance of phenolics and especially monophenolics is well known in compost, especially in the early stages, when there is an equilibrium between soluble low molecular phenols production and the polymerisation of the phenolics themselves (Saviozzi et al., 1986). These organic compounds can influence the solubility of heavy metals that are adsorbed or complexed onto the Fe, Mn and Al-oxides in compost and soil.

Ghosh et al. (1983) found after sterilising the soil in order to eliminate microbial activity, that humic substances are independently able to change the valency state of metal ions such as iron, copper and manganese. Takamatsu et al. (1983) found a reduction of Hg$^{2+}$ by humic acids during a chromatography test.

2.3.4 Transportation of metal - humic matter complexes through soil

From computer based models it has been shown that a complicated web of interactions can be expected in any natural water that contains hazardous concentrations of heavy metals along with reactive organic compounds (Sposito et al., 1982). The extent of solubilisation of heavy metals depends upon a number of factors, including the stability of the complex; the concentration of the complexing agent; pH; and the nature of the metal deposit. The situation is even more complicated in the soil solution.
The pH of the soil solution plays a major role in determining whether heavy metal-humic matter complexes become soluble and can be transported through the soil. Tan and Binger (1986) studied the effect of soil humic acid on aluminium toxicity in corn plants in a low pH sand culture. Addition of humic acids prevented a sharp reduction in dry matter production and aluminium toxicity symptoms disappeared. The high amount of aluminium had complexed with the insoluble humic acids at low pH. Hargrove (1986) found at pH values greater than 5 that Al-organic matter complexes could become solubilised and followed by Al absorption by plant roots.

Desorption of transition and heavy metals from organic matter, a process involving displacement of organic ligands by water, is one of the mechanisms which can cause release of metals from solid complexes into the soil solution. Often those metals that are adsorbed rapidly are desorbed very slowly. Desorption often needs a large activation energy to overcome the energy of adsorption, especially when the metal is a complex with an organic ligand as inner-sphere complex (McBride, 1989).

Lagas and Loch (1981) found that iron, zinc, nickel and lead were mobilised in synthetic landfill leachate using fatty acids.

2.3.5 Humic matter interaction with the soil mineral fraction

Humic substances are able to form complexes with minerals such as clay particles. These complexes are important in the cycling of chemical elements and formation of soil aggregates. Humus bound to soil mineral surfaces is relatively stable against biodegradation. Since the complex nature of humic substances, apart from the functional groups, is not fully understood, the reactivity with clay particles can be explained only in so far as the behaviour of functional groups is known.

A number of mechanisms exist for the association between organic functional groups and soil minerals. The two main ones are cation exchange and ligand exchange. Others include protonation, water and cation bridging, hydrogen bonding and van der Waals interactions.

The cation exchange mechanism can be represented by the following reaction:

\[ \text{B}^+_{(aq)} + \text{M} \equiv \rightarrow \text{B} \equiv + \text{M}^+_{(aq)} \]
where B is a quaternised nitrogen atom, usually a protonated amino group (NH$_3^+$), in an aliphatic chain or heterocyclic aromatic ring. M$^+$ is a monovalent exchangeable metal cation bound to a clay mineral surface (s) (Schnitzer and Khan, 1972).

The ligand exchange mechanism forms direct bonds between carboxylate groups and either Al or Fe(III) in a soil mineral bearing hydroxyl groups. The general reaction equations can be expressed as:

\[- \text{MOH}_\text{H}_\text{(s)} + \text{H}^+\text{(aq)} \rightarrow \rightarrow - \text{MOH}_\text{H}_\text{(s)}^2^+\]

followed by,

\[- \text{MOH}_\text{H}_\text{H}_\text{(s)}^2^+ + \text{S} - \text{COO}^- \rightarrow \rightarrow - \text{MOOC} - \text{S}_\text{(s)} + \text{H}_2\text{O}_\text{(l)}\]

Where \(- \text{MOH}\) represents 1 mol of reactive hydroxyls bound to a metal M (= Al or Fe) in a soil mineral and \(- \text{S} - \text{COO}^-\) is 1 mol of humus carboxylate groups. The initial protonation reaction is thought to promote the actual ligand exchange reaction (OH$_2^+$ for COO$^-$). Thus ligand exchange is favoured at low pH. Further reactions would see MOOC - S$_\text{(s)}$ transfer from the mineral surface to the soil solution, which demonstrates the role of organic matter in chemical weathering (Sposito, 1984).

Roy (1971) found that small amounts of humic matter could disperse kaolinite particles in suspension, possibly by neutralisation of the hydrogen bonds by the low humic matter electronegativity at low concentrations. On the other hand, humic matter could conceivably cement clay particles together to form stable aggregates (Jackson, 1975), in accordance with the aforementioned mechanisms.

Tan (1975) made an attempt to investigate the complex formation between clay and humic and fulvic acids to obtain more detailed information. After studying infrared spectra from the clay particles and the humic and fulvic acids he concluded that humic acids might have attacked the clay mineral, liberating and complexing Si and Al ions from tetra- and octahedral positions.

Both cation and ligand exchange mechanisms are relevant to interaction of organic matter with red mud since red mud is saturated with monovalent exchangeable cations (Na$^+$) and a major part of the mineral fraction consists of Al and Fe oxides.
2.3.6 Photo physical characteristics of humic materials as a measure for compost maturity

2.3.6.1 Introduction

The visible and ultraviolet (UV) regions in the electromagnetic spectrum are from 800-400 nm and from 400-200 nm respectively. The visible and UV spectra of organic compounds are associated with transitions between electron energy levels. The transitions are generally between a bonding or lone-pair orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength at which the light is absorbed is then a measure of the separation of the energy levels of the orbitals concerned (Williams, 1966).

In general, humic substances yield uncharacteristic spectra in the visible and ultraviolet regions. Absorption spectra of alkaline and neutral aqueous solutions of humic acids (HA) and fulvic acids (FA) and of acidic aqueous FA solutions are featureless, showing no maxima or minima; the optical density usually decreases as the wavelength increases.

Occasionally an indication of a maximum can be discerned in the 260 - 300 nm region. Sposito et al. (1976) found this in fulvic acid spectra from sewage sludges in a NaHCO₃ solution. It is noteworthy that UV spectra of humic substances of different origins are very similar in spite of differences in elementary composition, sedimentation characteristics and other properties.

Light absorption by humic substances appears to increase with an increase in (a) the degree of condensation of the aromatic rings which they contain; (b) the ratio of carbon in aromatic "nuclei" to carbon in aliphatic or alicyclic side chains; (c) total carbon content; and (d) molecular weight (Choudry, 1984b). During stabilisation the higher molecular weight humic acids (>10,000) are broken down into the lower molecular weight fulvic acids. The spectra for fulvic and humic acids can be expressed in % transmittance or in optical density (cm⁻¹). Sposito et al. (1976) used % transmittance.

Several researchers investigated the use of photophysical properties of the soluble organic matter fraction as an indicator for compost maturity (Kononova, 1966; Schnitzer and Khan,
1972; Witter and Lopez-Real, 1986). During stabilisation the higher molecular weight humic acids (>10,000) are broken down into the lower molecular weight fulvic acids.

2.3.6.2 Absorption laws

Two empirical laws have been formulated about the absorption intensity.

Lambert’s law: The fraction of the incident light absorbed is independent of the intensity of the source.

Beer’s law: The absorption is proportional to the number of absorbing molecules.

The equation of Lambert - Beer: \(10 \log (I_0/I_t) = E \cdot l \cdot c\)

\(I_0 = \) Intensity of the incident light.
\(I_t = \) Intensity of the transmitted light.
\(E = \) Molar extinction coefficient.
\(l = \) Path length of absorption solution (cm).
\(c = \) Concentration (mol/l).

(Bolt and Bruggenwert, 1978)

2.3.6.3 \(E_4/E_6\) ratio

The ratio of optical densities (OD) or absorbances of dilute aqueous HA and FA solutions at 465 and 665 nm, known as the \(E_4/E_6\) ratio, is often used for the characterisation of humic substances. The \(E_4/E_6\) ratio or well-index is used as an indicator for the maturity or state of humification of organic material (Kononova, 1966; Schnitzer and Khan, 1972; Almendros et al., 1983; Chen et al., 1977).

The \(E_4/E_6\) ratio is independent of the concentration of the humic materials, but varies for humic substances extracted from different soils, sludges and compost (Choudry, 1984b). A two- or threefold dilution of the extract should not affect the ratio; this expectation is based on the Lambert-Beer law’s validity for the humic material (Sposito et al., 1976).

A large number of soils have been characterised by means of their \(E_4/E_6\) ratio, however no reference standards have been developed. Fulvic acids generally have a \(E_4/E_6\) ratio varying
between 5 - 11. The $E_4/E_6$ ratio for humic acids is lower and varies between 2 - 6. Humic acids have a higher molecular weight and a higher level of condensation. Generally the FA's have higher ratio's than the HA's (Schnitzer and Khan, 1972).

Chen et al. (1977) concluded that the $E_4/E_6$ ratio of HA's and FA's was:

(I) mainly governed by the molecular size or weight;
(II) affected by the pH;
(III) correlated with the free radical concentration, contents of O, C, COOH, and total acidity in as far as these parameters are also functions of (I);
(IV) apparently not directly related to the relative concentration of aromatic condensed rings; and
(V) independent of HA and FA concentrations, at least in the 100 - 500 ppm range

(Choudry, 1984b).

In research by Witter and Lopez-Real (1986) the $E_4/E_6$ ratio was used as a measure for the compost stability during monitoring the composting process. Witter and Lopez - Real found that the $E_4/E_6$ ratio of the humic acids increased during composting, and in a pattern very similar to that of dry solid losses. This indicated that significant qualitative changes occur in the humic acid fraction during the composting. The values they found ranged from 1.3 to 7.5.

Saviozzi et al. (1986) did research on compost maturity by examining water extracts and found that the $E_4/E_6$ ratios increased as composting progressed. The composting process is the biochemical decomposition of organic matter, during which insoluble substances are decomposed into soluble components by oxidation, part of which are subsequently metabolised into microbial cells. The trends they found in $E_4/E_6$ values for the water soluble components seemed to reflect a progressive relatively smaller molecular size (Chen et al., 1977) and a lower degree of humification, of the water soluble organic matter. Nevertheless, the classic analysis of humified organic matter, accomplished by spectroscopic measurements for characterisation purposes, is not likely to be satisfactory in this context, since changes in this parameter should give a measure for the maturity of compost, and the progressive increases of the optical densities are principally the reflection of the decreasing carbon content of the solutions (Saviozzi et al., 1986). The latter statement
is partly supported by Chen et al. (1977) who showed a correlation between the carbon content of humic matter and the $E_4/E_6$ ratio.

In general, humification of organic matter is reflected in an increase in the $E_4/E_6$ ratio.

2.3.6.4 ΔLogK

Another parameter that has been used to monitor the maturity of organic substances is Δlog K (Almendros et al., 1983; Chen et al., 1977). The definition of this parameter is the difference in the logarithmic absorbances at 400 and 600 nm of 0.01% humic or fulvic acid solutions prepared by dissolution in 0.1 M NaOH.

Usually the Δlog K value in soil organic matter becomes smaller as humification proceeds. This was found by Takamatsu et al. (1983). The values they determined were between 0.4 and 1.2. They also found indications that the combining strength of humic acids and metals increases as humification proceeds, probably reflecting increased amounts of carboxyl and carbonyl groups as humification progresses.

Saviozzi et al. (1986), who did research on compost maturity by water extract analyses, found increasing values for Δlog K as the composting process progressed. They found values between 1.10 and 1.30 but in their article they did not provide details on the preparation of the samples, didn’t state whether fulvic or humic acids were used or a mixture and did not follow the alkaline extraction procedure which forms part of the definition of Δlog K.

2.3.7 Conclusion

During its biochemical decomposition during composting, organic matter is oxidised and soluble organic acids containing functional groups are formed. These functional groups are easily ionised in solution and give the organic acids an anionic character. The soluble organic acids can form strong complexes with metals in solution. Since in a soil environment these complexes are more stable than the exchangeable metal complexes with the inorganic soil fraction, the organic acids are important scavengers of metals from solution as well as from the inorganic phase and function as a carrier for metals in the
environment. This process is not desirable from an environmental viewpoint. In order to reduce the role of soluble organic acids as metal carriers, two mechanisms are available: firstly by reducing the metals available for adsorption to organic acids by strong complexation of the organic acids with an inorganic fraction and secondly by reducing the solubility of the organic acids. Al- and Fe-oxides and clay particles can form complexes with soluble organic acids with the result that the solubility of the latters is reduced.

2.4 Bauxite refining residue

Section 2.4.1 is an adaptation of a review on the subject by Wong (1991).

2.4.1 Bauxite refining residue production

Virtually all alumina (Al₂O₃) is refined from bauxite via the Bayer process developed by Karl J. Bayer in 1887 (Hudson et al., 1983). The Bayer process takes advantage of the fact that gibbsite (Al(OH)₃) and boehmite (AlOOH) are soluble in sodium hydroxide (NaOH). In Western Australia, the bauxite is high in gibbsite. Crushed bauxite is digested in a strong caustic soda solution at a temperature of 143°C and a pressure of at 250 kPa (Robson, 1982).

The clay minerals, consisting of reactive silica, mainly as kaolinite, in Darling Range bauxite dissolve and recrystallise under high temperature and pressure as relatively insoluble sodium-aluminium-silicates known as the "Desilication Product (DSP)". DSP is not a single compound but a series of zeolites (Leiteizen et al., 1975). The DSP is saturated with sodium.

With the Al₂O₃ in solution, the next step is to remove the solid residue by sedimentation and filtration. This separation must be as complete as possible because any remaining solids will contaminate the product. The coarse fraction of the residue larger than 100μm can be removed easily by liquid - solid cyclones or more primitive settling chambers. The desanded slurry is then pumped to a thickener which removes the remaining residue by sedimentation.

The residue, both sand and mud, are separately washed with residue pond water by countercurrent decantation. The aim of washing the residue is to minimise the amount of
soluble salt in the residue and the reduced cost of drying by evaporation that the dilution introduces. After washing, the residue is discarded to tailing ponds (Hudson et al., 1987).

The fine fraction of size < 150μm is called red mud. Fine bauxite residues mainly consist of very fine particles with a diameter smaller than 0.02 mm (Table 2.3). This particle distribution classification gives red mud a very high specific surface on which both anions and cations can be adsorbed.

The dried red mud is being trialled as an amendment to the local sandy soils to improve its water and nutrient retention capacity. However due to the high alkalinity in the red mud (pH 12) it is amended with 10% gypsum prior to its use as an amendment to form so called red mud - gypsum which has a lower pH of 8.2 (Barrow, 1982).

Table 2.3 Particle size distribution of bauxite refining residue from different refineries.

<table>
<thead>
<tr>
<th>Fraction (mm)</th>
<th>Point Comfort¹</th>
<th>Kwinana²</th>
<th>Mobile³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (2-0.02)</td>
<td>8</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Silt (0.02-0.002)</td>
<td>66</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Clay (&lt;0.002)</td>
<td>26</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

¹Hossner et al., 1984; ²Thornber et al., 1985; ³Parekh and Goldberger, 1978

The major environmental concern of alumina production is disposal of the bauxite residue. The production of residue averages 1 tonne per tonne alumina and varies according to the type of bauxite. In Western Australia, the total bauxite residue produced was about 12 million tonnes in 1986 (Glenister, 1987).

2.4.2 Metal binding ability of fine bauxite residue

2.4.2.1 Ion exchange

The permanent charge sites of layer silicate clays retain cations by non specific electrostatic forces. Empirical ion exchange selectivity diagrams suggest a very high preference of clays
for higher charge cations at low ionic strength (McBride, 1989). This high selectivity does not arise from a specific bonding mechanism, but is a consequence of the stoichiometry of the ion exchange equation. For example Cu$^{2+}$/Na$^+$ exchange (McBride, 1989):

$$\text{Cu}^{2+} + 2 \text{Na}^+ -\text{clay} \rightleftharpoons \text{Cu}^{2+} -\text{clay} + 2 \text{Na}^+$$ (6)

The selectivity coefficient:

$$K_s = \frac{(m_{\text{Na}})^2 \times n_{\text{Cu}}}{m_{\text{Cu}} \times (n_{\text{Na}})^2}$$ (7)

$m_{\text{Na}}, m_{\text{Cu}} = \text{molarity of metal in solution phase.}$  
$n_{\text{Na}}, n_{\text{Cu}} = \text{fraction of clay exchange sites occupied by these ions.}$

If the cations behave as an ideal solution in the clay phase, then $K_s$ should remain relatively constant with changing ionic strength. Every different electrolyte concentration and clay concentration will produce a different adsorption isotherm.

In the red mud matrix, heavy metals must compete with Na$^+$, Al$^{3+}$ and Ca$^{2+}$, in cases where gypsum has been added, for exchange sites. Based on available evidence it is unlikely that clay exchange sites limit trace or heavy metal solubility in soils, generally (McBride, 1989). No specific ion exchange data are available for red mud, though many of its minerals are common in soils. More selective mechanisms are indicated to operate in red mud considering the low extractability of metals from red mud. Nevertheless, in metal polluted soils, exchange sites have an important role in attenuating the movement of metals through the soil (McBride, 1989). Thus red mud can be suitable to reduce the mobility of metals in a compost matrix.

The colloidal fraction of the red mud, consisting of clay particles (fraction < 2 μm), amorphous oxides and hydroxides of Fe and Al, acts as an ion exchanger. Metal ions in solution compete for the ion exchange sites of red mud. The amount of a specific cation which will adsorb onto the solid phase depends on the cation exchange capacity (CEC) of the red mud, the concentration of this cation in solution and, if there are different species of cations in solution, on the charge and the size of the cations. The CEC is the maximum
amount of exchangeable cations a soil mineral can hold expressed in milli-equivalent per 100 g dry soil. Under certain conditions, one finds that certain ions are preferentially adsorbed, sometimes giving rise to partly irreversible reactions ((Bolt and Bruggenwert, 1978).

The CEC of red mud can assist in reducing the mobility of soluble heavy metals by attenuation of a considerable amount of heavy metals on the exchange sites. The coarse sandy soils of the Swan Coastal plain have a low clay content and hence a low CEC.

The exchange of cations on red mud is determined by two groups of minerals, the zeolites (DSP, 11%) formed during the refining process and the non-zeolites such as haematite (Fe₂O₃, 14%), goethite (FeOOH, 15%), gibbsite (Al(OH)₃, 9%), Al-goethite (AlOOH, 5%) and clay minerals such as muscovite (10%) (ALUTERV - FKI, 1983).

The cation exchange sites can be classified as surface exchange sites and internal exchange sites. The DSP framework consists of a network of very fine channels that only allow passage of monovalent cations. It has been found that 70 % of the sodium in red mud is adsorbed on the internal sites. The internal exchange capacity was found to be about 50 meq/100 g. These sites are not accessible for the much larger divalent or trivalent heavy metals (Wong and Ho, 1988).

The surface exchange sites of the non-zeolitic minerals and the DSP have a combined cation exchange capacity of about 25 meq/100 g. These sites are available for adsorption of heavy metals by cation exchange (Wong and Ho, 1988).

2.4.2.2 Precipitation

A free metal ion Meⁿ⁺ in the soil solution will precipitate when the solubility product (Kₛ) with its reaction partner Rᵐ⁻ is exceeded. If the ion concentrations reduce and the solubility product is not exceeded the precipitate will redissolve.

\[ m \text{Me}^{n+} + n \text{R}^{m-} \rightleftharpoons \text{Me}_m \text{R}_n \]  \hspace{1cm} (8)
In this way metal precipitates of hydroxide, carbonate and phosphate can be formed. The solubility of the metal ion Me\textsuperscript{n+} can be calculated with the solubility-product \textit{K}_s (eq. 9):

\[
\textit{K}_s = (\text{Me}^{n+})^m \cdot (R^{m-})^n
\] (9)

The brackets indicate ion activities, not concentrations, since concentrations depend on the ionic strength of the solution.

\[-\log (\text{Me}^{n+}) = \frac{1}{m} \frac{1}{pK_s} + \frac{n}{m} \log (R^{m-})\] (10)

if R\textsuperscript{m-} = OH\textsuperscript{-}, then (with pH + pOH = 14):

\[-\log (\text{Me}^{n+}) = pK_s + n(pH - 14)\] (11)

There is a direct correlation between the metal concentration and the pH of the solution, because the solubility product is a constant. The negative logarithm of solubility products of relevant heavy metal ions with OH\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} are given in Table 2.4.

Table 2.4 Negative logarithm of the solubility product of metal precipitates (pK\textsubscript{s}).

<table>
<thead>
<tr>
<th>Metal</th>
<th>OH\textsuperscript{-}</th>
<th>CO\textsubscript{3}\textsuperscript{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>20.3\textsuperscript{®}</td>
<td>6.2\textsuperscript{®}</td>
</tr>
<tr>
<td>Cr</td>
<td>30\textsuperscript{#}</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>13.8\textsuperscript{®}</td>
<td>8.5\textsuperscript{®}</td>
</tr>
<tr>
<td>Ni</td>
<td>15.2\textsuperscript{*}</td>
<td>6.9\textsuperscript{*}</td>
</tr>
<tr>
<td>Pb</td>
<td>17.8\textsuperscript{®}</td>
<td>4.7\textsuperscript{®}</td>
</tr>
<tr>
<td>Zn</td>
<td>16.8\textsuperscript{®}</td>
<td>7.9\textsuperscript{®}</td>
</tr>
</tbody>
</table>

\textsuperscript{®} activity constants, independent of concentration, Lindsay, 1979

\textsuperscript{*} ionic strength 0.5, Smith and Martell, 1976

\textsuperscript{#} Aylward and Findlay, 1971

There is a general consensus that in soils, the amount of transition and heavy metals in solution is not controlled by the solubility product of a pure solid phase. Nevertheless,
-there are cases where precipitated solid phases may determine the amount of metals in solution, usually in situations of high metal loadings.

An underlying problem associated with adsorption experiments is distinguishing true chemisorption and cation exchange processes from precipitation (McBride 1989), since precipitation of metals for example as their hydroxide (Cr) or sulphate (Pb) could incorrectly be attributed to adsorption of these metals.

The incorporation of red mud - gypsum into compost is likely to increase the pH in the top layer of a soil to which this 'red mud - compost' is applied. The high alkalinity in red mud is due to the presence of NaOH, Na₂CO₃, NaHCO₃ and Na₂(AlO)₃ in the entrained liquor. These compounds are formed as a result of atmospheric exposure in the red mud impoundment where the residual hydroxide reacts with carbon dioxide to form bicarbonate and subsequently carbonate depending on the pH. Heavy metals in compost mixed with red mud thus have the opportunity to precipitate as metal hydroxides or carbonates and so can be prevented from leaching out or being available for plant uptake. Red mud with a pH higher than 9.6 contains a large amount of CaCO₃. But because the pH of red mud - gypsum is lower than 9.6 (ie. 8.2), there is just a small amount of CO₃²⁻ in solution, therefore precipitation of the heavy metals as metal hydroxides is more likely than as metal carbonates. Both hydroxide and carbonate precipitates of heavy metal have a very low solubility and are thus useful in controlling the release of immobilised metals, along with pH control.

2.4.2.3 Chemisorption

There is no lack of evidence that transition and heavy metals in soils when present at trace levels are retained largely in non exchangeable forms by covalent bonds with soil particles. Schemes for complete metal extraction require extreme treatments, including the oxidative degradation of organic matter and dissolution of Fe and Mn oxides. It is now established that metal oxides and hydroxides as well as amorphous alumino - silicates provide surface sites for chemisorption of heavy metals (McBride, 1989). Indirect evidence for the formation of surface metal bondings includes:

1. the release of as many as two H⁺ ions for each M²⁺ adsorbed;
2. the high degree of specificity shown by oxides for particular metals; and
3. changes in the surface charge properties of the oxide as a result of adsorption.

It is very unlikely that all oxides bind the heavy metals by a similar mechanism. UV-visible spectroscopy and other less direct techniques indicate that Ni$$^{2+}$$ and Co$$^{2+}$$ are adsorbed on silica as the hydrated metal, in contrast to their behaviour on Al and Fe oxides. Confirming evidence shows Cu$$^{2+}$$ to be adsorbed on silica at low pH, but there are indications that this surface complex is unstable relative to Cu(OH)$_2$. As the pH is raised, adsorption on oxides inevitably merges into precipitation (McBride, 1989).

Oxide surfaces possess selectivity for certain heavy metals, and although the order of preference is roughly consistent with the tendency of the metals to hydrolyse, there are notable exceptions. Metal affinities for amorphous Fe-hydroxides have been reported to be in the following order:

Pb$$^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} >= Co^{2+} > Sr^{2+} > Mg^{2+}$$

Amorphous Al-hydroxides produce a somewhat different sequence:

Cu$$^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} >= Cd^{2+} > Mg^{2+} > Sr^{2+}$$

Metal affinity for the silanol groups of silica follows the order:

Pb$$^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} = Cd^{2+} > Sr^{2+} > Mg^{2+}$$ (McBride, 1989)

A complicating factor for models of metal adsorption on oxides is the formation of so-called ternary complexes. Although some metal-complexing ligands such as EDTA suppress metal adsorption, others enhance adsorption by forming stable surface-metal-ligand (ternary) complexes. Inorganic as well as organic ligands can be involved in ternary complex formation. For example Zn$$^{2+}$$ adsorption by Fe/Al oxides, clays and soil is enhanced by the presence of phosphate or sulfate. Also, phosphate adsorption by gibbsite is enhanced by the presence of metals such as Cu$$^{2+}$$ and Cd$$^{2+}$$, again suggesting the adsorption of a metal phosphate complex (McBride, 1989).

Mixtures of compost with red mud - gypsum contain relatively high concentrations of sulphates (gypsum), phosphates (compost), and Al- and Fe-hydroxides (red mud). It is thus likely that both chemisorption and the formation of ternary complexes would play a significant role in the attenuation of heavy metals by a red mud - gypsum - compost matrix.
The precipitation of metal phosphates or of metal hydroxides on which phosphate subsequently might adsorb may confuse the issue of ternary complex formation involving phosphate and other oxy-anions. However, monomeric metal-phosphate pairs do appear to form at oxide surfaces, which suggests that metal-enhanced phosphate adsorption and phosphate-enhanced metal adsorption are dependent on this same reaction (McBride, 1989).

It is difficult to distinguish the processes of metal chemisorption, co-precipitation and electron transfer on the oxides, as all have the effect of strongly scavenging heavy metals from solution.

**Reversibility**

Different measures of reversibility or lability are used in assessing metal extractability. These include:

1. exchangeability of metals by cations that do not specifically adsorb;
2. exchangeability of metals by specifically adsorbing cations;
3. pH reversibility;
4. isotope exchangeability;
5. desorbability by chelating agents; and

Desorption is a function of the stability constant of the complex, cation exchange equilibrium and the pH. However, when metal sorption is achieved by increasing metal concentrations, a lowering in metal concentration generally results in very little desorption (McLaren et al., 1986). Whether this refers to true irreversibility or a very slow rate in the reverse direction is unclear. This process was demonstrated for Pb$^{2+}$ in a goethite suspension by Hayes and Leckie (1986).

Adsorption through chemisorption may or may not require an activation energy, $E_a$, but desorption always requires an activation energy, $E_d$, since desorption necessitates that the energy of adsorption, $\Delta H$, be overcome (Adamson, 1976). Thus the activation energy for desorption energy can be described as:

$$E_d = E_a + \Delta H$$
Thus the activation energy for desorption is much higher than that for adsorption resulting in a much slower rate of desorption. Since $\Delta H$ is higher at lower levels of chemisorption, the desorption rate is even slower at low sorption levels. The often reported hysteresis in metal sorption reactions may thus reflect a non equilibrium condition caused by slow desorption instead of true irreversibility (McBride, 1989).

Desorption rate is an important factor in the concept of immobilising heavy metals in a productive soil environment, in order to assess the future fate of these metals. Accumulation of metals in the soil as a result of continued application of red mud compost is undesirable. However, the release of these metals at rates that ensure that the reactive metal concentrations in soils remain below such levels that they do not pose a threat to environmental and human health is a way of safely returning the metals to the environment.

2.4.2.4 Adsorption isotherms

The adsorption of heavy metals onto the solid phase of a soil can be described by using adsorption isotherms. As was shown in the previous sections, there are various mechanisms available to red mud to remove metals from solution. Adsorption isotherms can be obtained by adding a solution with a high adsorbate concentration to a fixed amount of adsorbent (batch process). After the system has reached equilibrium, the amount of adsorbate in the solution can be measured and then the amount adsorbed can be calculated. The results are usually graphically presented as a plot of the amount adsorbed (mg/100 g) vs. equilibrium concentration in the solution (mg/l) at a certain temperature and pressure. The plots can be classified in four classes (S, L, H and C-curves) each representing a different adsorption behaviour. Figure 3.1 shows the different curves of the classes.

The S-curve isotherm suggests an increasing affinity of the adsorbent for the adsorbate after a few molecules have been adsorbed. The L-curve, however, shows that the adsorbate adsorbs rapidly even in a dilute solution. The H-curve is similar to the L-curve but the initial part of the curve is nearly vertical which implies that the adsorbate in dilute conditions is completely adsorbed. Finally the C-curve shows an adsorbate which is partitioned equally over both the liquid and the solid phases.
Adsorption and desorption isotherms can be very useful in predicting the behavior of heavy metals in solution when a solid phase is present. Adsorption isotherms do not distinguish between any particular adsorption mechanism, such as chemisorption, ion exchange or even whether adsorption, as opposed to precipitation, actually has occurred.

Figure 2.7 Representative examples of the 4 curves of the different classes of adsorption (Sposito, 1984).

Two equations are widely used to describe these isotherms. These are the Freundlich and Langmuir equations (Harmsen, 1979).

**Freundlich equation**

The amount of cations adsorbed can be described by:

\[ q = k \cdot C^{1/n} \]

in which:  
- \( q \) = amount of cations adsorbed on adsorbent (mg/100 g)  
- \( C \) = equilibrium concentration of cation in solution (mg/l)  
- \( k \), \( n \) = constants (\( n > 1 \))
This equation can be written in double log form, so that \( k \) and \( n \) can be easily determined.

\[
\log q = \log k + \frac{\log C}{n}
\]

The constants \( k \) and \( n \) can be found by plotting \( \log q \) versus \( \log C \). The slope of this line is \( 1/n \) and the \( y \)-intercept \( \log k \).

The shortcomings of the Freundlich equation are:

1. The equation does not express \( q \) as a linear function of \( C \) at low concentrations.
2. The equation does not provide for a maximum in the value of \( q \).

Langmuir equation

According to the Langmuir equation the extent of adsorption is dependent on the maximum adsorption capacity of the adsorbent.

\[
q = \frac{K \cdot Q \cdot C}{(1 + K \cdot C)}
\]

in which:

\( q \) = amount of cations adsorbed on adsorbent (mg/100 g),
\( Q \) = maximum amount of cations which can be adsorbed on the adsorbent (mg/100 g),
\( C \) = equilibrium concentration of cations in solution (mg/l),
\( K \) = constant, which is a measure of the binding strength of the adsorption sites for the cations adsorbed.

The Langmuir equation is often written in the linear form:

\[
\frac{C}{q} = \frac{C}{Q} + \frac{1}{K \cdot Q}
\]

from which it can be seen that a plot of \( C/q \) against \( C \) yields a straight line with an intercept of \( 1/(K \cdot Q) \) and a slope of \( 1/Q \).

2.4.2.5 Metal mobility

The mobility of metals in a soil can be assessed on the basis of distinguishing the following levels of extractability of metals; exchangeability by cations that do not specifically adsorb
(CaCl₂), desorbability by extraction using the chelating agent diethylene triamine pentaacetic acid (DTPA) (Lindsay and Norvell, 1978) and dissolution by concentrated acids to obtain a total metal content in the matrix.

The metals extractable form a soil matrix with a CaCl₂ solution are metals that appear in the normal soil solution as well as the very weakly bound metals. These metals easily leach out of the soil into the groundwater aquifer and are also available for uptake by plants. Since plants are capable of extracting cations from soil complexes, the total plant available amount of cations is higher than that is present the soil solution. The metals extracted with DTPA thus include the CaCl₂ extractable metals. The acid extraction supplies the total metal content of the compost, which is essential as a reference for the leachable and plant available metal fractions.

2.4.3 Gypsum as an amendment of bauxite residue

Red mud can be considered a sodic soil due to the saturation of its adsorption sites with sodium and its high pH and dispersed nature. Thus red mud is unsuitable as a productive soil or soil amendment unless its sodicity and pH are reduced. In general, the addition of acidic ameliorants to a sodic soil can initiate permeability increases due to both electrolyte concentration and cation exchange effects (Miyamoto et al., 1975; Loveday, 1976; Shainberg, et al., 1982; Cates et al., 1984). Increases in the electrolyte concentration in soil solutions reduce the dispersion of clay in soil which results in a higher soil permeability. The displacement of sodium by other cations such as calcium can reduce the exchangeable sodium percentage (ESP) in soil, which in turn enhances the water permeability of soil. In a general strongly alkaline soil, the cation exchange effect of replacing sodium by other particularly divalent cations seems to be more important for permanent improvement in soil properties than just increasing the hydraulic conductivity as it permanently reduces the ESP in the soil (Gupta and Singh, 1989).

Different ameliorants including FeSO₄, FeS, S and CaSO₄ have been used to neutralise the alkalinity and reduce the sodicity of bauxite residue (Meecham and Bell, 1977; Fuller et al., 1982; Barrow, 1982; Ward, 1983; Ward 1986; Ho et al., 1985; Hossner et al., 1984). In Western Australia, waste gypsum from a phosphate fertiliser plant in Kwinana, located near Alcoa's refinery is readily available as product for neutralisation of bauxite residue.
The chemical reaction of red mud and entrained liquor with gypsum is shown below:

\[ \text{Na}_2\text{X} + \text{CaSO}_4 \rightarrow \text{CaX} + \text{Na}_2\text{SO}_4 \] (13)

In which \( X \) in weathered bauxite residue exists mainly as carbonate. Hence \( \text{CaCO}_3 \) forms as the end products of the above reactions, since the solubility product of \( \text{CaCO}_3 \) is much lower than that of gypsum (\( \text{CaSO}_4 \)). Since the carbonate is effectively insoluble, the reaction equilibrium moves to the right.

Gypsum is a commonly used amendment for remediation of sodic and alkaline soils because of its low cost and general availability. Through the precipitating of \( \text{CO}_2^{2-} \) as \( \text{CaCO}_3 \), gypsum dissolution can reduce soil pH to a level similar to that in a calcareous soil (Barrow, 1982; Ward, 1983). The theoretical pH of a soil buffered with calcium carbonate in equilibrium with atmospheric carbon dioxide is about 8.3 (Bolt and Bruggenwert, 1978). Moreover, \( \text{Ca}^{2+} \) dissolved from gypsum increases soil electrolyte concentration and can exchange with sodium in the exchangeable sites. The replacement of sodium from the exchange sites has a permanent effect in reducing sodium in the soil. This will reduce soil ESP and increase the rate of water infiltration.

Gypsum has been found to be an effective ameliorant for red mud. A 5% w/w gypsum addition was found to be sufficient to neutralise the alkalinity of red mud (Barrow, 1982). Excess gypsum must be applied due to the slow release of the potential alkalinity from red mud which may result in a gradual increase in pH, sodium concentration and sodium adsorption ratio (SAR) (Ho et al., 1985; Hossner et al., 1986). Excess gypsum can provide red mud neutralisation capacity to counteract further release of alkalinity.

2.4.3.1 Effect of gypsum on red mud amended organic matter

The reduction in alkalinity of red mud is of importance to the stability of organic matter when mixed with red mud. High alkalinity reduces the stability of organic matter and thus increases solubilisation of organic matter. This may lead to mobilisation of metals that had formed stable complexes with the organic matter. The increase in the divalent/monovalent or \( \text{Ca}^{2+}/\text{Na}^{+} \) ratio in the electrolyte has a flocculating effect on the soluble organic matter fraction. Thus the addition of gypsum counters the dispersive effect of high sodium levels.
in the red mud and reduces organic matter solubilisation. The reduction in pH also increases phosphate adsorption by reducing competition for adsorption sites with hydroxyl ions.

2.4.3.2 Effect of gypsum on metal adsorption capacity of red mud

The addition of CaSO₄ to red mud should enhance the heavy metal adsorption capacity of the red mud matrix. A number of researchers have found that Zn²⁺ adsorption by iron and aluminium oxides, clays and soil is enhanced by the presence of phosphate or sulfate through the formation of Zn-sulfate or -phosphate surface complexes (Stanton and Burger, 1970; Newton, 1971; Bolland et al., 1977; Moraes, 1982; Shuman, 1986). The same has been found for cadmium (Benjamin and Leckie, 1982).

Indirectly, CaCO₃ which is formed following gypsum amendment of red mud, acts as a chemisorption site for cadmium, zinc, lead, and for copper which forms malachite (Cu₂CO₃(OH)₂) (McBride, 1979, 1980; Brummer et al. 1983; McBride and Bouldin, 1984). The metals displace Ca²⁺ at the hydrated CaCO₃ surface to form a metal carbonate. The reaction is very fast, is enhanced at higher CaCO₃ levels in suspension and proceeds even if the solution is undersaturated with respect to solid metal carbonate e.g. CdCO₃ (Davis et al., 1987). The reaction thus conforms with an adsorption rather than a precipitation process.

2.5 Conclusions

The complexity of the mechanisms controlling the mobility of metals in a red mud - organic matter matrix makes difficult to obtain a clear insight. The conclusions of research in this area vary and are not always consistent.

The main mechanisms that should be looked into in research concerning red mud addition to compost are precipitation - dissolution, adsorption - desorption and the organic matter - metal complexation in these materials.
As for the metal-organic matter complexes, recent literature gives a variety of results, specially for the structures and formation of soluble humic substances and the behaviour of specific metals.

Heavy metal immobilisation by mixing compost with red mud can take place through a number of processes:

- precipitation of metal hydroxides or carbonates;
- adsorption to iron and aluminium oxides in red mud;
- adsorption to the surface sites of the DSP in red mud;
- adsorption to clay minerals in red mud;
- complexation of heavy metals to humic and fulvic acids;
- precipitation of the soluble organic matter with calcium (Ca-humates); and
- adsorption of humic or fulvic acids containing heavy metals to red mud.

For red mud the preferred reaction would be inferred to be the adsorption of heavy metals to the mineral fraction, the aluminium and iron oxides and clay minerals, which are most stable and are not subject to decomposition to the extent the metal-organic matter complexes are. Metal adsorption to the mineral fraction can take place to reach a significant rate at normal soil pH.

The conditions that determine which of these reactions take place are primarily dependent on the heavy metal distribution in the organic matter, the pH, and the nature of the minerals present.
Interaction of heavy metals with bauxite refining residue.

3.1 Introduction

In the microbiological treatment of organic waste, contamination of the waste with heavy metals can cause significant problems during the process and with the marketing or further disposal of the resulting stabilised organic matter. It is often the mobility of heavy metals in a receiving soil that prevents the stabilised organic waste from being used to return organic matter and nutrients to the soil.

It was hypothesised that reducing the mobility of these metals might reduce the environmental impact of recycling organic waste. Reducing the mobility of heavy metals can be achieved by increasing the pH, which promotes precipitation of insoluble metal hydroxides and carbonates, by chemisorption onto Fe- and Al- oxides and by adsorption, through cation exchange, onto the diffuse double layer of clay particles and also Fe and Al oxides.

Red mud has a high alkalinity as a result of its high sodium and carbonate content and has a high content of Fe oxides (31%) and Al oxides (21%) (section 2.4.2.1). This makes red mud potentially very suitable as an agent to immobilise heavy metals. Its high pH (12) requires neutralisation to pH 8 - 8.2 to make red mud suitable for addition to organic waste without affecting the microbial activity during the organic decomposition.

The immobilisation of heavy metals through precipitation by the alkalinity in red mud can be determined theoretically by using the relevant metal solubility products at the prevailing pH level. However, the adsorption of heavy metals through cation exchange or sorption by the Fe or Al oxides is extremely complex and can only be determined empirically.

Therefore the objective of this experiment was to determine the capacity of red mud to remove heavy metals from a solution. This would enable quantification of the metal adsorption capacity of pH neutralised red mud. This is important in relation to the ability of red mud to immobilise heavy metals in liquid form as well as in organic waste and soils,
and in determining whether the metals can be desorbed from the red mud matrix in the longer term in the open environment.

This segment of the study consisted of the following three experiments. In the first experiment the adsorption capacity of red mud for copper and zinc (range 0 - 40 mg/l) was determined after dissolving the desilication product (DSP) and the carbonates in the red mud by briefly reducing the pH to 1 with acid before neutralisation to pH 7, which was chosen as the pH at which the isotherms would be determined to simulate a neutral soil. The time dependency of the adsorption to red mud and effect of metal addition on the settling rate was also determined in this experiment for Cu, Ni and Zn, to assess the flocculating effect of the divalent cations on the dispersed red mud particles.

The second experiment examined the difference in the extent of adsorption of heavy metals between gypsum neutralised red mud and acid neutralised red mud. In addition to the metals examined in experiment I, this study included lead, nickel, chromium and cadmium. The range in metal concentrations in solution used was increased to 0 - 400 mg/l, since red mud was found to have a very high adsorption capacity for metals. In order to determine the preferential adsorption sequence of the metals to red mud, a solution containing all six metals was also equilibrated with red mud.

In the final experiment the adsorption isotherms were determined at a pH range of 7 - 7.4 with a metal concentration range of 0 - 1000 mg/l in an attempt to exhaust the metal adsorption capacity of the red mud matrix.

The three experiments are described individually in the Materials and Methods and Results section, though the discussion of the results is combined for all three experiments.

3.2 Materials and methods

3.2.1 Experiment I

3.2.1.1 Red mud preparation

A representative sample of red mud used in the adsorption isotherm experiment was collected from red mud lakes of the Alcoa of Australia Kwinana refinery and its pH was
neutralised before use, as follows. Air dried red mud was added to a plastic container filled with deionised water. An excess of concentrated nitric acid was added until a pH of 1 was reached in the mixture. At this pH, all the DSP in the red mud is destroyed. Carbonates present are removed as well. DSP has a high CEC for monovalent cations only (Wong and Ho, 1988) thus the removal of DSP does not affect the adsorption capacity for divalent cations. The iron- and aluminium oxides were dissolved during the acidification, but would have reprecipitated during pH neutralisation, thus maintaining or even increasing their metal adsorption capacity. The cation exchange capacity (CEC) of the red mud used in this experiment varied from 15 - 45 meq/100 g (Barrow, 1982; also section 2.4.2.1). The DSP present in the red mud contributed to a large extent to the CEC. When the DSP is destroyed the CEC is estimated to be only 10 meq/100 g (Wong and Ho, 1988). The pH was readjusted with a diluted sodium hydroxide solution to a pH of 7.5 which was sufficiently low to avoid precipitation of metal hydroxides. The red mud was then washed with deionised water to remove soluble salts. The red mud mixture was centrifuged several times until the supernatant had lost its high electrical conductivity. The neutralised red mud was washed and oven dried at 105°C before use.

3.2.1.2 Time dependence of heavy metal adsorption

To determine the time necessary to reach equilibrium between the Cu and Zn in solution and the amounts adsorbed onto the red mud, a batch experiment was carried out. To each of 4 500 ml flasks 20 g of neutralised red mud (pH 7.6) was added, followed by addition of 500 ml of a 10 ppm Cu or Zn solution. A combined solution of these heavy metals (each 10 ppm) was put in the fourth flask. The flasks were placed on magnetic stirrers in a constant temperature room (20°C). In this way a homogeneous mixture was obtained. The flasks were covered with parafilm to prevent evaporation. Pieces of cardboard were placed between the magnetic stirrers and the flasks to prevent heat transfer between the stirrers and the samples. Over a period of 8 days samples were taken each day. One ml of each sample was diluted with deionised water to 5 ml, except in the case of the sample taken on the first day which was diluted to 10 ml. These diluted samples were each filtered using a 0.45 μm membrane filter. To preserve the samples a drop of concentrated sulfuric acid was added to each filtered sample. The samples were analysed for the relevant metals using a GBC-901 atomic absorption spectrophotometer (AAS) with a hydrogen background correction lamp.
3.2.1.3 Adsorption isotherms

Two grams of neutralised red mud were put in plastic dilution tubes and 10 ml of Cu, Ni or Zn solution were added. The concentrations of Cu, Ni and Zn in each solution were respectively: 2.5, 5.0, 10.0, 20.0 and 40.0 ppm. The experiment was carried out in triplicate. The samples were shaken on a Coulter mixer for 5 days (120 hrs) in a constant temperature room (20°C). After shaking, the mixtures were poured into 20 ml measuring columns and the settling velocities in the different mixtures were determined by measuring the fall in the supernatant/suspension interface over time. Thereafter the samples were filtered using a 0.45 μm membrane filter. A drop of concentrated H₂SO₄ was added to preserve the filtrate obtained. The levels of Cu, Ni and Zn present in the filtrate were measured as in section 3.2.1.2.

3.2.2 Experiment II

3.2.2.1 Red mud preparation

For determination of the extent of adsorption of heavy metals on to red mud, the pH in the red mud was reduced to 5.5, in order to exclude precipitation from taking place. In practice gypsum is used for neutralisation of red mud. The pH of red mud amended with 4% gypsum (RMG) was 8.3. At this pH metal precipitation is likely to take place, resulting in inaccurate metal adsorption data. Therefore the adsorption of heavy metals was also determined onto red mud with pH below 7, so that the solubility product for the respective metal hydroxides would not be exceeded.

To obtain red mud with a pH of approximately 5.5 (RMA), air dried red mud was washed first with deionised water. Then the red mud was mixed with deionised water. Concentrated nitric acid was added until a pH of 4.5 was reached. Wong and Ho (1988) found that the pH in an acidic red mud suspension will increase over time (Figure 3.1). The pH was measured regularly. When the pH had increased more acid was added to maintain a pH of 5.5. After the pH remained at 5.5 for one day, the red mud was washed with deionised water. The mixture was centrifuged and the supernatant was poured out. The red mud was dried in the oven at a temperature of 105°C.
Figure 3.1 The time dependence of the change in pH of red mud as a function of increasing HCl addition (Wong and Ho, 1988).

3.2.2.2 Adsorption isotherms

The extent of the adsorption of Cu, Zn, Pb, Cd, Ni and Cr onto red mud neutralised with gypsum (RMG) and red mud neutralised with concentrated HNO₃ (RMA) was determined. A 1000 mg/l of metal stock solution was prepared in a volumetric flask for each metal, using the following quantities and metal salts: 3.929 g CuSO₄, 4.398 g ZnSO₄, 1.599 g Pb(NO₃)₂, 2.745 g Cd(NO₃)₂, 4.757 g Ni(NO₃)₂·6H₂O and 5.125 g Cr(Cl)₃·6H₂O. The working solutions were prepared by dilution of the stock solutions. The metal concentrations of the solutions used were respectively: 0, 50, 100, 150, 200 and 400 mg/l. Two grams of neutralised red mud were put in plastic dilution tubes and 10 ml of the heavy metal solution was added. Each sample of the series was prepared in duplicate. Also a solution containing a mixture of these metals was added to both types of neutralised red mud in order to determine the preferential adsorption sequence. The concentration of each of the metals in these solutions was respectively: 0, 8.5, 17, 25.5, 34, 68 mg/l, so that the total metal concentration remained 0, 50, 100, 150, 200 and 400 mg/l in the series.
From experiment I, it was found that equilibrium between the cations adsorbed onto the red mud and the cations in solution was reached within 24 hrs. Therefore the samples were shaken on a Coulter mixer for 24 hours in a constant temperature room at 20°C. After shaking, the samples were centrifuged for 10 minutes at 5000 rpm and the supernatant was pipetted off. The pH was measured in the supernatant. Then a drop of concentrated H₂SO₄ was added to the supernatant to preserve the samples prior to analysis on AAS.

3.2.3 Experiment III

The isotherms for the adsorption of copper, cadmium, chromium, nickel, lead and zinc onto red mud - gypsum were determined using two different ratios of red mud to solution (w/v), but with the same metal concentration range as in section 3.2.2.2. This was to ensure saturation of the metal adsorption sites of red mud. It also allowed collection of data on the effect of the solid concentration on adsorption isotherms.

Gypsum neutralised red mud (4%) was ground and sieved to a size < 2 mm. Two series of six sample tubes were filled with respectively 2 and 0.1 gram of neutralised red mud per metal. Then 10 ml of each of the metal solutions, containing respectively 0, 100, 200, 500, 800 and 1000 mg/l was added to the tubes. The metal solutions were prepared as described in section 3.2.2 except nickel which was prepared by weighing 6.728 g ammonium nickel sulphate (NH₄)₂SO₄NiSO₄·6H₂O, as this nickel salt remained in crystalline form during oven drying. The pH was measured in the solution after 3 hours equilibration and adjusted to 7.0 - 7.4 using 10 N HCl or 10 N NaOH. The mixtures were shaken for 24 hours at 20°C on a Coulter mixer. After shaking the samples were centrifuged at 3500 rpm for 15 minutes and the supernatant collected. The pH in the supernatant was measured before a drop of concentrated sulphuric acid was added in order to preserve the samples before analysis for the relevant metals on AAS.

3.3 Results

3.3.1 Experiment I

3.3.1.1 Equilibrium time

The adsorption equilibrium of heavy metals onto the red mud was reached rapidly. After approximately 5 - 10 minutes when the first sample was taken, the levels of Cu, Ni and Zn
in the metal mixture solution were respectively 5.6, 9.5 and 9.5 ppm while the concentrations found in the separate Cu, Ni and Zn batches were 0.0, 5.0 ppm and 2.3 ppm respectively. This indicated that red mud had an increasing preference of adsorbing metals in the order: Ni < Zn < Cu.

After 24 hours no heavy metals were detected in the solutions, indicating that all heavy metals had adsorbed onto the red mud.

3.3.1.2 Adsorption isotherms

The concentrations of heavy metals used the determination of the Cu and Zn adsorption isotherms were too low after equilibration. After 5 days no Cu and Zn could be detected in their supernatants.

After shaking of the red mud/metal solution mixtures, a significant improvement in the settling rate of the red mud was noticed (Table 3.1). This is attributed to the flocculation of the colloids by condensation of the double layer.

This finding deserves further experimental research to obtain more detailed information about the use of divalent cations (Ca^{2+}, mg^{2+}) rather than heavy metals for increasing the setting velocity of neutralised red mud.

Table 3.1 Settling velocity (m/hr) of red mud at different initial heavy metal concentrations.

<table>
<thead>
<tr>
<th>C (ppm)</th>
<th>Settling velocity (m/h)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>0</td>
<td>nd</td>
</tr>
<tr>
<td>2.5</td>
<td>nd</td>
</tr>
<tr>
<td>5.0</td>
<td>0.11</td>
</tr>
<tr>
<td>10.0</td>
<td>0.20</td>
</tr>
<tr>
<td>20.0</td>
<td>0.30</td>
</tr>
<tr>
<td>40.0</td>
<td>0.23</td>
</tr>
</tbody>
</table>

nd = not determined (too slow)
In the ≥ 10 ppm solutions the red mud had a flocculent character and a clear solution was present after the red mud had settled. The settling velocity of the 20 ppm Cu solution was highest, indicating a dependence on heavy metal concentration and type. In the 5 ppm Cu and Zn solution the settling of the red mud particles was still reasonable but the solution was light orange coloured after the red mud had settled. In the 0 and 2.5 ppm solutions settling of red mud was not measured because of the very slow settling rate. A dark coloured precipitate was formed over a one day period leaving an orange supernatant.

3.3.2 Experiment II

The results of the experiments are presented separately for each of the four treatments. The data for each experiment can be found in Appendix 3.Ia - d.

3.3.2.1 Metal adsorption isotherms for gypsum neutralised red mud

The extent of the removal of the metals from the solutions was very high. No chromium, copper and lead could be detected in solution after equilibration. Thus adsorption isotherms could not be constructed for these metals. The minimum adsorption capacity for these metals is thus 200 mg/100g red mud. The adsorption isotherms based on avaraged concentrations for cadmium, nickel and zinc are given in Figures 3.2 - 3.4. The prevailing pH in each solution are also shown in the Figures. The pH in the solutions at equilibrium varied around 8 and generally decreased with increased metal concentrations in solution, due to the acidic nature of the metal salts, despite the buffer capacity of red mud.

From the experimental data the constants for the Langmuir and Freundlich equations were calculated, as well as the correlation coefficient (r²) of the linear relationship between the models and the experimental data. These are presented in Appendix 3.II. The resulting models of both equations are drawn for each metal in the graphs. The symbols on the graphs are used only to distinguish them and indicate calculated data points only, as opposed to the measured points. The calculated data for each model are given in Appendix 3.Ia.

For all three metals, the adsorption to red mud was extremely high, resulting in low metal concentrations in the solutions. This indicates the even stronger adsorption of the other
metals, copper, chromium and lead, which were completely removed from the supernatant. The adsorption was such that saturation of the red mud adsorption matrix was not achieved, since the isotherms did not show horizontal levelling at the maximum concentrations in solution.

Figure 3.2 The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for cadmium with red mud gypsum, including the pH of the equilibrium solution.

Figure 3.3 The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for nickel with red mud gypsum, including the pH of the equilibrium solution.
Figure 3.4 The measured and calculated adsorption isotherms according to the Langmuir and Freundlich equation for zinc with red mud gypsum, including the pH of the equilibrium solution.

The high extent of adsorption suggests a degree of irreversible adsorption of Cd, Ni and Zn; moreover so for Cr, Cu and Pb, since the adsorption was not driven by the establishment of an equilibrium between solid and solution, but complete removal of the metals from solution. This type of adsorption can not be expressed in an adsorption isotherm. The order of the level of adsorption for the individual metals appears to be Zn > Cd > Ni (Appendix 3.1a); Cr, Cu and Pb are more strongly adsorbed than Zn. The measured data correlate closely to both the Langmuir and Freundlich models.

3.3.2.2 Adsorption isotherms of acid neutralised red mud.

The results of this experiment differed from the results of the previous experiment as a result of a lower pH during equilibration which reduces adsorption and may affect the stability of the Al- and Fe-oxides.

Adsorption isotherms could be developed for every metal analysed for, except lead. The measured isotherms and their Langmuir and Freundlich models are shown in Figures 3.5 - 3.9. It is indicative of the strong adsorption of lead by neutralised red mud that even in the
acid neutralised red mud (RMA) at low pH, all lead was removed from the solution by red mud upon equilibration with RMA.

The adsorption process when using RMA as an adsorbent takes place at considerably lower pH levels than when using RMG (Figures 3.5 - 3.9). A low pH reduces the adsorption capacity due to increased levels of ionisation and increased competition between cations and protons (H⁺) for exchange sites. The metal adsorption capacity of RMA appears to be lower than that of RMG for Cd, Ni and Zn. The adsorption isotherms for all 5 metals show an approach to metal adsorption saturation level on the solid fraction at high metal concentration. Since initial solution concentrations are the same as with the experiments with RMG, the adsorption capacity of RMA is lower, since the saturation level was not approached with RMG. The lower pH at equilibrium would be the main cause of the lower adsorption capacity of RMA. The pH reduced at increased metal salt concentration in the solutions due to the acidic nature of the salts. The decrease in pH in the increasing metal concentration solutions counteracts the adsorption of metals. The pH reduced from approximately 6 down to 5 for Cd, Ni and Zn. The pH range in the Cr and Cu samples was more acidic, i.e. respectively pH 6 to 4.5 and 6 to 5.

The empirical equation had a high correlation with the Langmuir and Freundlich equations for all metals, except Cr for which the Langmuir appears inaccurate at solute concentrations < 10 ppm (Appendix 3.II).

![Figure 3.5](image)

**Figure 3.5** The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with acid neutralised red mud, including the pH of the equilibrium solution.
Figure 3.6 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with acid neutralised red mud, including the pH of the equilibrium solution.

Figure 3.7 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with acid neutralised red mud, including the pH of the equilibrium solution.
Figure 3.8 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with acid neutralised red mud, including the pH of the equilibrium solution.

Figure 3.9 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with acid neutralised red mud, including the pH of the equilibrium solution.
3.3.2.3 Preferential adsorption of metals onto red mud - gypsum.

In the supernatant of gypsum neutralised red mud equilibrated with a mixed metals solution only cadmium, nickel and zinc were found. The cadmium adsorption isotherm for the mixed metal solution is shown in Figure 3.10. The data can be found in Appendix 3.1c. A maximum cadmium adsorption of 34 mg/100 g red mud occurred with a very low cadmium concentration left in solution (0.07 mg/l). Nickel and zinc were found in very low concentrations, < 0.05 and 0.11 respectively (Figures 3.11 - 3.12). Zinc was more strongly adsorbed than nickel. Copper, chromium and lead were not detected in solution after equilibration. This confirmed the high levels of adsorption of these metals to red mud - gypsum. The Langmuir and Freundlich constants can be found in Appendix 3.1I.

The pH levels measured in the samples in this experiment were less affected by the increasing metal concentration than those measured in the individual metal adsorption samples, as they ranged from 8.0 to 8.1. Since the pH was the same for each metal in solution, the preferential metal adsorption order could be determined. The graphs show the following order of preference: Cd > Zn > Ni; Cr, Cu and Pb were preferentially adsorbed to over Cd, but their respective positions in the order of preference could not be established.

![Graph showing preferential adsorption isotherms](image)

**Figure 3.10** The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions.

- 67 -
Figure 3.11  The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions.

Figure 3.12  The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with red mud gypsum in a mixed heavy metal solution, including the pH of the equilibrium solutions.
3.3.2.4 Preferential adsorption onto acid neutralised red mud

Due to the complete removal of Cr, Cu and Pb from solution, no adsorption isotherm could be produced for these metals. The isotherms for Cd, Ni and Zn are given in Figures 3.13 - 3.15 and the data in Appendix 3.1d. Since the adsorption equilibrium for each metal was established at the same pH value, the level of adsorption of individual metals can be compared on an even basis. The pH in the solution at equilibrium is shown on in each Figure. The residual concentrations of Cd, Ni and Zn were relatively high, considering the complete removal from solution by adsorption of Cr, Cu and Pb.

The pH levels though the same for each metal in the mixed solution are a function of the combined metals concentration in the supernatant. The pH reduced from 6 to 5.2 as a result of the increasing metal concentrations (Figures 3.13 - 3.15).

The constants for the mathematical isotherm equations fitted to the experimental data are in Appendix 3.11. For the nickel Langmuir equation, the last measured data point was omitted from the model calculation since the model could not assimilate the concept of reduced adsorption at higher metal concentration. This occurred in the case of nickel due to the pH reduction at higher metal concentrations (Figure 3.14). The Q value in the Langmuir equation along with the experimental results show the order of preference to be the same as with RMG except lower due to the acid treatment (lower pH): Cd > Zn > Ni (Table 3.4).

![Figure 3.13](image-url) The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions.
Figure 3.14 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions.

Figure 3.15 The measured and calculated preferential adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with acid neutralised red mud in a mixed heavy metal solution, including the pH of the equilibrium solutions.
3.3.3 Experiment III

This experiment aimed to determine adsorption saturation levels on RMG only and examine the effect of adsorbate concentration by comparing the adsorption isotherms determined with a red mud to solution ratio of 5 and 100. The raw data for each experiment are in Appendix 3.III.

3.3.3.1 Solid: Solution Ratio of 5

The results of this experiment allowed the production of the adsorption isotherm for each metal involved. The isotherms can be found in Figures 3.16 - 3.21 and the data in Appendix 3.IIIa. The graphs include the measured isotherm, the isotherm based on the Langmuir and Freundlich models and the pH at the point of equilibrium.

The isotherms generally demonstrate a high level of adsorption of metals by red mud, though strongly varying per metal. An adsorption saturation plateau was only achieved for nickel, which was in the previous RMG metal adsorption experiments found to be adsorbed at the lowest levels of the six metals analysed.

The experimental Cr isotherm shows a dip which seems an irregularity. The dip coincides with a peak of the pH in the solution. This feature is caused by the fact that the Cr concentration in the supernatant was lower for the 150 ppm solution (0.06 ppm) than for the 100 ppm solution (0.07 ppm). Thus the adsorption at equilibrium at 0.06 ppm was higher than at 0.07 ppm. The fact that the pH was slightly higher in the 0.06 ppm supernatant implies the influence of the pH either by increasing the adsorption capacity or through Cr precipitation. The increased pH in the higher Cr concentration solution indicates an experimental irregularity.

In the blank solutions low concentrations of Pb, Ni and Zn were found. This desorption, or negative adsorption, caused a problem when an attempts were made to fit an isotherm of the Langmuir type to the measured data, since it resulted in a negative value of C/q (See section 2.3.2.4). The Langmuir model is not suitable if q is negative. In order to use the Langmuir model the end concentration in the blank (Ce) was assumed to be 0.
The alkaline nature of red mud and the relatively low solution to red mud-gypsum ratio of 5 (10 ml/2g) resulted in an alkaline pH in the supernatant after 24 hours equilibrium. The pH decreased again as a result of the acidity of the solutions with high metal concentrations, in the range of 7.5 - 8.5. The order in preferential adsorption was: Cr > Pb > Cu > Zn > Cd > Ni.

![Graph showing pH and [Cd] in solution mg/100g](image)

**Figure 3.16** The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.

![Graph showing pH and [Cr] in solution mg/100g](image)

**Figure 3.17** The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.

- 72 -
Figure 3.18  The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.

Figure 3.19  The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for lead with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.
Figure 3.20 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.

Figure 3.21 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with red mud gypsum with a solution/solid ratio of 5, including the pH of the equilibrium solution.

3.3.3.2 Solid : solution ratio of 100

An increased solution solid ratio of 100 as opposed to 5 has the effect of a higher metal loading onto the adsorbate and thus stronger competition for sites, on the red mud matrix.
This allows an assessment of the effect of solid concentration on adsorption and an attempt to assess the saturation level.

The samples had a residual metal concentration (Ce) in solution for each metal upon reaching equilibrium, so that isotherms could be drawn for each metal. The isotherms are presented in Figures 3.22 - 3.27 and the data is in Appendix 3.IIIb. The isotherms for Cu, Pb, Ni and Zn appear to be of the S-curve type. This indicates that different adsorption mechanisms or sites are involved, or enhanced adsorption as a result of increased surface adsorption of metals (Harmsen, 1979).

The adsorption process took place at a lower pH than with the solution to solid ratio of 5 due to the lower buffer capacity of the solution as a result of the lower concentration of red mud. A pH adjustment was made after three hours equilibrating for all samples, except the blanks, to maintain a pH of 7.2 in all solutions, using a caustic soda solution. The reduction in pH levels was caused by the acidic metal salts used.

Cadmium is the only metal that approached its adsorption saturation level (Figure 3.22). The pH in the Cd equilibrium solutions was lower than those in the lead and zinc solutions. The level of metal adsorption in a solution to RMG ratio of 100 was approximately an order of magnitude higher than the adsorption with a solution to RMG ratio of 5 (Appendix IV). A similar result of the effect of adsorbent concentration on adsorption was found by DiToro et al. (1986). He observed metal desorption from clay particles by reducing the solution to adsorbent ratio through increasing the adsorbent (montmorillonite) concentration after an equilibrium was established.

At a higher ratio of solution/red mud, the ionic strength of the solution is reduced due to less salinity released in solution from red mud. The preferential order was: Cu > Cr > Pb > Zn > Ni ≥ Cd.
Figure 3.22 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for cadmium with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.

Figure 3.23 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for chromium with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.
Figure 3.24  The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for copper with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.

Figure 3.25  The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for lead with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.
Figure 3.26 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for nickel with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.

Figure 3.27 The measured and calculated adsorption isotherms, according to the Langmuir and Freundlich equations, for zinc with red mud gypsum with a solution/solid ratio of 100, including the pH of the equilibrium solution.
3.4 Discussion

The experiments clearly show that red mud has a very high capacity to remove large amounts of heavy metals from a solution. The removal of the metals cannot be attributed to one single mechanism alone, and includes chemisorption, cation exchange and possibly some precipitation. The solubility products calculated for each metal at equilibrium concentration and pH show that the $K_{sp}$ values for their hydroxides and carbonates are not exceeded.

The following discussion covers the metals adsorption adsorption capacity of red mud and the influence of red mud concentration in solution, the pH and the level of competition for adsorption sites. In addition, the correlation between the adsorption isotherms and the Langmuir and Freundlich models are discussed. Finally, the effect of metal adsorption on red mud properties is discussed.

3.4.1 Adsorption isotherms

In Table 3.2 are listed the metals for which adsorption isotherms could be developed from the experimental data. Cadmium, nickel and zinc were the only metals for which an adsorption isotherm could be developed from each experiment. Thus, the isotherms of these metals can be used to make a comparison between the different treatments and conditions.

The reason for not being able to develop an isotherm for the metals not mentioned in Table 3.2, is that no metal ions were could be detected in solution after equilibration, thus an independent variable (x) required for the development of an isotherm was not available. the complete removal from solution of these metals suggest the metal adsorption was not driven by the establishment of an equilibrium.

Figures 3.2 - 3.27 show that the different red mud treatments and pH levels resulted in considerable differences in adsorption behaviour for each metal. In none of the experiments saturation of the red mud adsorption complex by metals was achieved.
Table 3.2 Metals for which experimental adsorption isotherms could be determined.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>solution/solid ratio (ml/g)</th>
<th>concentration range (ppm)</th>
<th>metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMG® single metal</td>
<td>5</td>
<td></td>
<td>Cd, Ni, Zn</td>
</tr>
<tr>
<td>RMG mixed metal</td>
<td>5</td>
<td></td>
<td>Cd, Ni, Zn</td>
</tr>
<tr>
<td>RMA* single metal</td>
<td>5</td>
<td></td>
<td>Cd, Cr, Cu, Ni, Zn</td>
</tr>
<tr>
<td>RMA mixed metal</td>
<td>5</td>
<td></td>
<td>Cd, Ni, Zn</td>
</tr>
<tr>
<td>exp III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMG single metal</td>
<td>5</td>
<td></td>
<td>Cd, Cr, Cu, Pb, Ni, Zn</td>
</tr>
<tr>
<td>RMG single metal</td>
<td>100</td>
<td></td>
<td>Cd, Cr, Cu, Pb, Ni, Zn</td>
</tr>
</tbody>
</table>

@RMG = red mud gypsum (4%); * RMA = Acid neutralised red mud to pH = 5.5.

3.4.2 Correlation of the isotherms with the Langmuir and Freundlich models.

Each isotherm in this study was modelled according to both the Langmuir and the Freundlich equation. The correlation coefficients ($r^2$), given in Table 3.3 and in Appendices 3.II and 3.IV apply to the linear relationship within of the Langmuir and Freundlich equations and their respective relationship with the experimental data.

Table 3.3 The correlation coefficients between the isotherms of red mud gypsum (RMG) and red mud acid (RMA) and the Langmuir and Freundlich equations for both single metal and preferential adsorption.

<table>
<thead>
<tr>
<th>Metal</th>
<th>RMG</th>
<th>RMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>individual</td>
<td>mixed</td>
</tr>
<tr>
<td></td>
<td>L  F</td>
<td>L  F</td>
</tr>
<tr>
<td>Cd</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>Zn</td>
<td>0.87</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Both models generally showed a high correlation to the measured isotherm, and thus both equations are applicable to metal adsorption onto neutralised red mud. The close correlation indicates that the process follows conventional adsorption dynamics, including the establishment of a solid/solution equilibrium as a driving force. However, this observation could not be made in all experiments for Cr, Cu and Pb in the cases where these metals were completely removed from solution, indicating fixation rather than formation of an equilibrium.

The maximum metal adsorption capacity (Q) determined using the Langmuir model showed a much higher adsorption capacity for a ratio of 100 than for a ratio of 5 (Table 3.4).

3.4.3 Effect of red mud neutralisation method

During the preparation of acid neutralised red mud (RMA) the DSP complex would be expected to be completely destroyed during the acidification of the red mud to pH < 2. The subsequent neutralisation of the red mud would have been expected to result in recrystallisation of the Al- and Fe- oxides, both of which have a high metal adsorption capacity. The pH neutralisation would not have recrystallised the DSP complex. According to the literature, DSP has a high CEC, though for monovalent cations only (Wong & Ho, 1988). Thus in regard to the red mud neutralisation method the main adsorption sites, Al- and Fe- oxides and clay minerals, are present in using either the acid or gypsum neutralisation method. However, the pH in the equilibria with RMA is 2 - 3 pH points lower. This lower pH level will result in a reduced metal adsorption, which has to be taken in consideration when comparing the differently neutralised red mud adsorbents.

By comparing the adsorption of metals into red mud - gypsum and RMA some insight into whether DSP plays a role in the adsorption of heavy metals can be obtained. The difference in pH levels must be taken into account, since the maximum adsorption plateau of a metal is pH dependent. Adsorption is generally stronger as the pH increases.

Gypsum amendment of red mud increases the soluble sulphate content of the matrix which can form, when solubilised, precipitates with metals, e. g. lead sulphate ($K_{sp} = 1.08 \times 10^{-8}$). However, the solubility of gypsum ($K_{sp} = 2.45 \times 10^{-5}$) is also low, thus only $4.9 \times 10^{-3}$ of sulphate will be in solution. Thus, for lead sulphate precipitation to occur, the lead
concentration must exceed 0.46 mg/l. This concentration could not be found in the supernatant of even the highest equilibrium concentration (400 mg/l). Thus lead removal through sulphate precipitation is unlikely.

When Figures 3.2 and 3.5, showing cadmium, are compared, it is obvious that RMG has a much higher adsorption capacity for cadmium than RMA, resulting in very low cadmium concentrations in solution. This difference in adsorption capacity is likely to be the result of the lower pH at equilibrium with RMA.

The maximum individual metal adsorption capacity is a factor 3 - 4 higher for RMG than for RMA in the 0 - 400 ppm range (Table 3.4). This is most likely caused by the lower equilibration pH for RMA and a possible loss of adsorption capacity as a result of the dissolution of CaCO₃.

In the preferential adsorption experiment it appeared that Cr, Cu and Pb were completely adsorbed with remaining sites being occupied by Cd, Ni and Zn (Table 3.4). The concentrations of Cd, Ni and Zn in the supernatant showed that in this situation, RMG metal adsorption capacity was much higher than RMA.

Table 3.4 Maximum metal adsorption capacity (Q) for RMG and RMA for individual and mixed metal solutions according to the Langmuir equation in mg/100g red mud for different concentration ranges and dilutions.

<table>
<thead>
<tr>
<th>metal</th>
<th>RMG-ind.</th>
<th>RMA-ind.</th>
<th>RMG-mix</th>
<th>RMA-mix</th>
<th>RMG5®</th>
<th>RMG100®</th>
</tr>
</thead>
<tbody>
<tr>
<td>cadmium</td>
<td>417</td>
<td>135</td>
<td>-29.4*</td>
<td>22.2</td>
<td>625</td>
<td>4000</td>
</tr>
<tr>
<td>chromium</td>
<td>√</td>
<td>196</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>14500</td>
</tr>
<tr>
<td>copper</td>
<td>√</td>
<td>164</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>15600</td>
</tr>
<tr>
<td>lead</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>27.3</td>
<td>√</td>
</tr>
<tr>
<td>nickel</td>
<td>417</td>
<td>83</td>
<td>34.5</td>
<td>4.2</td>
<td>476</td>
<td>4170</td>
</tr>
<tr>
<td>zinc</td>
<td>385</td>
<td>112</td>
<td>34.5</td>
<td>17.5</td>
<td>592</td>
<td>8930</td>
</tr>
</tbody>
</table>

®RMG5 and RMG100 represent red mud gypsum with a solution: solid ratio of 5 and 100 respectively.
* Langmuir invalid due to negative slope;
√ not possible to calculate, as Ce = 0.
In the third experiment, where solutions with much higher metal concentrations (0 - 1000 ppm) were used and different solution to solid ratios were tested for RMG, it was shown that the higher metal concentrations and a higher solution: solid ratio further increased the maximum adsorption capacity. This indicates that some form of equilibrium is involved in the adsorption process, and that the stability constants of the adsorption complexes are very high.

3.4.4 Solid concentration

According to DiToro et al. (1986) the solid concentration, ie. the ratio between adsorbent and solution (w/v), influences the adsorption of metal to the adsorbent. He found that at lower clay concentrations proportionally more metals could be adsorbed by the clay. It was suggested that inter - particle associations somehow induced metal adsorption. This would mean that the metal adsorption capacity of a soil could be much lower in - situ, than in an equilibrium solution using the same soil.

This hypothesis can be tested on the results of this experiment by comparing the results of cadmium, nickel and zinc for the experiments where a solution/solid ratio of 5 and 100 was used. The results with the ratio 5 for cadmium, nickel and zinc are in Figures 3.16, 3.20 and 3.21 respectively. For the ratio 100 the results are in Figures 3.22 (cadmium) and 3.26 (nickel) and 3.27 (zinc).

The comparison shows that for all metals the adsorption to red mud is higher with a solution/soil ratio of 100 despite the equilibrium being established at a slightly lower pH value. Metal adsorption is generally positively correlated with pH. A lower pH reduces metal adsorption due to increased ionisation of Al and Fe oxide adsorption sites and higher proton concentration. This confirms the finding of DiToro et al. (1986). The metal adsorption capacity at a solution/red mud ratio of 100 ratio is extremely high. For copper and zinc, red mud can adsorb up to approximately 15% of its dry weight.

3.4.5 Preferential metal adsorption

Apart from obtaining information on the adsorption behaviour of individual metals, it is important to study the adsorption behaviour of metals in a mixed solution, so as to assess
their adsorption behaviour in a competitive environment. This situation more closely resembles real-life situations. It provides information on preferential adsorption of the metals to the red mud.

Since equilibrium of all metals with red mud is attained in the same solution, the pH is eliminated from the process as a variable. Preferential adsorption of metals was determined for red mud - gypsum and acid neutralised red mud.

The results for red mud gypsum (Figures 3.10 - 3.12) show the following sequence of preferential adsorption: Cd > Ni > Zn. Chromium, copper and lead were completely removed from solution, thus are more strongly adsorbed than Cd. The individual metal isotherms determined in experiment III (0 - 1000 ppm) for chromium, copper and lead show the adsorption to be in the order: Cr > Pb > Cu (Figures 3.23 - 3.25). The pH levels are not the same, but are in fact in reverse order: pH(Cu) > pH(Pb) > pH(Cr). Thus this order is not likely to change given adsorption at a comparable pH for these metals. The order of preferential adsorption for RMG is thus: Cr > Pb > Cu > Cd > Ni > Zn.

A different preferential order of metal adsorption was found for acid neutralised red mud (Figures 3.13 - 3.15): Cd > Zn > Ni. As in the case of RMG, all Cr, Cu and Pb were removed from solution, thus no adsorption isotherms could be developed for these metals. However from the results of the individual isotherms of Cr and Cu (Figures 3.6 and 3.7) an indication of their preferential adsorption can be extracted. Pb could not be detected after equilibration in either experiment. The preferential adsorption sequence on this basis, considering the different pH levels of the first three metals, is: Pb > Cr > Cu > Cd > Zn > Ni.

These preferential adsorption sequences do not follow the order reported for either iron oxides: Pb > Zn > Ni > Cd, or for aluminium oxides: Cu > Pb > Zn > Ni > Cd (Kinniburgh et al. 1976), (see also section 2.4.2.3).

An explanation could be the fact that red mud contains a mixture of these minerals, thus the preferential adsorption sequence found for red mud can be expected to be a combination of the separate adsorption sequences. The relative positions of the three metals that occur in all three orders, namely Zn, Ni and Cd, are comparable, except that Cd is more strongly adsorbed in RMG than Zn and Ni which is different for iron and aluminium oxides (RMA).
Pb is strongly adsorbed in all, only surpassed in RMA by copper. Other factors in red mud which can interfere in determining metal adsorption could be the presence of sulfate from gypsum, which is insoluble with lead, and clay minerals, such as muscovite, which are able to adsorb metals.

3.4.6 Effect of metal adsorption on red mud

Red mud behaves as a highly dispersed suspension in a water solution. The main cause of this is its high sodium content. The alkali-like reaction that sodium causes can result in the dispersion of inorganic negatively charged colloids such as iron and aluminium oxides. These colloids are held in suspension by the opposing forces of their nett negative charge in the diffuse double layer. The sodium, as a monovalent cation, reduces the repulsive forces that would keep suspended oxides apart, but insufficient to flocculate. The addition of divalent cations to such a suspension can cause a flocculation reaction as a result of the neutralisation of the opposing electrical forces between the colloids. The effect of this reaction on red mud was clearly demonstrated during this experiment. A pure red mud suspension in water can take up to seven days to settle. In experiment I, the red mud settling time was reduced to less than 10 minutes (Table 3.1) by addition of a metal solution. This property could have a significant application in improving the settling rate of red mud in storage ponds and improving the properties of red mud as a soil amender.

3.4.7 Metal removal mechanism

It was discussed in section 2.4.2 that three main metal removal mechanisms were possible when red mud was present in a metal solution:

- precipitation;
- ion exchange; and
- chemisorption

It is of interest to determine to what extent each mechanism is responsible for the strong metal removal capacity of red mud - gypsum from solution, and how each of the metals behave with these mechanisms relative to each other.
Precipitation

The first step is to examine whether the solubility product in the equilibrium solutions were reached or exceeded, since this suggests precipitation. This can be done by comparing the solubility data in Table 2.4 with the experimental $K_s$ data in Appendix 3.Ia-d and 3.IIIa-b.

The results of experiment II show that no precipitation of metal hydroxides or carbonates occurred with red mud gypsum as the adsorbent and that with acid neutralised red mud as the adsorbent, precipitation played at most a minor role since the $K_s$ was only exceeded at the highest concentration (400 ppm) for Cr, Cu, Ni and Zn, except for Cd where the $K_s$ was exceeded for all metal solutions. Pb could not be detected in the supernatant thus is likely to be adsorbed. A comparable result was found in the preferential adsorption experiment.

The results of experiment III showed that at higher red mud concentration and resulting higher pH (Appendix 3.IIIa), the likelihood of precipitation is less since the $K_s$ was only exceeded for some metals (Cd and Cr).

For some metals the solubility product with their hydroxide was exceeded by a number of magnitudes. This indicates a supersaturation of metals in solutions. A possible explanation for this is that the prevailing pH was the result of a dominant presence of $\text{HCO}_3^-$ as opposed to $\text{OH}^-$ and a relatively high ionic strength of the solutions, which would affect the solubility product. The fact that at higher pH levels and higher availability of adsorption sites lower equilibrium metal concentrations were achieved indicates the prominent role of sorption processes and the high stability of the bonds they form. The increased pH appears to stimulate adsorption activity more than precipitation.

Only at very high metal loading, combined with a resulting lower pH, some metals (Cd, Cr, Pb and Zn) were precipitated. Cu and Ni which have slightly higher equilibrium pH levels are 6 orders of magnitude below their $K_s$ value.

McBride (1979; 1980) also found that adsorption processes were able to maintain metal solubility at a level too low for precipitation to occur. Thus, in the experiments it appeared that precipitation played a minor role in metal removal.
Chemisorption results in metal bondings with high stability constants often partly irreversible and independent of concentration in solution (McBride, 1989).

In a red mud metal adsorption experiment, in the presence of organic matter, described in Chapter 6, it was found that only 70 - 80% of the metals adsorped by red mud, except Cr, could be recovered with a concentrated acid extraction (Table 6.7), thus 20 - 30% was irreversibly complexed. In total only 65 - 80% of the metals were extractable with acid but not with 0.01M CaCl$_2$ or DTPA, a metal complexing agent. It can be assumed that this fraction of metals was predominantly chemisorbed, and a minor fraction exchangeable since neither the CaCl$_2$ nor the DTPA extraction can fully recover the exchangeable metals. In a separate experiment without organic matter, the metals were 100% recovered. These metals must have been chemisorbed in an acid extractable form which appears to account for ±50% of sorbed metals. The non acid extractable fraction caused by the presence of organic matter is likely due to the presence of phosphates which can coprecipitate with metals onto Fe and Al oxides (McBride, 1989).

Cr, Cu and Pb appear to have a strong preference for this type of sorption as none of these metals could be detected in equilibrium solutions with red mud - gypsum (Appendix 1a & c), ruling out precipitation as well as ion exchange.

*Ion exchange*

Ion exchange is positively correlated to cation (metal) concentration, and the resulting equilibrium solute concentration of a given solution is mainly dependent on the stability constants of this type of sorption.

In section 2.4.2.1, the cation exchange capacity of red mud was given as 25 meq/100g or 12.5 mmol divalent cations/100g. In the case of Cu this means 787.5 mg/100g adsorbent. This represents less than 10% of the maximum metal adsorption capacity found for Cu (9307 mg./100g) and absence of precipitation was established (Figure 3.24; Appendix 3.IIIa).
For Ni, where no precipitation occurred either (Appendix 3.IIIa), the ion exchange capacity would be equal to 862.5 mg/100 g. This represented circa 25% of the highest Ni adsorption found (Appendix 3.IIIb). These fractions are dependent on ion exchange being the sole mechanism of metal removal. Since chemisorption is the dominant mechanism, since even in this case of Cu and Ni, 90% and 75% respectively is chemisorbed, ion exchange is likely to play a minor role, up until the chemisorption capacity of red mud for a particular metal is exhausted. The increasing metal concentrations at equilibrium of Cu and Ni (3 and 651 mg/l respectively) indicated that ion exchange starts to play a more significant role once chemisorption capacity has reached its potential. In the case of Cu, no Cu could be detected in the while red mud had adsorbed 200 mg Cu/100g (section 3.3.2.1).

The pH dependency of chemisorption is stronger than precipitation in the experiments described here, since precipitation only plays an increasing role at a lower pH when the higher metal concentrations left in solution can exceed their solubility product with hydroxide.

3.5 Conclusions

The ability of neutralised red mud in suspension to remove heavy metals from solutions is very high. A number of different processes is involved in the removal of these metals. These processes are: 1) precipitation of insoluble metal compounds, such as hydroxides, carbonates and sulphates; 2) chemisorption, involving iron and aluminium oxides; and 3) cation exchange with ions from the diffuse double layer of the clay minerals. Some adsorption processes involving heavy metals are irreversible. The equilibrium that is established between red mud particles and a heavy metal solution is the result of all of the above mentioned processes that affect metal solubility. Equilibrium between heavy metals in solution and heavy metals adsorbed onto the red mud was reached within 24 hours.

Chemisorption accounts for at least 75 - 90% of the metal removal, and seems to be a more dominant mechanism at alkaline pH levels than precipitation. The chemisorption capacity of red mud varies considerably between metals. After saturation of the chemisorption capacity, ion exchange becomes the main adsorption mechanism and forms an equilibrium with the remaining metals in solution. Precipitation is minor and occurs mainly at lower
pH levels (<6.5) when the chemisorption and ion exchange capacities of red mud are largely exhausted.

More specific research is required to achieve a more accurate resolution of how each process contributes to metal removal from solution. In particular the distinction between precipitation, cation exchange and fixation is of interest since there is great difference in stability of the complexes formed during each of these processes. This will affect the long term mobility of the heavy metals in the matrix.

The red mud matrix shows preferential adsorption of different metals. The preferential adsorption sequence is: Cr > Pb > Cu > Cd > Ni > Zn.

Heavy metal ions are able to increase the settling velocity of neutralised red mud considerably. The presence of these ions gives the red mud a flocculent character.
The effect of bauxite refining residue (red mud) on the solubility of heavy metals in municipal compost.

4.1 Introduction

In order to address the problem of heavy metal mobility in soils when metal contaminated compost is applied, it was hypothesised that bauxite refining residue ('red mud') could be a suitable amendment to compost, because of its high sorption capacity for heavy metals (chapter 3). An additional advantage is that the adsorption capacity of red mud can be used to retain applied fertiliser, reducing nutrient leaching.

To improve the dispersed structure of the red mud particles which is a result of sodium saturation, and to neutralise the alkalinity in red mud, the effect of gypsum (CaSO$_4$.2H$_2$O) amendment of red mud was included in the study.

Two processes were thought to be active in reducing the mobility of heavy metals. The hydroxides and carbonates present in red mud could reduce metal ion concentrations by precipitation. This process is regulated by the pH in the medium. The other process is adsorption onto the red mud adsorption complex of slowly released metals, which result from the decomposition of organic complexes and the dissolution of precipitated metal hydroxides.

The role of pH in reducing metal concentrations in solution requires clarification, in order to assess the metal adsorption potential of red mud, as opposed to the reduction of metals in solution through precipitation.

The objective of this study was to gain insight into the distribution of a range of metals in municipal waste compost over the humin and soluble organic matter fraction and the free ionic metal fraction. In addition the effect of red mud and red mud - gypsum on the metal distribution was studied with the objective of reducing the level of mobile metals, ie. the free ionic metals and the metals associated with the soluble organic matter fraction which are available for leaching or uptake by vegetation.
4.2 Methodology

4.2.1 Introduction

The study had a four way approach. After analysis of a municipal compost from Auckland for its metal content the following experiments were carried out. The first step was to assess the effect of red mud on the extractability of a selection of environmentally relevant metals from the Auckland municipal compost, using calcium chloride (CaCl₂), barium chloride (BaCl₂), diethylene triamine pentaacetic acid (DTPA) and hydrochloric acid (HCl) as extractants.

In the second part, the interaction of heavy metals with soluble organic acids was studied through fractionation of the soluble fulvic and humic acids and metal analysis of each fraction.

The third part consisted of two experiments. In the first experiment, the effect of red mud on the dissolution of organics and heavy metals from compost was assessed. This experiment simulated a field situation and provided an overall result of metal retention and organic matter dissolution processes. The second experiment was designed to give more information about adsorption of soluble organic matter and heavy metals onto red mud and about precipitation of metals as a result of the increasing pH associated with red mud addition. The distribution of metals in solution was studied by removing the humic substances according to Holtzclaw et al. (1976; 1978).

Finally percolation columns were used to determine the effect of red mud and red mud-gypsum amendment of municipal compost on the leaching of metals from the compost.

4.2.2 Analysis of Auckland municipal compost

Compost was obtained from the municipal composting plant in Auckland, New Zealand. The compost was produced in a Dano composting plant, using as a feedstock a combination of the organic fraction of presorted mixed domestic waste and sewage sludge. The compost was analysed for pH, ash content (loss on ignition), and its concentration of the following metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, by HClO₄ -
HNO₃ digestion. The compost was oven dried at 80°C to minimise metal evaporation until a stable dry weight was achieved and ground prior to its use in the experiments.

4.2.3 Effect of red mud on metal speciation in compost

Two series of mixtures were prepared from compost with respectively 0, 5, 10 and 15% w/w red mud (RM) or red mud neutralised with gypsum (RMG). Each sample weighed 5 grams. The mixtures were extracted by mechanical shaking for two hours in a 10:1 liquid to solid ratio with 50 ml of a 0.5 M BaCl₂ solution and with a 0.1 M HCl solution. This was to determine the amounts of lead and zinc that were easily soluble and exchangeable (0.5 M BaCl₂) and the exchangeable, organically complexed and the metals associated with Fe- and Mn-oxides (0.1 M HCl) (Lagas and Loch, 1981). After extraction, the samples were centrifuged in a Sorvall ultracentrifuge at 2000 rpm for 15 minutes and filtered using a 0.45 µm membrane filter.

Two other series of mixtures, consisting of compost with respectively 0, 10, 20, 30, 40 and 50 % w/w RM or RMG, were extracted in an identical manner with 0.005 M DPTA, at pH 7.3, to determine plant available metals (Lindsay and Norvell, 1978), and with 0.01 M CaCl₂ to determine the soluble and weakly bound amounts of cadmium, copper and nickel.

4.2.4 Effect of red mud on the fractionation of organo-metallic complexes

The fulvic and humic acids were extracted by adding 200 ml of a 0.1 M sodium hydroxide solution to 50 grams of air dried and ground compost with respectively 0, 5, 10 and 15 gram red mud added to it. The samples were extracted for two hours on a Coulter mixer. Then the samples were centrifuged at 5000 rpm for 20 minutes on a Sorvall RC-5B ultra centrifuge to remove particulate matter. The supernatants were filtered using a 0.45 µm membrane filter.

The humic acids were separated from the extracts by reducing the pH to 1 with 6 M HCl, allowing the humic acids to precipitate for one hour, and subsequent centrifugation at 15,000 rpm for 20 minutes (Holtzclaw et al., 1976, 1978). The humic acids were washed with 0.1 M HCl and redissolved in 0.1 M NaOH.
The UV-visible spectra (200 - 800 nm) of the fulvic and humic acids extracts were measured. In order to indicate the maturity of the compost by determination of the $\Delta \log K$ value (see section 2.3.6.6) and the $E_4/E_6$ ratio (see section 2.3.6.5), the absorbances of the extracts at wavelengths 400, 465, 600 and 665 nm were measured.

One ml aliquots of the extracted fulvic and humic acids solutions were fractionated over a Sephadex G 10 gel filtration column, with a column bed height of 54 cm, bed volume of 205 cm$^3$, a void volume of 74 cm$^3$ and a pressure head of 81 cm. The void volume was determined by percolation of 5 ml Dextran Blue 2000. The different fractions were analysed for UV absorbance on-line at a wavelength of 254 nm with a LKB 8300 Unicord II UV-analyser and the results recorded on a Rikadenki pen recorder. The organic acid fractions were collected by a LKB fraction collector and stored for analysis. The compost extracts and the fractions were analysed for cadmium, copper, nickel, lead and zinc.

The behaviour of the solute was characterised by determining the eluent parameter $K_{av}$ according to the formula:

$$K_{av} = \frac{(V_e - V_0)}{(V_t - V_0)}$$

where

- $K_{av}$ = the fraction of the stationary gel volume which is available for diffusion of a given solute species.
- $V_e$ = volume of eluent collected from the time of application of the sample to the time of the eluted peak of the extract,
- $V_t$ = total bed volume,
- $V_0$ = void volume.

4.2.5 Effect of red mud on the leachable metals and soluble organic matter

Extracts from municipal compost with red mud or red mud - gypsum were prepared in duplicate by adding respectively 0, 1, 5 gram of red mud or red mud - gypsum to 5 g of compost in 125 ml polyethylene bottles. As a control 1 and 5 grams of red mud was used. The compost, red mud and the mixtures were extracted with 25 ml of a 0.01 M CaCl$_2$ solution by shaking for two hours on a Coulter mixer in a constant temperature
room at 20° ±1°C. The solid and liquid phases were separated by ultracentrifuge, for 10 min at 9000 rpm and 20°C and subsequent vacuum filtration over a 0.45 μm membrane filter to obtain a clear extract (Ernc).

Compost water extracts were made by adding 375 ml deionised water to 75 gram compost (liquid : solid = 5 : 1) in a 500 ml centrifuge bottle and red mud water extracts were made using 1 and 5 grams of red mud with 25 ml deionised water in 50 ml phials. The bottles and phials were shaken for two hours on a Coulter mixer at 20°C. The bottles were centrifuged for 10 minutes at 9000 rpm. Subsequently, batches of 25 ml extract were added to respectively 0, 1, 5 grams of red mud in 50 ml phials. These red mud and compost extract mixtures were shaken for 2 hours on the Coulter mixer. All extractions were centrifuged for 5 minutes at 9000 rpm and filtered over a 0.45 μm membrane filter to obtain a clear supernatant for analysis (Ec+rm).

The extracts were analysed for cadmium, copper, nickel, lead and zinc. In all extracts the pH was measured to enable the calculation of the solubility products for the metal hydroxides. UV and visible light spectra (200 - 800 nm) and the peak absorbance at the most sensitive wavelength (highest absorbance) were measured in the extracts using a Shimadzu double beam spectrophotometer.

After these measurements the humic acids were removed from the extract as described in the previous section. In order to remove the precipitated humic acids the acidified extracts were membrane filtered (0.45 μm). The metal analysis was repeated and new UV and visible spectra and peak absorbance were determined. The initial water extract and the extracts after having been shaken with 1 and 5 gram red mud, were analysed for total organic carbon (TOC), using the dichromate method, in order to determine the extent of organic matter adsorption onto red mud and to quantify the effect on the UV and visible light absorbance of the extracts.

4.2.6 Effect of red mud on metal leaching from percolation columns

Two percolation columns (50 mm Ø x 1000 mm) were constructed and filled to a height of 500 mm with a mixture of compost and red mud or red mud - gypsum in a ratio of 60 : 40, and with a porosity of 75% (96.6 cm³). The mixtures were leached with 0.01 M CaCl₂
using a Mariotte bottle set-up to maintain a constant pressure head. The leachate was collected in a LKB fraction collector and each fraction was analysed for cadmium, copper, nickel and zinc.

All metal analyses were performed on a GBC atomic absorption spectrophotometer. For all optical measurements a Shimadzu double beam spectrophotometer was used.

4.3 Results

4.3.1 Auckland municipal compost analysis

The results of the compost analysis for heavy metals, pH and ash content are given in Table 4.1. The metal levels are rather high by international standards (see Table 1.1). This was probably due to the organic waste fraction having been mixed with inorganic waste before sorting and to the subsequent mixing with sewage sludge, which generally contains significant levels of heavy metals as a result of industrial discharges into municipal sewerage systems (Stephenson, 1987).

Table 4.1 Results of Auckland municipal compost analysis; metals in mg/kg dry matter, unless otherwise indicated.

<table>
<thead>
<tr>
<th>metal</th>
<th>mg/kg</th>
<th>pH</th>
<th>ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>cadmium</td>
<td>6</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>copper</td>
<td>380</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>nickel</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lead</td>
<td>608</td>
<td></td>
<td></td>
</tr>
<tr>
<td>zinc</td>
<td>1460</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chromium</td>
<td>225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iron</td>
<td>1.6 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>manganese</td>
<td>560</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pH is slightly alkaline, which is normal for mature compost due to the ammonium content and the high degree of oxidation of organic matter.

-95-
The ash content provides a measure of the volatile solids content, which is mainly organic matter in the case of compost. Volatilisation of non biodegradable contaminants such as some metals and plastics makes it inaccurate to credit the loss on ignition solely to the organic matter content. Nevertheless the organic matter content is close to 60% which is high for municipal compost.

4.3.2 Effect of red mud on metal speciation in compost

4.3.2.1 Exchangeable and weak-acid extractable cations

The $\text{BaCl}_2$ solution was able to extract 2.8% of the total zinc content of compost. The presence of red mud resulted in a decrease (41 to 18 mg/kg) in extractable zinc, down to 1.2% of total zinc content (Table 4.2). The decrease was presumed to be caused by zinc adsorption onto red mud, since zinc-organic matter complexes are relatively instable compared to other metals. Addition of red mud would have increased the adsorption capacity of the compost mixtures by providing more adsorption sites.

Table 4.2 The effect of red mud on the extractable zinc and lead (mg/kg) in municipal compost.

<table>
<thead>
<tr>
<th>% red mud</th>
<th>$\text{BaCl}_2$</th>
<th>$\text{HCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>zinc</td>
<td>lead</td>
</tr>
<tr>
<td>0</td>
<td>41</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>29</td>
<td>1.6</td>
</tr>
<tr>
<td>10</td>
<td>22</td>
<td>1.9</td>
</tr>
<tr>
<td>15</td>
<td>18</td>
<td>bd</td>
</tr>
</tbody>
</table>

$\text{bd} =$ below detection limit (0.1 mg/l).

The $\text{HCl}$ extractable zinc concentration in the compost decreased from 55 to 8 mg/kg (85%) as a result of red mud addition to the compost. A considerable part of this reduction may be attributed to partial neutralisation of the $\text{HCl}$ by the alkalinity in the added red mud, resulting in a reduced strength of the $\text{HCl}$ solution and thus its ability to extract from or dissolve cations in the mixtures.
BaCl₂ extractable lead was low, ie. only a maximum of 0.4 % of the total lead content. This was expected as lead forms very stable complexes with organic matter, particularly with humic acids (see section 2.3.3 and 4.3.4), unlike zinc. Red mud addition reduced the extractable lead significantly, and no lead was detected in the extract of compost with 15 % red mud (Table 4.2). A clear trend however could not be established due to the scatter of the data.

During extraction with BaCl₂ it is likely that barium ions would prefer to exchange with the sodium adsorbed to red mud as opposed to lead from organic matter, since it is more easily available for adsorption. A combination of high concentrations of sodium, which has a dispersive effect on organic matter, and excess barium in solution may assist in extracting lead from its stable organic matter complex. Increased red mud addition would increase the cationic strength of the solution by release of sodium and it also increases the available cation exchange capacity for adsorption of metals.

Acid extractable lead was nearly twice the amount of exchangeable lead. This shows that some organically complexed lead was extracted. The reduced acid extractability of lead as a result of red mud addition can partly be attributed to adsorption of lead to red mud, though acid neutralisation by the red mud would have affected the lead extraction as well. The lead found in the 10% red mud sample extract (2.6 mg/kg) could have originated from red mud itself since it contains appreciable lead levels (Table 6.6). However, lead was not found in the compost sample with 15% red mud, thus it may have been erroneous contamination. Nonetheless, in both the BaCl₂ and the HCl compost extractions, red mud addition reduced the amount of solubilised zinc and lead.

4.3.2.2 Plant available and soil solution soluble metals

DTPA extraction showed that red mud addition might have different effects on the plant availability of heavy metals (Table 4.3). Cadmium decreased significantly, copper increased slightly, whereas nickel did not appear to be affected. The degree of complexation of heavy metals with organic matter, metal adsorption to red mud and preference for complexation by DTPA interact to determine the extractable amount of metal from compost. The slight increase in plant available copper is likely to be associated with the increased solubilisation of the organic matter, and the metals bound
to it, as a result of the red mud addition. Copper is known to be very strongly bound to organic matter (Emmerich et al., 1982). Plant availability is high for nickel, 9 mg/kg (25 % of total) and cadmium, 2.1 mg/kg (35 % of total). This suggests a relatively low stability constant for nickel and cadmium complexes with the organic matter fraction.

Table 4.3 The effect of red mud on plant available and soil solution soluble cadmium, copper and nickel concentrations (mg/kg).

<table>
<thead>
<tr>
<th>% red mud</th>
<th>plant - available (DTPA)</th>
<th>leachable (CaCl₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cadmium</td>
<td>copper</td>
</tr>
<tr>
<td>0</td>
<td>2.2</td>
<td>8.6</td>
</tr>
<tr>
<td>10</td>
<td>1.9</td>
<td>8.9</td>
</tr>
<tr>
<td>20</td>
<td>1.7</td>
<td>8.9</td>
</tr>
<tr>
<td>30</td>
<td>1.5</td>
<td>8.9</td>
</tr>
<tr>
<td>40</td>
<td>1.3</td>
<td>9.7</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>10.3</td>
</tr>
</tbody>
</table>

*Not detectable

The results of the CaCl₂ extraction showed that addition of red mud did not affect the level leachable metals in compost. Metal removal from solution through precipitation could be ruled out since the concentrations did not exceed the solubility product with their hydroxides. The leachable nickel was 5 - 5.5% of its total content in compost, and copper 0.44%, reflecting their different affinity for organic matter. Cadmium was not detected in the extracts. The results of the batch extraction tests suggest that most heavy metals leached from compost are bound to solubilised organic matter and are not in free cationic form, otherwise red mud addition would have had a more significant effect on heavy metal removal from the leachate.

4.3.3 Effect of red mud on the fractionation of organo - metallic complexes

4.3.3.1 Characterisation of humic and fulvic acids

The UV-scan of the humic and fulvic acid solutions extracted from compost over the range 200 - 800 nm shows a similar UV absorbance pattern for both humic and fulvic
acids (Figure 4.1). Absorbance remains constant in the range 200 - 270 nm and is lower for fulvic acids (0.65) than for humic acids (1). From 270 to 320 nm absorbance increased to a maximum. From 350 nm absorbance reduced again to reach a minimum (0) at 800 nm.

![Absorbance graph](image)

Figure 4.1 The UV and visible absorbance spectra of fulvic and humic acids in compost.

It was confirmed that the high adsorption in the 270 - 320 nm range was not caused by the soluble anionic zinicate by a separate measurement in a zinicate solution.

Table 4.4 UV absorbance at four wavelengths and the $E_4/E_6$ ratios and $\Delta \log K$ values of fulvic (FA) and humic (HA) acids in compost.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength (nm)</th>
<th>$\Delta \log K$</th>
<th>$E_4/E_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
<td>465</td>
<td>600</td>
</tr>
<tr>
<td>Fulvic acids</td>
<td>0.90</td>
<td>0.29</td>
<td>0.04</td>
</tr>
<tr>
<td>Humic acids</td>
<td>1.94</td>
<td>0.83</td>
<td>0.17</td>
</tr>
</tbody>
</table>

In Table 4.4, the $E_4/E_6$ ratios and $\Delta \log K$ values are given for the fulvic and humic acids. The threefold higher $E_4/E_6$ ratio for fulvic acids than for humic acids and the eightfold higher $\Delta \log K$ value for humic acids indicate a well matured compost.
4.3.3.2 Fractionation of soluble organic acids

4.3.3.2.1 Fulvic acid

Fractionation of the fulvic acid extract by gel filtration resulted in three distinctive molecular weight fractions with absorbance peaks at 254 nm (Figures 4.2, 4.3). The distribution coefficients \( K_{av} \) were determined for each peak (Table 4.5). Only three organic matter fractions could be distinguished with the G-10 gel, because of the predominance of high molecular weight fractions. The \( K_{av} \) for the first peak approaches zero. This indicates that the molecular weight of the largest fulvic acid fractions exceeds 700 g/mol (Baham et al., 1978). This is in agreement with the results of Giovanozzi-Sermanni (1982), who separated compost humic and fulvic acids on a Sephadex G-100 column. It can be inferred from Figures 4.2 and 4.3 that red mud reduces the level of heavy metals in solution. The levels of cadmium, nickel and lead in the extracts were below their detectable limits on AAS.

Table 4.5 shows that the addition of red mud had no influence on the distribution coefficient and the absorbance pattern of the organic matter (maximum and 0.5 x peak width). The red mud thus did not change either the molecular weight distribution or the concentration of fulvic acids.

Table 4.5 \( K_{av} \) values of fulvic acids obtained from compost/red mud mixtures separated on a Sephadex G-10 column.

<table>
<thead>
<tr>
<th>red mud (g)</th>
<th>( K_{avI} )</th>
<th>( K_{avII} )</th>
<th>( K_{avIII} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
<td>0.37</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>0.34</td>
<td>0.45</td>
</tr>
<tr>
<td>10</td>
<td>-0.01</td>
<td>0.34</td>
<td>0.47</td>
</tr>
<tr>
<td>15</td>
<td>0.0</td>
<td>0.34</td>
<td>0.47</td>
</tr>
</tbody>
</table>

mean (stand. dev.): 0.0 (± 0.01); 0.34 (± 0.01); 0.46 (± 0.02)
The zinc peaks show that most of the zinc in the extract was not complexed to the organic matter fraction that shows an absorbance at 254 nm, since the zinc only eluted after twice the elution volume had passed (Figure 4.2). This indicates either that cationic zinc is adsorbed to soluble organic matter with a higher molecular weight than could be separated or that the zinc is in solution as Zn(OH)$_4^{2-}$ or Zn(OH)$_4^{4-}$. The pH of the sample applied to the column is 10.2, but the elution liquid has a pH of 13 (0.1 M NaOH) resulting in a pH value of the eluted sample approaching 13, at which pH the presence of zinctate is likely. Zinc in anionic form could be adsorbed onto red mud by Al and Fe oxides in a similar manner to PO$_4^{3-}$.

![Graph showing UV absorbance and [Zn] vs. elution volume (ml)](image)

**Figure 4.2** The effect of red mud on the distribution of zinc over the different molecular fractions of a compost fulvic acid extract. ($V_0 = 74$ cm$^3$, $V_1 = 205$ cm$^3$, pH=±13)

Addition of red mud to the compost prior to extraction resulted in a consistent decrease in zinc in the extracts from 1.45 to 0.1 mg/l (93 %). This reduction is likely to be due to adsorption of Zn(OH)$_4^{2-}$ onto aluminous goethite in red mud. Zinc removal through precipitation of Zn(OH)$_2$ is unlikely since the reduction in Zn concentration is independent of the pH. Thus non-organically bound zinc will stay in solution during the fractionation with 0.1 M NaOH. Zinc was not detected in the humic acid extract. The interaction of zinc with the gel matrix cannot be excluded as a contributing factor for zinc reduction in the effluent, as zinc retention by gel was established by Kron (1986).
The elution diagrams (Figure 4.3) show that copper elutes at the same time as soluble organic matter at wavelength 254 nm. All copper must be presumed to be adsorbed to organic matter, since any ionic copper in solution would precipitate as Cu(OH)2 at the elution pH of approximately 13. The copper must be strongly adsorbed, as sodium will compete strongly for adsorption sites on the functional groups of the organic acids. Increasing red mud addition resulted in a reduction in copper concentration in the extracts from 2.37 to 0.8 mg/l or 66%. Chen et al., (1977) found from a soil column percolation experiment that the absorbance of soluble organic matter in the leachate, measured at 265 nm, peaked at the same elution volume as copper and the electrical conductivity (salt leaching) at pH 8 (Ks = 3.6 *10^-11). It can thus be concluded that all copper leached from the G - 10 column is chelated to the fulvic acids.

![Graph showing elution volume vs. copper concentration and UV absorbance](image)

**Figure 4.3** The effect of red mud on the distribution of copper over the different molecular fractions of a compost fulvic acid extract. (V₀ = 74 cm³, Vₜ = 205 cm³, pH = ± 13)

4.3.3.2.2. Humic acids

The fractionation of the humic acid extract on a G - 10 column was inadequate, due to the high the inability of G - 10 gel to separate molecular weight fraction exceeding 700 g/mol, to provide more information about the molecular weight distribution. Thus the
humic acids had a molecular weight exceeding 700 g/mol. The tailing of the peak showed that there is a range of fractions with a molecular weight close to 700 g/mol. In Table 4.6 the Cu and Zn concentrations found in the humic acid extract eluent are given.

Red mud appears to remove metals from solution through adsorption of free cations, e.g. zinc, and seems also capable of reducing the amount of copper bound and adsorbed to the humic acids, without an increase in free ionic copper. This shows that red mud is able to immobilise metals through adsorption of cations as well as soluble organic fraction to which metals are complexed.

Figures 4.2 and 4.3 and Table 4.6 show that only a small amount of metal was adsorbed onto the humic and fulvic acids, compared to the total amount in the compost. Zinc was in solution as zincate, due to the high pH. Copper can not be present in free ionic form, as it would precipitate. Most metals were complexed to the insoluble organic matter fraction (humins). The leachable copper in ionic form could not be measured due to precipitation.

Table 4.6 The distribution of copper and zinc (mg/kg) in the soluble organic fraction of compost.

<table>
<thead>
<tr>
<th>red mud (g)</th>
<th>Copper</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fulvic</td>
<td>humic</td>
</tr>
<tr>
<td>0</td>
<td>24.2</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>17.4</td>
<td>0.65</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>0.38</td>
</tr>
<tr>
<td>15</td>
<td>10.7</td>
<td>-</td>
</tr>
</tbody>
</table>

*bd = below detection limit (Cu 0.05 mg/l; Zn 0.01 mg/l).

4.3.4 Effect of red mud on the leachable metals, the soluble organic matter and its optical characteristics

4.3.4.1 Effect of red mud on the leachable heavy metals in municipal compost

Increasing the amount of red mud has different effects on the solubility of the metals analysed for. This effect of red mud is demonstrated by the results of the removal of the
humic acid fraction where metal levels in solution are selectively reduced. The results are shown in Figures 4.4 and 4.5 and the data are tabulated in Appendix 4.I.

The cadmium levels were close to the detection limit which makes interpretation of the effect of red mud addition on Cd behaviour difficult. The cadmium concentration slightly decreased after the first red mud addition (1g). Further addition of red mud left the concentration unaffected. Lead levels were not affected by red mud addition.

Zinc levels decreased as a result of increasing red mud addition. The largest reduction (50%) occurs with the first addition of red mud. The amount of solubilised zinc is relatively very low.

The release of nickel from compost was more than 10% of the total nickel content in compost. Nickel levels in the compost extracts showed a slight increase as a result of red mud addition, possibly due to increased solubilisation of humic acids to which soluble Ni is adsorbed.

![Graph showing metal levels in CaCl₂ compost extract](image)

**Figure 4.4 Effect of red mud addition on metal levels in a CaCl₂ compost extract (Ecrm) before and after (*) humic acid removal.**

Relatively little copper was found in the extracts; only 1% of the total content. The extracts showed a decrease in copper as a result of increasing red mud additions.
The removal of humic acids from the extracts after the equilibration of the extracts with red mud showed a slight increase in copper and zinc levels, but complete removal of cadmium, lead and nickel. This demonstrated the strong and complete complexation of cadmium, lead and nickel with humic acids. The increase in copper and zinc could be experimental error though the consistency suggests a release of these metals from the humic acid matrix during the acidification step to pH 1. Even at this pH cadmium, lead and nickel remained complexed to the precipitated humic acids.

Precipitation of metal hydroxides did not contribute to the reduction in metal concentrations, since the solubility products were not exceeded (Appendix 4.1).

![Figure 4.5](image)

**Figure 4.5** Effect of red mud-gypsum addition on metal levels in a CaCl₂ compost extract (ECmg) before and after (*) humic acid removal.

4.3.4.2 The effect of gypsum on metal solubilisation

Addition of gypsum to red mud had no noticeable effect on the extractable metals when Figures 4.4 and 4.5 are compared. Only the level of nickel in solution increased. No nickel could be found after analysis of gypsum.

Gypsum amendment of red mud at 4% w/w to neutralise red mud alkalinity had no effect on the pH of the red mud - compost extracts (Figure 4.6). The organic acids in the
compost seemed sufficient to neutralise red mud alkalinity, since gypsum addition did not make a difference. The pH graph of the compost extract, to which red mud was added confirmed this, since red mud addition increased the pH of the extract significantly, due to the absence of the buffer capacity of the solids in compost.

![Graph showing pH vs. red mud added (g)]

Figure 4.6 Effect of gypsum amendment to RM on the pH in a red mud-compost water extract and the effect of RM addition to a compost water extract on the pH.

4.3.4.3 Adsorption of soluble heavy metals and organic acids onto red mud

The total organic carbon content (TOC) of the compost extract reduced by ±70% after addition of red mud from 1430 to 390 mg C/l (Table 4.7). An additional reduction in TOC of 100 g C/L was observed in the extract without humic acids (i.e. fulvic acid extract) as a result of red mud addition. It can therefore be inferred that 90% of the total reduction in TOC was caused by adsorption of humic acids to red mud, while only approximately 10% of the fulvic acids were adsorbed and the rest remained in solution.

Table 4.7 Total organic carbon concentrations (mg C/l) in compost extracts equilibrated with red mud and the effect of humic acid (HA) removal.

<table>
<thead>
<tr>
<th>red mud (g)</th>
<th>Total Extract (TE)</th>
<th>TE minus HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1435</td>
<td>480</td>
</tr>
<tr>
<td>1</td>
<td>390</td>
<td>380</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>500</td>
</tr>
<tr>
<td>5</td>
<td>380</td>
<td>-</td>
</tr>
</tbody>
</table>
The humic acid fraction that was adsorbed is likely to have been the hydrophobic lipidic fraction, which lacks the ability to adsorb metals (Kron, 1986). The metal binding humic acid fraction is more hydrophilic and less polymerised. The result suggests a considerable, though selective, capacity of red mud to adsorb soluble organic matter.

The results in Figure 4.7 demonstrate the effect of the addition of red mud to a compost water extract on the removal of soluble metals and organic acids from solution. The removal of metals from solution is either by direct adsorption onto red mud or by adsorption onto red mud of fulvic or humic acids with contain metals, ie. Cu - fulvic and Cd, Ni, Pb - humic acid.

![Graph](image)

**Figure 4.7** The effect of red mud addition to a compost - water extract (Ec+rm) and removal of humic acids (*) on the metal levels in solution.

The zinc concentration reduced by >95% with 1 gram red mud addition but did not reduce further by higher red mud additions. This indicates that most zinc in the extract was in a readily adsorbable form, though a small amount remained strongly adsorbed to soluble organic acids, probably fulvic acids, not available for adsorption. It is possible that some zinc desorbed from fulvic acids and subsequently was adsorbed by red mud. The copper concentration was reduced by each increased red mud addition up to a maximum of 70%. The biggest reduction occurred after the first red mud addition. This suggests that some copper was in solution in ionic form and that red mud when
present in sufficient amounts appears to be able to extract copper from the fulvic acids
or adsorbed Cu - fulvates, since it was shown in chapter 3 that any ionic copper would
be removed from solution by red mud. The addition of red mud had no effect on the
lead and nickel which are entirely complexed to the humic acid fraction. The cadmium
concentration in the extract was below detection level.

4.3.4.4 Role of humic acids in soluble metal retention

The removal of the humic acids from the compost - red mud and - red mud gypsum
(Ecrm and Ecrmg) extracts resulted in complete removal of cadmium, lead and nickel
from the solutions (Figures 4.4 and 4.5).

In the water extracts (Ec+rm) all lead and nickel was removed from solution through
humic acid removal. Thus lead and nickel can be inferred to be strongly complexed to
humic acids. No cadmium was found in these extracts. The concentrations of zinc and
copper were not affected by humic acid removal.

However, red mud addition did not reduce the concentrations of the metals that are
complexed to the humic acids. This indicates that the humic acid fraction that adsorbs
metals did not adsorb to red mud.

4.3.4.5 Effect of red mud on the optical properties of compost extracts

The results of the measurement of the UV and visible light transmission spectra of the
water and CaCl₂ extracts of compost, red mud and mixtures are shown in Figures 4.8
and 4.9. The results are plotted as 100% - %transmission to obtain peaks similar to the
previous absorbance graphs (figures 4.1 - 3). Transmission data can be converted to
absorbance using the equation of Lambert - Beer (section 2.3.6.2). It is clearly
demonstrated that for compost, water was a more efficient extractant than CaCl₂, since
100% - %transmission in the water extracts was much higher for compost (40% vs. 20%)
and for red mud (15% vs. 10%) below 250 nm. This is likely to be due to reduced
solubility of organic acids because of the flocculation properties of calcium.
The 100% - %transmission of the red mud only water extracts seems dependent on the red mud concentration, as increasing red mud from 1 to 5 g, increased the 100% - %transmission from about 4% to about 15%. This increase in 100% - %transmission is presumed to be caused by the dissolution of colloidal iron oxides (particle size < 0.45 μm) such as the yellow haematite (Fe₂O₃), which could not be removed by membrane filtration. These colloids can form complex species with the humic substances in compost. These complexes have a stronger light absorbance than the humic substances or iron oxides on their own. This is demonstrated in Figure 4.8, where the 100% - %transmission in the compost extract after red mud is added, is much higher than those of the individual extracts of either red mud or compost. For example, at 400 nm the 100% - %transmission of the compost extract was 20% and of 1 and 5 g red mud respectively 15% and 50%, but of the mixtures it is respectively 80% and 95% (Figure 4.8). This increase in 100% - %transmission reflects the different optical properties of the iron oxide - humic substance complexes as opposed to an increase in concentration, following their linear relation, since red mud addition reduced the TOC in the extracts.

In the compost extracts with 1 g red mud added, the spectrum was mainly influenced by the humic substances since the pattern of the spectrum was the same as the compost only extract, though with a higher 100% - %transmission, (approximately 40% vs. 80%) in the 200 - 250 nm range (Figure 4.8). The spectrum of the compost extract with 5 g red

Figure 4.8 The effect of red mud addition to compost water extracts on the UV/visible light spectra of the extracts. (CE = compost extract)
mud was more influenced by the red mud spectrum. At wavelengths above 350-380 nm the mud was lower in the mixed extracts due to the complexation of humic substances with soluble red mud minerals. Humic substances were also complexed to the solid red mud fraction and thus removed from the extract during filtration (Table 4.7).

The CaCl₂ extraction of red mud + compost mixtures resulted in a value of 100% - %transmission in the extracts that was in between the value of the 5g red mud extract, and the compost extract but the value was much lower in the 1g red mud sample (Figure 4.9). Calcium ions from CaCl₂ form soluble complexes with the soluble compost fraction, which competes for the calcium with red mud, if present. A high percentage of colloidal particles were coagulated in the presence of calcium and precipitated, hence the lower 100% - % transmission in the calcium extracts.

Red mud addition to compost decreased the 100% - transmission in the extract because of adsorption of organic acids to red mud, thus reducing the organic acid concentration. Since the relationship between concentration and transmission is logarithmic, a two fold increase in transmission requires a hundred fold reduction in concentration. At 400 nm the value of 100 - %transmission of the compost extract is only 75% while addition of 1 and 5 g red mud decreased this value to respectively 55% and 45% (Figure 4.9).

![Figure 4.9 The effect of red mud addition to compost on the UV/visible light spectra of CaCl₂ extracts.](image-url)
The results of the maximum absorbance measurements and the Δlog K and E₄/E₆ ratios are shown in Table 4.8. The E₄/E₆ quotient was not affected by red mud addition to compost. However, the solutions were not buffered and variations in pH (7.5 - 8) may have affected the result, since absorbance is pH dependent. The E₄/E₆ ratios need to be determined in the pH range 7 - 8 (Kononova, 1966). The E₄/E₆ ratio could be considered rather high, indicating a low degree of aromatic condensation and the presence of relatively large proportions of aliphatic structures. Red mud - gypsum reduced the ratio at 1g red mud addition possibly through adsorption but increased at higher additions (5g) which can possibly be explained by increased condensation due to the added alkalinity. The same was observed when red mud was added to a compost water extract.

Table 4.8 The effect of red mud on the Δlog K and E₄/E₆ values of compost extracts.

<table>
<thead>
<tr>
<th>wavelength</th>
<th>400</th>
<th>600</th>
<th>465</th>
<th>665</th>
<th>Δlog K</th>
<th>E₄/E₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>red mud added (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>organic matter - red mud extracts (Ecrm):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.54</td>
<td>0.02</td>
<td>0.19</td>
<td>0.007</td>
<td>1.43</td>
<td>27.1</td>
</tr>
<tr>
<td>5</td>
<td>0.44</td>
<td>0.013</td>
<td>0.14</td>
<td>0.005</td>
<td>1.52</td>
<td>28.0</td>
</tr>
<tr>
<td>organic matter - red mud gypsum extracts (Ecrmg):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.49</td>
<td>0.02</td>
<td>0.17</td>
<td>0.01</td>
<td>1.39</td>
<td>17.0</td>
</tr>
<tr>
<td>5</td>
<td>0.57</td>
<td>0.10</td>
<td>0.27</td>
<td>0.008</td>
<td>0.75</td>
<td>33.8</td>
</tr>
<tr>
<td>red mud organic matter adsorption (Ecr+rm):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.20</td>
<td>0.11</td>
<td>0.13</td>
<td>0.10</td>
<td>0.26</td>
<td>1.30</td>
</tr>
<tr>
<td>1</td>
<td>0.79</td>
<td>0.28</td>
<td>0.52</td>
<td>0.23</td>
<td>0.44</td>
<td>2.26</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>0.27</td>
<td>0.52</td>
<td>0.23</td>
<td>0.44</td>
<td>2.26</td>
</tr>
</tbody>
</table>

4.3.4.6 Role of Humic acids

In Table 4.9 the results of the measurements of the maximum absorbance and the most sensitive wavelength are presented. The absorbance in the fulvic acid solution were slightly higher than the original extracts (note the dilution factors). This result may be a combination of the following processes, i) red mud may adsorb humic acids during the
extraction, resulting in mainly fulvic acids in the extracts, and ii) red mud has an effect on the chemical structure of fulvic acids, resulting in an increased absorbance at 276 nm (Table 4.9). This indicates either a direct effect of red mud on the organic acids through iron oxide complexation and chelation with calcium ions.

Even though the wavelengths where maximum absorbance was observed were not the same for the compost - red mud and compost water extracts, possibly because of the pH difference, the absorbances were similar, considering the dilution factor of the compost - red mud extract. The absorbance in the compost water extracts decreased approximately by 70% as a result of humic acid removal. The same reduction was observed in TOC concentration after humic acid removal (Table 4.7), confirming the linearity between concentration and absorbance.

Table 4.9 The effect of increasing red mud (C1-C5) and red mud-gypsum (Cg) additions to compost and to water extracts of compost on the absorbance (range 0 - 3) of the extracts at their most sensitive wavelength (\( \lambda \) in nm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>FA &amp; HA</th>
<th>FA</th>
<th>FA &amp; HA</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda )</td>
<td>abs*</td>
<td>( \lambda )</td>
<td>abs#</td>
</tr>
<tr>
<td>C0</td>
<td>276</td>
<td>1.06</td>
<td>276</td>
<td>1.24</td>
</tr>
<tr>
<td>C0</td>
<td>312</td>
<td>0.58</td>
<td>277</td>
<td>1.35</td>
</tr>
<tr>
<td>C1</td>
<td>312</td>
<td>0.41</td>
<td>277</td>
<td>0.94</td>
</tr>
<tr>
<td>C2</td>
<td>312</td>
<td>0.41</td>
<td>276</td>
<td>0.90</td>
</tr>
<tr>
<td>C4</td>
<td>312</td>
<td>0.39</td>
<td>276</td>
<td>0.92</td>
</tr>
<tr>
<td>C5</td>
<td>312</td>
<td>0.38</td>
<td>277</td>
<td>0.85</td>
</tr>
</tbody>
</table>

| Cg1     | 312 | 0.43 | 277 | 2.02 |
| Cg2     | -   | -    | -   | -    |
| Cg3     | 312 | 0.42 | 277 | 0.94 |
| Cg4     | 312 | 0.42 | 277 | 0.95 |
| Cg5     | 312 | 0.44 | 277 | 0.98 |

* after 10 fold dilution; # after 5 fold dilution
4.3.4.7 The effect of gypsum addition

The incorporation of gypsum into red mud was to fulfil three functions. The acidic nature of gypsum assists in neutralising the free alkalinity of red mud. The calcium content can improve the soil properties of the clay fraction in red mud e.g. structure and hydraulic conductivity (chapter 2). The calcium can also react with the soluble organic matter to form a calcium - humate precipitate, thus reducing the mobility of the metals adsorbed to the organic matter (Gorbunov, 1971). This was confirmed in this study since gypsum - red mud addition resulted in a lower optical density of the extracts that was similar to the optical density found in the tenfold diluted red mud only compost extracts. The first addition of 1 gram red mud - gypsum resulted in a 25 % reduction in absorbance. The addition of 5g red mud had no further reducing effect on the absorbance. Thus gypsum addition has a considerable effect on reducing the solubility of organic matter. Since gypsum did not influence the pH, the effect is likely to be the result of formation of insoluble calcium - humate precipitates.

4.3.4.8 Adsorption of soluble organic acids to red mud

The addition of red mud to the compost extracts resulted in a large reduction in absorbance of the total red mud - compost extract. The reduction in absorbance in the fulvic acid solution is considerably lower. This leads to the conclusion that the reduction is mainly caused by humic acid removal from solution. This agrees with the TOC results (Table 4.7). Red mud, and in particular gibbsite (Al - oxides) and goethite (Fe - oxides), are capable of adsorbing organic acids (Schnitzer and Skinner, 1966).

4.3.5 Effect of gypsum on metal leaching from red mud - compost percolation columns

The percolation experiment showed that gypsum amended red mud reduces heavy metal leaching compared to unamended red mud (Figures 4.10, 4.11, 4.12). This result was not found in the batch extraction experiment (Figures 4.4 and 4.5). The quantities of metals leached are shown in Table 4.10. The reduction in leaching is in the order of Cu > Zn > Ni. The reduction was not caused by a change in pH, because the pH of the leachates did not appear to be affected by gypsum addition.
After approximately 2 pore volumes no more copper and nickel was found in the leachate from the RMG column, while zinc continued to appear in the leachate for the duration of the experiment. This shows a different metal retention mechanism between these metals and the compost mixture. The leachable copper and nickel in the RMG column is likely to have been in ionic form. The reduction in concentration of these metals in the leachate is likely to be attributed to the precipitation of the metal fraction that is strongly complexed to soluble organic acids in the presence of calcium from gypsum. These are likely to be both humic (Ni) and fulvic (Cu) acids.

![Graph](image)

Figure 4.10 Nickel leaching from red mud (RM) and red mud - gypsum (RMG) amended compost.

![Graph](image)

Figure 4.11 Copper leaching from red mud (RM) and red mud - gypsum (RMG) amended compost.
Zinc leaching from the RMG column appeared to be a function of the cation exchange process trying to maintain an equilibrium between zinc that was adsorbed and that in solution which continued to leach, therefore the long tailing in the peak.

The RMG amended compost column produced a lighter coloured effluent than the red mud amended compost column, indicating a lower soluble organic matter content in the leachate. This confirms the gypsum effect of reducing solubility of organic matter, as was found in the optical study (section 4.3.4.7 and Table 4.9). In addition, the leached metals are either in ionic form or complexed onto the soluble organic matter. The coinciding reduction of soluble organic matter and leached metals confirm the effect of gypsum on organic matter solubility and thus metal solubility.

Table 4.10  Effect of gypsum amendment of red mud on total metal leaching, in mg, from a red mud - compost percolation column.

<table>
<thead>
<tr>
<th>Metal</th>
<th>red mud</th>
<th>red mud - gypsum</th>
<th>reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>202</td>
<td>99</td>
<td>51</td>
</tr>
<tr>
<td>Copper</td>
<td>143</td>
<td>35</td>
<td>76</td>
</tr>
<tr>
<td>Zinc</td>
<td>302</td>
<td>84</td>
<td>72</td>
</tr>
</tbody>
</table>
An additional explanation for lower organic matter solubilisation can be a higher ratio of divalent/monovalent cations in the mixture through addition of calcium in gypsum. A high calcium to sodium ratio prevents the dispersion of organic acids. Additionally the acidic character of gypsum has a considerable capacity to reduce the alkalinity of red mud, as a 5% gypsum amendment reduces the pH of red mud from 12 to 8.3 (Ho et al., 1984). A reduction in the alkalinity of the red mud will reduce the solubilisation of organic acids which would otherwise buffer the pH.

4.4 Discussion

The results of the different experiments presented in this chapter at first glance seem to have little in common. The experiments will first be discussed individually before a proposed theory to provide a consistent explanation for the combined results is discussed.

The amount of leachable, plant available and exchangeable metals extracted from municipal compost was relatively low (section 4.3.2). Thus approximately 90-95% of the total metal content is complexed to the humin fraction. The humin fraction thus functions as a store for metals which will be released as the fraction further decomposes in soil. It appears that differences exist in the behaviour of the various metals. This can be attributed to the specific characteristics of each metal e.g. charge, hydration properties (ion exchange), radii, etc.

It appears that amending compost with red mud has a different effect on the solubility of each metal. In both the extraction and adsorption experiments (section 4.3.3), red mud addition reduced the zinc concentration by 50%. So zinc was approximately 50% in solution in a form directly reactive with red mud, as zinc did not appear to be adsorbed to humic acids. The residual 50% in solution was complexed with fulvic acids or in another form, that is non reactive with red mud. The slight reduction in zinc concentration as a result of increasing red mud additions might be caused by ion exchange, when zinc desorbs from fulvic acids and preferentially adsorbs onto red mud particles. Red mud did not reduce plant availability of heavy metals. It is likely that DTPA forms a stronger complex with metals than red mud does.
Copper behaviour is similar, except for the more gradual decrease of copper in solution as a result of increasing red mud additions. This might indicate that copper is complexed to soluble organic acids, as copper is known to have high stability constants with soluble fulvic acids (McBride, 1989). No copper was found to be adsorbed to humic acids. Of the total copper >99% is complexed in the insoluble humin fraction. Copper-humic matter complexes have very high stability constants similar to lead-humic matter complexes, in particular those complexes with the soluble fulvic acids formed at an alkaline pH. Copper fulvate complexes have stability constants 10 times greater than those of cadmium-fulvates (Saar & Weber, 1982).

All lead, nickel and cadmium in solution was adsorbed to humic acids. These metals must have been strongly bound to the humic acids, since red mud proved incapable of reducing their concentration by adsorption. A reduction in soluble TOC did not lead to a reduction of these metals in solution (Figures 4.4 and 4.5). Research described in chapter 6 shows that red mud can reduce TOC levels in compost extracts, through adsorption of organic acids (Table 6.6). It appears that TOC reduction is mainly due to a reduction in humic acid. The absence of Cd, Ni and Pb removal indicates that the TOC reduction by humic acid adsorption to red mud is caused by adsorption of the hydrophobic humic acid fraction (lipids) which do not adsorb metals, while the hydrophilic fraction which contains carboxylic functional groups that can bind metals stay in solution (Kron, 1986).

The increase in nickel concentration in the extract is probably the result of desorption of nickel from red mud and/or gypsum. The suggestion that nickel is strongly bound to humic matter is supported by the fact that only 10 % of the total nickel was dissolved and that all dissolved nickel was removed as a result of humic acid removal.

As with nickel, all extractable lead in solution was adsorbed by humic acids. Red mud addition, however, did not decrease the lead levels in the extract. Lead was not adsorbed by red mud. The behaviour of lead and nickel suggests that red mud adsorbs only hydrophobic humic acids. The cadmium concentrations in the water extracts were too low to show an effect of the red mud addition.
Gypsum addition to red mud has no significant effect on the metal solubility in batch extractions. However, gypsum amendment of red mud reduced metal leaching (> 50%) from municipal compost compared to red mud only amendment in percolation columns. This is probably due to a reduction in organic matter dispersion into water as colloids. The mixture consisting of a combination of municipal compost and red mud - gypsum leached the lowest amounts of metals during percolation.

The five metals that were studied in the extracts can be divided into two groups. Firstly the metals that are fully complexed to humic acids i. e. Pb, Cd and Ni, since humic acid removal eliminated these metals from solution. The others, Cu and Zn, are associated with fulvic acids particularly Cu, and/or in ionic form. Cu - fulvate bonds are stronger than Zn - fulvates bonds.

The results of the TOC analysis in the compost water extract to which red mud was added showed that addition of red mud combined with humic acid precipitation reduced the TOC in solution by approximately 1000 mg C/l. This suggests that all humic acids, as opposed to fulvic acids, are adsorbed to red mud. This is likely to be due to the hydrophobic nature of humic acids as a result of polymerisation and their high molecular weight.

However, in all extractions, the concentration of metals associated with humic acids did not decrease when red mud was added. The metals that are bound to fulvic acids (Cu, Zn) and/or are in ionic form (Zn) did reduce in concentration, suggesting that only fulvic acids are adsorbed by red mud.

Humic acids can contain a large fraction of hydrophobic lipidic compounds which can not adsorb metals, as well as a fraction that can bind metals and is, due to its ionic nature, hydrophilic. The hydrophobic fraction will preferentially adsorb to red mud causing a substantial reduction in TOC. However, the adsorption of this humic acid fraction will not lead to a reduction in metals associated with humic acids, but will be removed when the humic acids are precipitated.

Thus the likely scenario of red mud - organic acid - metal interactions is as follows. Red mud adsorbs the lipidic non - metal binding humic acid fraction and some fulvic acid in
a ratio of approximately 10:1 (Table 4.7), thus keeping Cd, Pb and Ni in solution since these are associated with the metal binding humic acid fraction in solution. Red mud would adsorb all ionic metal species which mainly applies to Zn which is mainly in ionic form in solution. In addition, red mud would adsorb some fulvic acids containing Cu or Zn. However some of these Zn-, Cu- fulvate complexes remain soluble.

Distilled water extracted 40 - 50% less humic acids indicated by the reduction in Pb, than the CaCl₂ extract, confirming the hydrophobic nature of humic acids. The higher pH of the water extracts (8.5) vs. the CaCl₂ extracts (7.5) suggests that phenolic functional groups are ionised and available as additional metal adsorption sites.

4.5 Conclusions

Only a relatively small fraction of the total metal content of municipal compost is soluble. Of the solubilised metals, it was established that the levels of copper and zinc in solution can be reduced by red mud addition. Cadmium, nickel and lead are strongly adsorbed to the humic acids and thus little is in ionic form.

The use of red mud as an amendment to municipal compost to reduce the mobility of heavy metals is centred around its ability to adsorb free cations strongly and to adsorb some soluble organic acids to which metals are complexed. Most heavy metals however are adsorbed or complexed onto the insoluble humin fraction. Red mud seems able to adsorb heavy metals complexed to the soluble organic matter, which is mainly fulvic acids. Because fulvic acids are soluble over a wide pH range (1 - 13), the use of pH as a tool to reduce metal leaching is ineffective.

The experiment has shown that red mud is not capable of extracting the majority of metals from municipal compost since the metals are strongly complexed to the predominantly insoluble and to a minor extent the soluble organic fractions which are formed during the composting process. In order to immobilise these metals longterm, they must be adsorbed to an inorganic fraction before the organic waste is sufficiently decomposed to be able to adsorb these metals.
5.1 Introduction

In order to study the effect of red mud on the composting process and the mobility of heavy metals, a system was designed to enable compost production under controlled conditions.

Composting is an exothermic and aerobic process (Section 2.2). This means that the process is dependent on oxygen supply. The oxygen is used by microbes to oxidise organic matter. The energy released as a result of the oxidation process is partly used by the microbes for their metabolism, but is mainly released to the environment in the form of heat. Due to the heat production resulting from the microbial oxidation process the temperature of the mass will increase (Battley, 1987). In a situation with insufficient heat removal the temperature will rise to such levels that the biological degradation reaction becomes temperature inhibited (Strom, 1985). In order to achieve maximum degradation rates it is thus necessary to balance the heat production and heat removal in such a way that an optimum temperature is present in the composting system (Finstein, 1983). Extensive research on various organic substrates has shown that at a temperature of between 55 - 60°C, decomposition rate and oxygen consumption is highest (MacGregor et al., 1981 and Kuter et al., 1985), so in order to maintain the composting process in an optimum situation, the following is required:

- excess oxygen to maintain aerobic conditions and high decomposition rate, and
- the temperature maintained at an optimum level (55°C) to achieve optimum decomposition rate.

The air supply can be used to control the temperature through the absorption of heat by the cooler air (convective cooling) and moisture evaporation (ventilative cooling). Maintaining the optimum temperature requires excess aeration of the substrate during the thermophilic phase, thus ensuring sufficient air supply for the microbes. The composting control system based upon temperature control through forced aeration is based upon the Rutgers' system (Finstein et al., 1983, 1986; MacGregor et al., 1981).
The present experimental research program involved parallel composting runs with various amounts of bauxite refining residue added. For reasons of scientific and statistical validity, it was essential that the composting process for the different mixtures takes place simultaneously. This meant that the design of the facility needed to incorporate as many composting incubators and associated control devices as possible. In the present program, 7 incubators were used, taking into account the experimental requirements and resources available.

The thermophilic stage of the composting process requires continuous monitoring. Therefore temperature control was performed, and acquired data recorded by computer.

This chapter describes the system that was developed and the testing of its capability to simulate the composting process, to maintain a set temperature and prevent anaerobic conditions through sufficient supply of air.

5.2 Composting incubators

The facility accommodated seven identical composting incubators. In Figure 5.1 a diagram of one incubator and its associated instrumentation is shown. Each incubator consisted of a black 30 litre high density polyethylene (HDPE) container with a Ø 28 cm screw-on lid.

The incubator had an artificial double bottom, to allow space for air supply and distribution. The artificial bottom which supported the substrate consisted of a steel mesh (10 mm) covered by a 1 mm nylon mesh to prevent substrate falling through. The air supply, (Ø 6.35 mm PE tubing) entered the incubator about 3 cm from the bottom and was distributed by a perforated 50 mm diameter coiled polyethylene drain tube. The drain tube supported the artificial compost support (roster). The airflow through the substrate was upwards; the air outflow tube was fitted in the centre of the lid.

The process temperature was measured with a platinum (Pt100) temperature probe (R = 100 Ω), fitted in the bin at 2/3 of the compost mass height. In order to minimise the conductive heat loss through the incubators' walls, and promote ventilative heat loss,
the incubator, including the lid, was insulated with 100 mm glass wool blanket covered with aluminium foil (Pink bats, ACI).

Figure 5.1 Diagram of one of the composting incubators and the associated monitoring and process control equipment.

5.3 Monitoring system

A diagram of the complete laboratory composting facility including air lines and control and monitoring equipment is shown in Figure 5.2.

The composting process control was centred around maintaining an optimum process temperature which involved cooling the substrate if the temperature exceeded 55°C. The temperature was monitored using Pt100 probes connected to a RIM1000 interface board. A Hyundai 286 SE computer read the changes in resistance and converted these readings into degrees Celsius through a calibration formula.

The temperature control was achieved by controlling the airflow rate through the substrate using solenoid valves. The air volume through the incubator was determined by setting a continuous basic airflow rate of 1 l/min and then using temperature activated on/off solenoid valves to add 2 l/min of flow when the temperature exceeded 55°C, to give a total airflow rate of 3 l/min. The time that the solenoid valve was open was recorded cumulatively. This allows for a more accurate calculation of the total loss
of carbon as CO₂, nitrogen as NH₃ and moisture since the valve position determined the flowrate. The flowrate and the concentration of each compound in the effluent gas were required to determine the amount of each compound lost through evaporation. Monitoring the loss of carbon and nitrogen also enabled the development of a nutrient balance and was essential to follow variations in the C/N ratio in the substrate which is an important process parameter.

The decomposition process was monitored by analysis of the gas produced during the process. During composting oxygen is used by the microbes to oxidise the organic fraction for their metabolism during which process carbon dioxide is given off. Carbon dioxide respiration is an accurate measurement of the level of metabolic activity. Oxygen uptake from the air can be higher than the carbon dioxide released due to the incorporation of oxygen into organic matter as part of the functional groups, which are rich in oxygen. Input air was drawn from the laboratory pressurised air mains It contained 79% nitrogen, 20.7% oxygen and a carbon dioxide content insignificant compared to the amount produced during the composting process. The air was led through a self draining air humidifier prior to the incubators to avoid excessive moisture loss from the substrate. The effluent gas was analysed on line for oxygen by a micro-fuel cell and for carbon dioxide by an infrared gas analyser (Teledyne 730). The measuring range was 0-20% (±1% full scale). The temperature and the oxygen and carbon dioxide concentration data were logged on a Hyundai 286 SE personal computer.

Loss of ammonia during composting is a common problem which results in a lower nutrient value of the final compost, an unbalanced C/N ratio and odour problems. Ammonia emission was monitored by the analysis of the condensate for ammonium after condensing the effluent gas at 10°C in condensers. The condensate was collected in a sulphuric acid trap to keep the ammonium in solution. The collected volume of condensate was noted for inclusion in the mass balance and for calculation of the nitrogen balance.

Using data on total organic carbon content (TOC), total nitrogen (TN) and moisture content in the solids and the loss of gaseous carbon and nitrogen compounds, a full mass balance could be made. An accurate mass balance is, however, difficult to achieve
Figure 5.2 Schematic diagram of the laboratory composting facility showing the composting incubators and process control system.
for the composting process due to its highly complex nature and its dependence on environmental conditions.

Twice weekly solid samples of 100 g of compost were removed from the incubator to be analysed for pH, total C and N, moisture content and the chemical oxygen demand (COD) of a water extract. The COD is an indicator for compost maturity.

5.4 Process control and data acquisition system

The process control system was designed to monitor oxygen, carbon dioxide and temperature and control the temperature in the composting incubators simultaneously (Figure 5.2), in order to be able to make a valid scientific comparison between different substrates.

A software program was written to control the temperature, monitor the process and log the temperature, oxygen and carbon dioxide concentration data. It also determined the position of the solenoid valves and monitored the time each valve was open. (see Appendix 5.1).

Each temperature probe was connected to the computer via a programmable analog to digital interface module (RIM 1000, Novatech). The computer software enabled the setting of any desired temperature. The temperature was controlled by a computer signal to the RIM 1000 which then sent a signal to the corresponding solid state relay in the 240 Volt AC output box. This action opened the appropriate solenoid valve (240 V AC, Burkett) and boosted the basic air flow. This increased the ventilative heat loss from the incubator through heat convection and water evaporation.

Switching between the seven incubators for gas sampling and analysis was enabled by an electrical 12-port stainless steel switching valve. Only seven ports were connected. The output of the valve was connected to a continuous gas sampling pump which supplied the carbon dioxide and oxygen analysers at a constant flow of 60 cc/min. The valve had two micro switches, one of which was activated by a computer signal and the other enabled the computer to monitor the valve position. The valve and the computer also
communicated through the RIM1000 which relayed activation signals to the power box to rotate the valve.

With this set up each incubator could be sampled over a set duration in a cycle of 12 valve positions. The five dummy positions were employed to calibrate the analyser in between cycles with a gas standard containing 10% CO₂ and 15% O₂. The sampling regime was set as follows; for the first 2.7 days each bin was sampled for 2.5 minutes (30min/12positions) every 30 minutes since oxygen respiration is highest early in the process. For the following 2.3 days each incubator was sampled for 5 minutes in a 1 hour cycle, and for the rest of the time, the incubators were sampled for 10 minutes each in a 2 hour cycle. The result of each analysis was recorded on the hard disk at the last moment of the sampling period to allow complete purging of the previous sample from the gas lines and maximum stabilisation time for the analyser.

Both oxygen and carbon dioxide analysis results were sent as analog signals (range 0 - 1 V) to the RIM 1000 interface which converted them to digital form for computer logging. The computer converted the digital signals into actual concentrations using predetermined calibration formulas (Appendix 5.1).

5.5 Materials and methods

To test the experimental set up, one of the incubators was filled with 10 kg of a substrate consisting of fresh grass clippings and sawdust in a 4:1 weight ratio. This mixture had a C/N ratio of 20 - 30 and a moisture content of 60 - 65%, which are optimum values for these relevant process parameters. The substrate had a fine particle size which increases the surface area to which the microbes have access. This improves the degradation rate. The temperature control was set at 55°C and the airflow was set to a basic continuous flow of 1 l/min and a boost flow of 3 l/min to control the temperature.

Twice a week a 100g sample was taken to be analysed for the parameters listed in Table 5.1 and the incubators were weighed to monitor changes in the nett total weight of the substrate. The weight figures function as a reference for the mass balance. From the result of the total organic carbon and total nitrogen analysis the C/N ratio could be calculated.
The volume of condensate was measured regularly in order to include it in the mass balance. The concentration of ammonium in the condensate was analysed to determine the loss of nitrogen and its effect on the carbon to nitrogen ratio in the substrate. Solid samples were analysed for moisture content and dry matter content. This completed the data required to enable the calculation of a mass balance.

Table 5.1 Compost process and maturity parameters and the analytical methods applied.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>drying 50g at 105°C</td>
<td>Loss of weight</td>
</tr>
<tr>
<td>pH</td>
<td>10g in 50 ml water extract</td>
<td>combined glass electrode</td>
</tr>
<tr>
<td>COD in water extract</td>
<td>chromic acid digestion</td>
<td>FAS* titration#</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>chromic acid digestion</td>
<td>spectrophotometer (Cr⁶⁺)#</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>Kjeldahl</td>
<td>NH₄⁺ on Auto Analyser®</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>on-line sampling</td>
<td>infra red detector</td>
</tr>
<tr>
<td>Oxygen</td>
<td>on-line sampling</td>
<td>micro fuel cell</td>
</tr>
</tbody>
</table>

* Ferrous Ammonium Sulphate ((NH₄)₂SO₄·FeSO₄·6H₂O); # (Page et al.,1982); @ (APHA, 1985)

5.6 Results

The results are separated into two groups. First results of monitoring the process parameters are presented for each parameter. Then the results of the mass balances are given. The accuracy of the mass balances is an indication for the ability of the system to monitor the overall composting process and account for all the biochemical conversions that are taking place.

5.6.1 Temperature

The change in temperature over time during composting is the most important process parameter as it is an overall indicator of the quality of the process. Any problems that may occur during the process will usually be expressed in a temperature drop, or incomplete development of the thermophilic phase of the process.
The pattern of temperature change in the substrate during this experiment is shown in Figure 5.3. The temperature is shown together with the results of the gas analysis. It must be remembered that the airflow rate increased threefold when the temperature exceeded 55°C. This causes a dilution of the carbon dioxide concentration. However, the concentration is in that case multiplied by 3 to obtain the amount of carbon dioxide as opposed to multiplication by 1 if the temperature is ≤ 55°C. The temperature and gas concentrations are shown combined to demonstrate the direct relationship between temperature and carbon dioxide release. An increase in temperature is the result of increased metabolism of organic matter and thus increased carbon dioxide release.

![Graph showing temperature and gas concentrations over time](image)

**Figure 5.3** The relationship between the level of oxygen and carbon dioxide in the effluent gas and the development of the temperature in the incubator.

The graph shows a very steep increase in temperature in the first 24 hours. This indicates the existence of optimal composting conditions provided by the substrate and the aeration. Despite increasing the level of aeration by increasing the rate from 1 l/min to 3 l/min of air, the aeration was inadequate to maintain the temperature at 55°C. Within hours of the increase in air flow the temperature continued to increase reaching well above 60°C. In previous trials the temperature was easily maintained at 55°C by increasing the flow rate to 3 l/min; however, the installation of the humidifier reduced the evaporative cooling capacity of the air, thus causing a greater reliance on convective cooling. This reduction in cooling capacity could be compensated for by increasing the...
flow rate even further (> 3L/min). After 4 days the temperature decreased to 55°C. This temperature was maintained for 1 day before further cooling reduced the temperature to 35°C. The sudden drop in temperature was probably caused by the malfunction of the humidifier. This resulted in aeration with drier air which has greater cooling capacity due to a higher moisture absorption capability. When the humidifier was operational again, the temperature gradually increased again to a maximum of 46°C. This was the end of the thermophilic phase since the temperature dropped slowly but irregularly to 25°C over the following 22 days.

5.6.2 pH

The pH is a relevant parameter because microbial activity is pH dependent and since pH is an important factor in controlling nitrogen loss from the substrate through ammonia volatilisation. The results of the pH measurements made during the composting process are shown in Figure 5.4.

The initial pH measurement was low (6.2). This indicated that the decomposition of the organic matter had already commenced resulting in the release of simple organic acids. This explanation is feasible since the grass clippings that were used in the composting substrate were several hours old and the mass had already achieved an above ambient temperature, indicating microbial decomposition, during the short storage time.

![Figure 5.4 The development of the pH in the substrate during composting.](image-url)
The pH of the compost increased consistently to reach above 8 over the first 2 weeks of composting. The pH slowly decreased after that to just below neutral at 5 weeks. This pH curve resembles a standard composting pH development (see Figure 2.1). The relevance of the pH in relation to loss of ammonia and temperature is discussed in section 5.6.5.

5.6.3 Respiration

During composting oxygen is used by microbes as an electron acceptor to oxidise carbon which functions as a source of energy. The uptake of oxygen and subsequent release of carbon dioxide is a good measure of the level of microbial activity. In addition to oxygen being used for metabolic purposes it is also chemically bound in the form of water, as a metabolic by product, in new microbial cell material, and as part of the functional groups in the organic fraction. For this reason the release of carbon dioxide is the more accurate measure for the rate of decomposition.

Since microbial carbon oxidation is an exothermic reaction, carbon dioxide release and temperature are positively related to and dependent of the level of microbial activity. The higher the level of microbial activity, the higher the rate of respiration and release of carbon dioxide and the greater the amount of released energy in the form of heat, resulting in an increase in temperature in the substrate.

The oxygen and carbon dioxide concentrations that were measured independently in the gas effluent from the incubator and their sum are graphically displayed in Figure 5.3, alongside the temperature during composting.

During the first day carbon dioxide concentrations of up to 10% were measured. When the temperature reached 55°C, the solenoid valve opened and increased the airflow rate from 1 to 3 l/min. This caused a drop in carbon dioxide concentration down to 2 - 3% due to dilution. The microbial populations quickly adjusted to the increased aeration and the carbon dioxide levels rose to 4.5 - 5% but now with an aeration rate of 3 l/min. After four days the temperature dropped below 55°C at which point the air flow rate was reduced back to 1 l/min. The carbon dioxide level stayed at 4 - 5%, which demonstrated reduction in carbon dioxide release rate. After five days the carbon dioxide level
dropped to 2.5 - 3% and this level was maintained for 14 days when the temperature dropped below 35°C.

The oxygen graph is almost a mirror image of the carbon dioxide graph. This is to be expected since the oxygen is predominantly converted into carbon dioxide. Thus a drop in oxygen concentration is accompanied by an increase in carbon dioxide concentration.

The validity of this hypothesis was tested by plotting the sum of both oxygen and carbon dioxide concentrations. According to the hypotheses the sum should be near constant. The results of the summation can also be found in Figure 5.3. The sum remains fairly constant around 22% but drops to 20-21% after 18 days. This seems to be mainly the result of a strong drop in carbon dioxide concentration to about 2%. The result of the summation was statistically analysed for mean and variations. The results are in Table 5.2. The oxygen graph shows less variation than the carbon dioxide graph.

**Table 5.2 Statistical analysis of the sum of the carbon dioxide and oxygen balance during the composting process.**

<table>
<thead>
<tr>
<th>Mean (%)</th>
<th>St. Deviation</th>
<th>St. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.98</td>
<td>0.69</td>
<td>0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Min.</th>
<th>Max.</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>22.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The analysis shows a variation of the sum around 21% which is close to the original oxygen concentration in air of 20.7%; This variation is consistent with the instrument error of ± 1% and acceptable for the purposes of the experiment.

The total amount of carbon lost as carbon dioxide was calculated as 851.9 grams or 71 moles (Table 5.5). The amount of oxygen taken up was calculated as 2261 grams or 141 moles of oxygen. According to Table 5.4, 256 ml of water or 14 moles were produced during the process which contain 192 grams of oxygen. It must however be considered that neither the influent nor the effluent air was analysed for moisture content and temperature, thus the figure of 256 ml can not be strongly substantiated. However it is
the only available indication of process water production. Thus about 2069 grams of oxygen would have been used for the formation of carbon dioxide. During oxidation, 1 mole of carbon reacts with 2 moles of oxygen to form carbon dioxide. The amount of oxygen lost, apart from the amount formed in water, is slightly less than the amount oxygen bound in the carbon dioxide released. It would be expected to have more oxygen taken up than that lost as CO₂ due to water formation and oxidation of non-volatile organics resulting in the formation of functional groups. The second one would, however, be only a minor fraction of that lost as carbon dioxide. It is therefore likely that some CO₂ was released from red mud.

5.6.4 Soluble organic matter

The amount of soluble organic matter, measured as the chemical oxygen demand of a water extract, increases during composting as the biomass is decomposed and polymeric organic acids with functional groups are formed. Their ability to ionise increases the solubility of these compounds, grouped as humic and fulvic acids.

The results of monitoring the soluble organic matter during composting are shown in Figure 5.5. There is a steep increase during the first seven days of the thermophilic phase during which oxygen consumption is highest.

![Figure 5.5 The chemical oxygen demand of a water extract of the compost during composting.](image-url)
The sample taken at day 11 showed a drop in COD level but the COD level had increased again by day 15. The 'dip' in COD at day 11 may be the result of pH dependency of the solubility of organic matter. Several samples were analysed to confirm the reproducibility of the low result.

5.6.5 Carbon to nitrogen ratio

The carbon to nitrogen (C/N) ratio is given by the quotient of the total organic carbon (TOC) and total nitrogen (TN). It is an important parameter since it expresses in one figure the nutrient status of the organic matter. The C/N ratio is reduced during decomposition at acid or neutral pH as a result of loss of carbon as carbon dioxide. At an alkaline pH the C/N ratio can remain stable or increase as a result of loss of nitrogen as ammonia (NH₃) resulting from the reaction:

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_3(aq) + \text{H}_2\text{O} \rightarrow \text{NH}_3(g) + \text{H}_2\text{O}. \]

The TOC and TN of the organic material were determined at time (T) = 0, 21 and 34 days. The results are given in Table 5.3.

Table 5.3 Total organic carbon (TOC), total nitrogen (TN) and the C/N ratio during composting.

<table>
<thead>
<tr>
<th>T (days)</th>
<th>TOC (mg/g)</th>
<th>TN (mg/g)</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>347</td>
<td>12.4</td>
<td>27.9</td>
</tr>
<tr>
<td>21</td>
<td>259</td>
<td>19.2</td>
<td>13.5</td>
</tr>
<tr>
<td>34</td>
<td>243</td>
<td>21.7</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The table shows that over 34 days a 30% reduction in the TOC in the organic matter occurred. The greatest loss of carbon took place in the first 21 days after which the loss of carbon slowed down. The reverse pattern is shown by TN, with a strong increase in TN in the first 21 days as a result of loss of dry matter (C). This increase slows down after 21 days. So a strong inverse correlation exists between loss of dry matter and nitrogen content. The fact that during the thermophilic stage a considerable amount of nitrogen
As lost as volatile ammonia, see Table 5.4, as a result of high temperature and pH, did not appear to influence this correlation.

The C/N ratio is reduced during the composting process from 27.9 to 11.2. Such a reduction is typical during composting. A C/N ratio of 11.2 in the final compost means that the compost when applied to soil will not have a nitrogen demand.

5.6.6 Carbon and nitrogen balance

In order to assess the overall accuracy of the monitoring and analyses a mass balance was calculated for carbon and nitrogen during the process. The results are given in Table 5.4. The C-CO₂ and N-NH₃ data are cumulative totals over the periods indicated, while the C and N in the solid fraction represents the amount present at the time shown.

Table 5.4 The carbon and nitrogen balance at three time intervals (grams).

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>C-solids</th>
<th>C-CO₂</th>
<th>Total C</th>
<th>N solid</th>
<th>N-NH₃</th>
<th>N total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1249</td>
<td>0</td>
<td>1229</td>
<td>44.6</td>
<td>0</td>
<td>44.6</td>
</tr>
<tr>
<td>21</td>
<td>557</td>
<td>728</td>
<td>1285</td>
<td>41.3</td>
<td>0.75</td>
<td>42.1</td>
</tr>
<tr>
<td>34</td>
<td>499</td>
<td>855</td>
<td>1354</td>
<td>44.5</td>
<td>0.75</td>
<td>45.2</td>
</tr>
</tbody>
</table>

mean       | 1289     |       |         | 43.9    |       |         |
(s. d.)*    | (62.6)   |       |         | (1.6)   |       |         |

* Standard deviation

Carbon was monitored by analysing the residual organic matter for its TOC content and the carbon dioxide content of the effluent gas. The nitrogen was measured as TN in the solids and as NH₃ - N in the acidified condensate in which evaporated water and NH₃ was trapped. The accuracy is within 10% for the carbon as well as the nitrogen balance.

5.6.7 Overall mass balance

The initial substrate of composting can be considered to consist of moisture and dry matter. During the decomposition dry matter is converted into compost and the by-
products water, carbon dioxide and ammonia as illustrated in Figure 5.6. The 
production of water from the dry matter contributes to the moisture in the substrate and 
can thus result in an increase in moisture content during composting if loss of water 
through evaporation is insufficient.

![Diagram of the conversion process and its products during composting.](image)

The mass of each of these products was measured independently except in the case of 
dry matter the mass of which was calculated as the difference between total weight and 
moisture content. The data allow us to construct an overall mass balance for the 
process. This enables a check to be made on the overall accuracy of the measurements. 
The results of the measurements are given in Table 5.5 and shown in Figure 5.7. The 
sample entry refers to the samples taken from the mass for analysis.

![The development of the mass balance during composting.](image)

Figure 5.6 Diagram of the conversion process and its products during composting.

Figure 5.7 The development of the mass balance during composting.

-135-
The low variation in the total mass demonstrates the excellent ability of the laboratory composting rig and the monitoring program to give an accurate picture of the changes taking place.

### Table 5.5 The mass balance during composting; mass in grams, time in days.

<table>
<thead>
<tr>
<th>Time</th>
<th>Moisture</th>
<th>Dry matter</th>
<th>Evaporation*</th>
<th>C-CO$_2^*$</th>
<th>Sample*</th>
<th>N-NH$_3^*$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6300</td>
<td>3600</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>10000</td>
</tr>
<tr>
<td>2</td>
<td>5643</td>
<td>3257</td>
<td>880</td>
<td>238</td>
<td>200</td>
<td>0.28</td>
<td>10218</td>
</tr>
<tr>
<td>6</td>
<td>3720</td>
<td>3780</td>
<td>1920</td>
<td>418</td>
<td>300</td>
<td>0.69</td>
<td>10139</td>
</tr>
<tr>
<td>10</td>
<td>4536</td>
<td>2664</td>
<td>2000</td>
<td>501</td>
<td>400</td>
<td>0.72</td>
<td>10102</td>
</tr>
<tr>
<td>14</td>
<td>4644</td>
<td>2556</td>
<td>2080</td>
<td>593</td>
<td>500</td>
<td>0.75</td>
<td>10374</td>
</tr>
<tr>
<td>21</td>
<td>4250</td>
<td>2150</td>
<td>2230</td>
<td>735</td>
<td>600</td>
<td>0.75</td>
<td>9966</td>
</tr>
<tr>
<td>34</td>
<td>4246</td>
<td>2054</td>
<td>2310</td>
<td>851</td>
<td>700</td>
<td>0.75</td>
<td>10162</td>
</tr>
</tbody>
</table>

*average 10081
st. dev. 114
*cumulative data
st. error 43

The standard deviation ($\sigma$) of the average total mass of 10,081 grammes was 114.5 g which is 1.13% of the mean value. The standard error ($\sigma/\sqrt{n}$) was calculated as 43.3. These error values can be considered acceptable for the purpose of this experiment.

### 5.7 Discussion

#### 5.7.1. Process simulation and control

One of the primary objectives of the study was to design a rig that would enable us to simulate and study the composting process.

The organic matter that was used to test the rig had started to compost from the time the incubators were connected to the air supply and monitoring system of the rig. This was convincingly shown by the steep increase in temperature in the substrate and the respiration of oxygen; i.e. aspiration of carbon dioxide. In addition, there was an increase in soluble organic matter as a result of the decomposition process.
The high temperature during the initial 6 day thermophilic stage of composting was accompanied by an increase in pH and a high loss of nitrogen as ammonia. After 6 days 92% of the total nitrogen released as ammonia had evaporated. The pH was however only just over 7. The loss of nitrogen as ammonia seems to be mainly associated with the high temperature in the substrate and headspace. This is in accordance with the findings of Hamelers et al. (1987) who found a strong positive correlation between ammonia emission and temperature in the headspace. Hamelers et al. (1987) used only one incubator that was developed along similar principles to the one described here. However this rig is designed to operate and monitor seven incubators in parallel.

The system functioned well, enabling the organic substrate to pass through the various composting stages. The incubation and mesophilic stage lasted less than one day, after which thermophilic conditions developed. The thermophilic stage was relatively short. This can be partly ascribed to a technical failure of the humidifier, that would have had the effect of shortening this period. The humidified influent air ensured prevention of drying out of the substrate and provided plenty of oxygen for the aerobic process to take place. However the humidified air had a significantly lower cooling capacity, since the extent of evaporative cooling was greatly reduced. The air had mainly a convective cooling capacity. This caused a problem in maintaining the temperature at around the preset 55°C. The heat release rate was higher than the convective cooling capacity at an airflow rate of 3 l/min. The effect of the humidifier on the cooling capacity of the air was demonstrated when it was briefly out of operation due to a technical problem. The temperature dropped almost 30°C from 70°C down to 40°C, though it remained briefly at 55°C when the air flow was reduced from 3 to 1 l/min. The reconnection of the humidifier caused a subsequent increase in process temperature (Figure 5.3). It was realised that in future trials the maximum airflow rate may have to be increased to maintain the process temperature at 55°C by matching the convective cooling capacity with the process heat release.

5.7.2. Process monitoring

The computer software program enabled automatic, continuous, monitoring of the temperature and two hourly recording of the oxygen and carbon dioxide concentration data of each incubator. The software program worked free of technical problems.
There was a problem however with the logistics of the changing airflow rate around the 55°C temperature mark and the effect this has on the oxygen and carbon dioxide concentrations in the effluent gas. An increase in flow rate dilutes the carbon dioxide concentration in the effluent gas. In addition, the air retention time in the incubator is 20 min at 1 l/min and 7 min at 3 l/min. The computer registers whether the solenoid valve is open or closed during gas analysis and recording. However, due to the 7 or 20 minute delay in the change in airflow rate reaching the analyser, it is possible that a measurement is taken based on a 1 l/min air flow rate while the computer records it as being based on an air flow rate of 3 l/min. This then affects the calculated amount of carbon lost as carbon dioxide from the system which is to be included in the mass balance. This occurs only when the temperature is fluctuating around 55°C when the solenoid valves open and close and thus cause the air flow rate to fluctuate from 1 to 3 l/min at a high frequency.

The large number of measurements taken (n = 512) in combination with the limited period for which a temperature of around 55°C was maintained, nevertheless give the data a sufficiently high degree of statistical validity.

In order to monitor physical and chemical quality parameters in the substrate with sufficient accuracy 100g samples were taken. Care was taken not to open the incubator while a gas sample for analysis was extracted to avoid an unrepresentative sample.

The mass balance had a high level of accuracy. All components were accounted for over time and the total mass closely agreed with the initial mass of 10 kg. The only weakness in the measurement of the components in the mass balance was the dry matter. The dry matter was determined as the difference between total mass and the moisture component. An accurate mass balance should ideally consist of independently quantified components. However the assessment of moisture content and dry matter is fairly straightforward and it is expected that their dependence did not have a significantly adverse effect on the accuracy of the mass balance.

5.8 Conclusion

The laboratory composting device was well suited to simulate and monitor the composting process. An accurate mass balance could be produced from the collected
data and a compost type material was collected from the incubators after the process was completed.

The problem of synchronising the gas analysis with the open/close position of the solenoid valves is inherent with the air retention time in the incubators and the changing flow rate in order to control the temperature. Temperature control can be improved by increasing the air flow rate when an air humidifier is used.
Laboratory study on the effect of red mud on mobility of heavy metals and rate of biodegradation during composting.

6.1 Introduction

A study was carried out to develop a technique that would reduce the mobility of heavy metals in stabilised organic wastes. The principle of the process consists of the stabilisation of organic waste by a modified composting process in which bauxite refining residue, a waste high in clay content and alkalinity, is added to the process. Previous research as described in chapter three and four where the effect of bauxite refining residue on the mobility of heavy metals in the soluble and solid fraction of municipal compost was studied showed that red mud showed a limited capacity to reduce the mobility of some metals (Hofstede and Ho, 1989 and 1991).

The reason that red mud was only partially capable of binding the heavy metals was because most metals had already been complexed to the organic fraction during the composting process. Red mud seemed incapable of fully transferring these complexed metals from the organic fraction into the inorganic red mud.

The idea of combining bauxite refining residue or clay with organic waste, prior to composting, to reduce metal mobility is the subject of this study. This idea consists of adding bauxite refining residue before the stabilisation process enabling contaminants to be immobilised by the clay before they can be complexed to the organic fraction, instead of adding it to already composted organic matter. The logical step is to mix the clay with the organic waste before composting. This combined composting of organic waste and clay is hypothesised to have the following advantages.

- Heavy metal mobility is reduced through strong adsorption to the clay particles and precipitation by alkalinity in the red mud.
- The final compost has greater stability and density.
- The half-life of the organic fraction of the product is several times higher due to the formation of very stable clay - organic matter complexes.
- Increased product volume for sale.
- Value-added process for industrial residue and organic waste.
- Improved water and nutrient retention capacity and alkaline buffering capacity, especially for sandy soils.
- Presence of an inorganic fraction that remains in the soil after decomposition of the organic fraction.
- The large amounts of carbon dioxide released during composting will be partly absorbed by the alkalinity in red mud through formation of bicarbonate ($\text{HCO}_3^-$). This reaction turns red mud alkalinity into increased buffer capacity for the end product and reduces CO$_2$ emissions during the composting process.
- Amendment with red mud does not only mean heavy metal adsorption, but red mud also dilutes the metal concentration in the mixture.

An experiment was conducted to verify the above hypothesis. The main aspect of the experiment was to determine the extent of reduction in the mobility of heavy metals through addition of red mud, while still maintaining a high decomposition rate of organic matter in the reactor. Red mud could have an adverse effect on the bacterial population as in previous research red mud was found to be highly efficient in removing E. coli from wastewater (Ho et al., 1991). Possible causes for this are the high salinity, and high alkalinity of red mud and the adsorption of microorganisms onto the fine particles of red mud. When comparing sand as a filter medium for microbes with red mud amended sands, the latter has a lower permeability, higher retention time and higher die-off rate for microbes. The high alkalinity can be overcome by the addition of gypsum.

In this context, the design of the experiment needs to be able to clarify:

1. The effect of red mud addition to organic matter on the metal mobility in the resulting compost.
2. The effect of red mud on microbial activity and thus the rate of decomposition.

It was anticipated that red mud would reduce the mobility of metals on the one hand and reduce the decomposition rate on the other. The objective was thus to find the optimum amount of red mud to add, such that the mobility of heavy metals would be
acceptable, from a legal and environmental health point of view, while maintaining a high decomposition rate to keep the required retention time in the reactor to a minimum.

Since the decomposition rate is used to assess the effect of different levels red mud addition on the composting process, it was essential that the decomposition rate be optimised with respect to other process parameters. This meant operating with optimum process temperature and aeration. For the purpose of investigating the effect of red mud, it was felt to be sufficient to produce the compost in a bench scale reactor. A bench scale approach enables better control and more accurate monitoring of the process parameters. The different mixture batches can be composted simultaneously and under identical conditions. This adds to the validity of the experimental results and makes the experimental design more efficient. Small scale batch reactors are most suitable to simulate and monitor the process. The laboratory scale compost process monitoring system, as described in chapter 5, was used to carry out the experiment.

6.2 Materials and Methods

6.2.1 Process

The seven incubators of the experimental composting installation, described in chapter 5, were filled with predetermined amounts of grass clippings, sawdust and red mud neutralised with 10% gypsum (RMG), according to the scheme shown in Table 6.1. Each substrate was mixed with the appropriate amount of red mud, spiked with heavy metals, except in the case of the control, and packed in each incubator in 10 portions of 1 kg organic matter to ensure an even distribution of metals and substrate bulk density. The control substrate consists of only grass clippings and sawdust and the blank is the same as the control though spiked with the metals. The control and the blank allow assessment of the effect of the metals spiking as well as red mud addition on the composting process. The other batches contained a metal spiked mixture of grass clippings and sawdust, and an addition of respectively 10, 20, 25, 30 and 40 % red mud w/w of the organic material. The batches were spiked with two solutions of heavy metals: 1) Pb, Cr, and 2) Ni, Cd, Zn, Cu (see Table 6.2), such that the concentration in the solids was, cadmium 10 mg/kg, nickel 20 mg/kg, lead and chromium 50 mg/kg, copper
100 mg/kg, and zinc 500 mg/kg. These values were based on typical municipal compost values. The metals were selected based on their common occurrence in municipal waste and their toxicity to humans and plants. The spiking with metals in a solubilised salt form meant that the metals were completely available to plants and soil solution at the start of the experiment.

Table 6.1 Substrate consistency of the batches in each compost reactor (kg).

<table>
<thead>
<tr>
<th>Batch</th>
<th>Grass</th>
<th>Sawdust</th>
<th>RMG*</th>
<th>Spiking#</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>8.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>Blank</td>
<td>8.0</td>
<td>2.0</td>
<td>-</td>
<td>√</td>
<td>10.0</td>
</tr>
<tr>
<td>RMG 10 %</td>
<td>8.0</td>
<td>2.0</td>
<td>1.0</td>
<td>√</td>
<td>11.0</td>
</tr>
<tr>
<td>RMG 20 %</td>
<td>8.0</td>
<td>2.0</td>
<td>2.0</td>
<td>√</td>
<td>12.0</td>
</tr>
<tr>
<td>RMG 25 %</td>
<td>8.0</td>
<td>2.0</td>
<td>2.5</td>
<td>√</td>
<td>12.5</td>
</tr>
<tr>
<td>RMG 30 %</td>
<td>8.0</td>
<td>2.0</td>
<td>3.0</td>
<td>√</td>
<td>13.0</td>
</tr>
<tr>
<td>RMG 40 %</td>
<td>8.0</td>
<td>2.0</td>
<td>4.0</td>
<td>√</td>
<td>14.0</td>
</tr>
</tbody>
</table>

*RMG= gypsum neutralised red mud (dry mixed); # See Table 6.2

Table 6.2 Metal concentrations in the spiking solution and compost, assuming a 60 % moisture content#. The total addition is 2 x 100 ml/10 kg fresh organic matter.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Metal</th>
<th>compost</th>
<th>solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg/kg dm*</td>
<td>mg/l</td>
</tr>
<tr>
<td>I.</td>
<td>Cd</td>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>100 ml/10 kg</td>
<td>Cr</td>
<td>50</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>50</td>
<td>2000</td>
</tr>
<tr>
<td>II.</td>
<td>Ni</td>
<td>20</td>
<td>800</td>
</tr>
<tr>
<td>100 ml/10 kg</td>
<td>Zn</td>
<td>500</td>
<td>20000</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>100</td>
<td>4000</td>
</tr>
</tbody>
</table>

* dm = dry matter; #average moisture content of grass clippings/sawdust mixture.

In a real situation using municipal refuse the mobility of the contaminants would not be as severe, since most metals are bound or complexed in their source material e. g.
metal hydroxides in alkaline batteries. Based on the red mud metal adsorption capacity under ideal circumstances, described in chapter 3, a minimum addition of 7% red mud is required to remove all the zinc (2000 mg) from the compost. Since the experiment consisted of a 7 batch serial run, invalid results were expected to show up in the series.

The laboratory composting system was operated using the same settings and conditions as described in chapter 5.

6.2.2. Analysis

Twice a week over a 21 day period experimental run, a 100 g sample was taken for analysis from each of the seven incubators. The samples were taken at a depth of about 15 cm to avoid the variation in the moisture content that was apparent in the substrate. The bottom section had a slightly lower moisture content due to the drying effect of the influent air while the top section appeared more moist. This was caused by condensation dripping from the lids of the incubators. At 15 cm depth the moisture content was stable and this was also near where the temperature probe was located so that temperature data closely relate to the sample collection region.

Care was taken during sampling not to open incubators that were being sampled by the automatic gas sampler for carbon dioxide and oxygen analysis.

Each time a fresh sample was used to measure the pH and the chemical oxygen demand. The pH of a 1g fresh sample in 10 ml distilled water extract was measured using a Metrohm combination glass electrode and an Orion meter. The chemical oxygen demand of a 5g fresh sample in 50 ml distilled water extract was determined using the potassium dichromate method (APHA, 1985). Both analyses were carried out in duplicate.

The rest of the fresh sample was oven-dried at 105°C until a stable dry weight was achieved; this was done to determine the moisture content. The dried sample was then powdered using a Cyclotec 1092 sample mill. The samples were stored dry in sealed plastic bags for further analysis as described below.
The fulvic and humic acids were extracted as described in section 2.3.6.7 and the $E_4/E_6$ ratio was measured as described in sections 2.3.6.5 and 2.3.6.8. The COD and the $E_4/E_6$ ratio of a compost extract gave an indication of the maturity and degree of humification of the compost.

Each compost sample was analysed for copper, nickel, cadmium, zinc, lead and chromium in regards to total metal content (HNO$_3$-HClO$_4$ digest), plant available metal content with DTPA, according to Lindsay and Norvell (1978) and the soil solution soluble (0.1 M CaCl$_2$) metal concentrations (Table 6.3). All metal extractions with CaCl$_2$ and DTPA and the acid digest were carried out in duplicate for each sample. The last sample taken was also analysed for calcium, potassium and magnesium. Since the mobility of these latter elements is not of environmental concern and are thus not relevant to the objective of the study, analysis for them was carried out only on the blank and the 20\% red mud sample. Red mud was analysed for total heavy metal content using the same acid digestion. A separate test was carried out for the recovery of heavy metals, by acid digest, from 30 g red mud after a 24 hour equilibration of red mud with 2.5 ml of the spiking solution diluted to 100 ml. All metal extracts were analysed on a GBC atomic absorption spectrometer.

The carbon to nitrogen (C/N) ratio of the compost was determined by measuring its total organic carbon (TOC) and total nitrogen (TN) content (section 5.5).

Apart from requiring a neutral to slightly alkaline pH for a compost to have a low metal mobility and be suitable as a soil conditioner, it is important that the pH is buffered, particularly to avoid acidification, since this will increase the metal mobility. For this reason it is important to measure the pH buffer capacity of the samples. The buffer capacity in the compost samples and red mud - gypsum was measured, in duplicate, as the amount of carbonate and bicarbonate following Scheibler (APHA, 1985). An increase in carbonate content is expected during the composting process as a result of carbon dioxide adsorption. This is relevant to the carbon balance.

The effluent gas of each incubator was analysed every two hours for carbon dioxide and oxygen content as described in chapter 5. The carbon dioxide release is an important parameter for the decomposition rate as it is a direct decomposition by-product. The
carbon dioxide data are needed for the calculation of the mass balance over each incubator.

Table 6.3 Relevant parameters and frequency of monitoring or analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frequency</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>twice weekly</td>
<td>pH probe in 10:1 extract</td>
</tr>
<tr>
<td>Moisture content</td>
<td>twice weekly</td>
<td>drying (2 hrs at 80°C)</td>
</tr>
<tr>
<td>Temperature</td>
<td>continually</td>
<td>Pt100 probe</td>
</tr>
<tr>
<td>Oxygen</td>
<td>continually</td>
<td>micro - fuel cell</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>continually</td>
<td>infra - red analyser</td>
</tr>
<tr>
<td>Salinity (conductivity)</td>
<td>start, end</td>
<td>E. C.in 10:1 dist. water: compost extract</td>
</tr>
<tr>
<td>Metals (Cd, Cr, Cu, Ni, Pb, Zn)</td>
<td>twice weekly</td>
<td>A.A.S. in DTPA, CaCl₂ and acid extracts</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>twice weekly</td>
<td>TOC/Kjeldahl - N</td>
</tr>
<tr>
<td>E₄/E₆ ratio</td>
<td>twice weekly</td>
<td>UV spectrophotometer</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>twice weekly</td>
<td>Chromic acid digest</td>
</tr>
<tr>
<td>Ca, K, Mg</td>
<td>Start, end</td>
<td>AAS. in acid digest</td>
</tr>
</tbody>
</table>

The salinity was measured in each sample, since red mud addition can cause a considerable increase in salinity and potentially restrict microbial activity. According to European compost specifications salinity needs to be below 2 g/L dry matter compost to avoid phyto-toxicity (Zucconi and Bertoldi, 1987). This means that an addition of 20% w/w of red mud to compost is the maximum, assuming a red mud salinity of 10 g/L. The salinity was measured, in duplicate, as the electrical conductivity in an extract of 1 gram sample and 10 ml distilled water. The electrical conductivity was measured with an electrode with a constant of k=1, connected to a Philips G49 conductivity meter.

During each sampling period the incubators were weighed in order to measure the weight reduction during composting in each incubator. Weight reduction takes place as a result of moisture evaporation and carbon dioxide release. From the total weight, the dry weight fraction and the water fraction were calculated using the moisture content, for inclusion in the mass balance. Weight reduction due to regular sampling was also taken into account. The dry matter mass was determined as follows. Firstly, the water
content was calculated by deducting the condensation loss from the initial water content (% moist * weight). This figure was then deducted from the nett organic weight at the end of the experiment. The nett organic weight is obtained by deducting the weight of the added red mud from the weight of the bins during sampling. A relationship between carbon dioxide production, moisture evaporation and the loss of dry weight could be established in the form of a mass balance by taking the moisture content of the compost into account.

After the thermophilic and cooling down phase of approximately 20 days, the fresh compost was taken out of the bins and stored in perforated black plastic bags.

6.3 Results

6.3.1 Introduction

The experiment produced a large quantity of data. Just the metals samples amounted to 1512 analyses i.e. 7 incubators x 6 samples x 3 different extractions x 6 metals, in duplicate. In order to achieve a comprehensive presentation of the results, the data are presented in four sections. Firstly, the results of the metal extractions carried out on the various compost samples will be given. These should show the effect of the metal spiking on the composting process and the effect of red mud amendment and time on the mobility of the heavy metals. A statistical analysis of the data was performed to analyse the variance and assess the significance of the effects of each factor. Secondly, the data that describe the quality parameters of the compost and the process are presented. These data enable an assessment to be made of the effect of red mud on the compost as well as on the composting process. Thirdly, the results of the oxygen respiration and carbon dioxide release measurements are shown graphically. Finally, an attempt was made to calculate the mass balances for each incubator. The results of this are shown in area graphs depicting dry organic weight, moisture content, moisture evaporation, carbon dioxide release and the weight of samples removed. The mass balances give an indication of the accuracy of the process measurements taken and can supply relevant information about how the process proceeded in each incubator.
Overall, the composting installation, as described in chapter 5, generally performed well. There were, however, a few technical problems and interruptions. Two days after commencement of the experiment, repair work on the mains air supply interrupted the air supply to the incubators for a few hours. Due to the sudden pressure increase on the liquid release valve mounted on the bottom of the humidifier column the release valve failed, when the air supply was reinstated, and the humidifier exploded under the pressure. As a result the experiment had to continue without humidification of the air. The drier air had a greater cooling capacity due to greater water absorption capacity, however it also resulted in drying out the bottom one third section of the substrate, confining the composting activity to the top two thirds of the substrate. Samples therefore were taken from an active section in the upper part of the substrate.

In the incubator with the blank, another interruption of air supply was caused by disconnection of the supply tubing due to a connection failure. This resulted shortly afterwards in an anaerobic condition in the incubator and a subsequent drop in heat production and thus the temperature, for about 24 hours.

It was observed that after the temperature in the incubators dropped below approximately 40°C following the thermophilic stage, fungi started to grow on the compost. The fungi were identified as belonging to the family of Aspergillus. This phenomenon was observed in the control, blank and 10% red mud incubators.

The slight variation in the moisture and nutrient content of the grass clippings in each incubator was insignificant within the objective of studying the effect of red mud on heavy metal mobility because they did not restrict the decomposition rate. The red mud, sawdust and metal spiking solution had consistent characteristics.

6.3.2 Heavy metal mobility

6.3.2.1 Quality of data

The data collected from each metal extraction has meaning in two dimensions; first it will demonstrate the effect of red mud addition and secondly the effect of time on metal mobility.
In order to assess the significance of the effect of red mud addition and time for each metal and extraction, a multiple analysis of variance was carried out for the dependency of metal mobility on red mud addition and time, using the SPSS-X program on a Vax computer. For the purpose of assessing the significance of the effect of red mud addition on metal mobility, the time dependent data for each treatment were treated as duplicates to form compounded single data points; the same was done with the red mud data to assess the significance of time. The data points that show the red mud effect consist of 12 observations each (6 samples in duplicate) and each time dependence data point consists of 10 observations (5 treatments in duplicate) (Appendix 6.II).

The significance of the effect of red mud addition was determined by calculating the level of significance, relative to the residual variance. The results are shown in Table 6.4.

Table 6.4 Test of the significance of the effect of red mud addition on the leachable and plant available heavy metals using analysis of variance. Measures over time (6 in 20 days) treated as replicates.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sum of Squares</th>
<th>Degrees Freedom</th>
<th>Mean Squares</th>
<th>F</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>18.7</td>
<td>5</td>
<td>3.73</td>
<td>343</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>94.3</td>
<td>5</td>
<td>18.9</td>
<td>10243</td>
<td>0.000</td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>1.09</td>
<td>5</td>
<td>0.22</td>
<td>4356</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>246</td>
<td>5</td>
<td>49.2</td>
<td>3044</td>
<td>0.000</td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>1.09</td>
<td>5</td>
<td>0.22</td>
<td>4356</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>246</td>
<td>5</td>
<td>49.2</td>
<td>3044</td>
<td>0.000</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>66.5</td>
<td>5</td>
<td>13.3</td>
<td>3231</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>1169</td>
<td>5</td>
<td>233.7</td>
<td>5368</td>
<td>0.000</td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>7.96</td>
<td>5</td>
<td>1.59</td>
<td>106</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>768</td>
<td>5</td>
<td>153.7</td>
<td>406</td>
<td>0.000</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>40335</td>
<td>5</td>
<td>8067</td>
<td>7460</td>
<td>0.000</td>
</tr>
<tr>
<td>plant available</td>
<td>957003</td>
<td>5</td>
<td>191401</td>
<td>6058</td>
<td>0.000</td>
</tr>
</tbody>
</table>
The table shows the high significance of the effect of red mud addition on metal mobility, as $\alpha = 0.05$. The time effect though marginally significant, was not relevant when considering metal extractability (see section 6.3.2.2). For this reason, it was valid to jump the time dependent data together when considering the red mud effect on the metal extractability.

In order to estimate the experimental error in the data the standard deviation ($\sigma$) and standard error ($\sigma/\sqrt{n}$) was calculated for both the time and mud dependent data. The standard deviations and standard errors of the data are included in the raw data table in Appendix 6.II. The standard error of the data was compared to the trends in the metal extractability as a function of red mud additions and time in order to establish the validity of the trends. The standard error was smaller than the trend in the effect of red mud on the metal mobility for all metals. This was not the case for the effect of time. The linear interpolation of the data was shown to be significant by the multiple analysis of variance. This showed the absence of a consistent trend with time.

6.3.2.2 Metal mobility as a function of time.

From the results of the three different extractions the respective levels of heavy metal mobility in the compost of the different treatments can be assessed (see section 2.4.2.4).

The mobility of each metal as a function of time is plotted in Figures 6.1 - 6.6 for plant availability, Figures 6.7 - 6.12 for leachable metals and in Figures 6.13 - 6.18 for the acid extractable metals. The data of each extraction in respectively can be found in Appendix 6.IIa - c. Each data point is the average of the results of five red mud additions in duplicate or 10 observations. The error bars express the standard error of the data. The initial spiking concentration ($C_i$) is given in the title of each Figure to demonstrate the relative leachable and plant available fractions.

Since during composting the organic dry matter is reduced, by transformation into carbon dioxide and water, an increase in total metal concentration can be expected in the blank, since the metal concentration is expressed in mg/kg dry matter. This increase
could to some extent also be reflected in an increase in the plant available and leachable metals. Thus the absence of this increase would imply a reduction in metal mobility.

The dry matter fraction in which the metal data from the red mud amended samples are expressed include red mud. Thus the dilution effect of red mud forms part of the effect of red mud addition on the metal mobility. Since the metals interact with red mud as well as with the organic fraction and the red mud is not separated from the organic matter after composting, the metal concentrations are expressed relative to mass of the complete matrix.

The Figures demonstrate that there is no significant effect of time on the level of extractable metals when red mud is present. This shows that the metals would have been immobilised by interaction with the red mud particles early in the composting process. In a conventional composting process, without red mud, the metal mobility is time dependent as a result of the required formation of functional groups on organic acids, formed during composting, before metal adsorption sites are present.

With respect to the leachable metal concentrations in the blank, there is a reduction in concentration for all metals over time (Figures 6.7 - 6.11), except lead (Figure 6.12). In the same sample, the plant available concentrations of zinc, chromium, copper and nickel appears to be clearly time dependent, whereas plant available lead and cadmium appear independent of time.

The reduction in plant availability of metals over time in the blank was not as high as the reduction in the leachable metals. In this respect it must be taken into account that leachable metal concentration forms part of the plant available metal concentration. This means that the reduction in plant availability could be the result of a reduction in the leachable amount only. For example, this could be the case for chromium where there is a 90% reduction (2.5 --> 0.2 mg/kg) in leachable metals and a 65% reduction (5.1 --> 1.7) in the plant available metals. If only the non-leachable plant available metal fraction is considered, the net reduction is only 42% i.e. 2.0 --> 1.5 mg/kg. This means that the mobility of the non-leachable plant available chromium less dependent on time than the leachable chromium. Zinc is also a good example of this, since the reduction in plant availability is relatively much lower than the reduction in leachable zinc.
The graphs also show the effect of red mud on the time dependence of the leachable and plant available metals. The mobility of each metal was lower in the red mud amended compost and not time dependent. The mobility of metals in the blank was clearly time dependent and reduced over time. The experiment did not last long enough to achieve a stabilisation of the metal mobility over time for all metals. In some cases, such as the leachable copper and cadmium, the concentrations reduced down to the levels that were

![Graph showing the effect of red mud addition on plant available zinc during composting.](image)

**Figure 6.1** The effect of red mud addition on plant available zinc during composting ($C_i = 500\ mg/kg$).

![Graph showing the effect of red mud addition on plant available chromium during composting.](image)

**Figure 6.2** The effect of red mud addition on plant available chromium during composting ($C_i = 50\ mg/kg$).
achieved instantly when red mud was applied. However this compost, when applied to the field will further decompose and release the adsorbed metals for plant uptake and ground water leaching. As mentioned in chapter 2 red mud is not subject to biological decomposition and metals release is governed by pH and metal concentration in soil solution.

![Graph](image)

**Figure 6.3** The effect of red mud addition on plant available copper during composting ($C_i = 100 \text{ mg/kg}$).

![Graph](image)

**Figure 6.4** The effect of red mud addition on plant available cadmium during composting ($C_i = 10 \text{ mg/kg}$).
Figure 6.5 The effect of red mud addition on plant available nickel during composting 
\( (C_i = 20 \text{ mg/kg}). \)

Figure 6.6 The effect of red mud addition on plant available lead during composting 
\( (C_i = 50 \text{ mg/kg}). \)
Figure 6.7 The effect of red mud addition on the leachable zinc during composting ($C_i = 500$ mg/kg).

Figure 6.8 The effect of red mud addition on the leachable chromium during composting ($C_i = 50$ mg/kg).
Figure 6.9  The effect of red mud addition on the leachable copper during composting 
($C_i = 100 \text{ mg/kg}$).

Figure 6.10  The effect of red mud addition on the leachable cadmium during 
composting ($C_i = 10 \text{ mg/kg}$).
Figure 6.11  The effect of red mud addition on the leachable nickel during composting
($C_i = 20$ mg/kg).

Figure 6.12  The effect of red mud addition on the leachable lead during composting
($C_i = 50$ mg/kg).
Figure 6.13 Effect of time on the acid extractable zinc \((C_i = 500 \, \text{mg/kg})\).

Figure 6.14 Effect of time on the acid extractable chromium \((C_i = 50 \, \text{mg/kg})\).

Figure 6.15 The effect of time on the acid extractable cadmium \((C_i = 10 \, \text{mg/kg})\).
Figure 6.16 The effect of time on the acid extractable copper ($C_i = 100$ mg/kg).

Figure 6.17 The effect of time on the acid extractable nickel ($C_i = 20$ mg/kg).

Figure 6.18 The effect of time on the acid extractable lead ($C_i = 50$ mg/kg).

The acid extractable metals represented the total metal content, which was not expected to change much apart from a small increase in accordance to the reduction in organic
matter during composting. The total metal levels remained fairly constant over time, though there was considerable fluctuation in chromium and copper (Figures 6.14 and 6.16). The metal levels measured in the blank were considerably higher, except of chromium, than the level of spiking for each metal would justify. Some of the increase is attributable to the metal concentration in the original substrate of grassclippings and sawdust. These data, measured in the control, can be found in Appendix 6II.c. Another contributing factor, as mentioned before, is the reduction in the dry matter mass during composting, resulting in a relative increase in metal concentration. The assumption of 60% moisture in the fresh substrate for calculation of the level of spiking proved accurate (Appendix 6.VII). However, particularly the consistently higher concentration for copper and nickel from the start of the experiment can not be fully explained by this.

The remarkable feature of these results is that the total levels in red mud - compost are consistently lower than the levels in the blank, except in the case of chromium. Since the data points of the red mud - compost are the average of the metal concentrations in the composts of respectively 5 incremental red mud additions (0, 10, 20, 25, 30, 40%), the average dilution factor is 25%. The total metal recovery from red mud - compost is well below that which could be attributed to the red mud dilution effect. Thus a fraction of the spiking metals appears to be irreversibly bound to red mud from the start of the composting process. The increased chromium recovery from red mud - compost compared to the blank is due to the high chromium content in red mud (Table 6.6), which will be discussed in section 6.3.2.3.3.

6.3.2.3 Effect of red mud addition on the mobility of heavy metals

Results showing the effect of red mud addition on the leachable metal content of compost are plotted in Figures 6.19 - 6.21 and, the effect on plant available metal content in Figures 6.22 - 6.24. In Figures 6.25 and 6.26 the effect of red mud on the acid extractable metals in the compost was plotted, since it was found that the presence of red mud affected the recovery of total metals from the compost. The acid extract was designed to fully digest the organic matter fraction to solubilise all the metals but not the complete dissolution of red mud, for metal recovery. Hydrofluoric acid and sodium bisulphate fusion would have been required to achieve red mud dissolution and complete metal recovery. 

-160-
6.3.2.3.1 Leachable metals

The extractability of metals by CaCl₂ was very low, absolutely and relative to the total content, even in the blank (Figures 6.19 - 6.21; Appendix 6.IIa). The concentration in the extracts of the blank and samples was in some cases very close to the lower limit of the detection range for the metals Cd, Cu, Pb. The amount of metal in the extracts (mg/l) is expressed per compost unit mass of dry matter (mg/kg) to allow a meaningful comparison with the results of the other two extracts. This conversion explains the high concentration values expressed in the graphs. The metal concentration in the actual extracts was in fact only a tenth of the levels shown in the graphs.

The leachability of each of the metals is reduced by incremental addition of red mud. For most metals the reduction is highest in the interval between 20 - 30% red mud additions. Overall, the addition of 30% results in the lowest concentration of metals in the CaCl₂ extract. The addition of 40% red mud results in an increase in nickel, copper and to a lesser extent zinc in the extract. This may be to do with the content of these metals in red mud (Table 6.6) and/or the stability of their bonding with red mud in a reducing environment with humic and fulvic acids from the decomposing organic matter. The amount of organic matter was the same in each of the incubators (10 kg); it was the amount of red mud that increased. Nevertheless since the formation of organic acids is time dependent and the metal mobility was shown to be independent of time for the red mud samples (section 6.3.2.2), the release of metals as a result of red mud addition is unlikely. The metal content of red mud is given and discussed in section 6.3.2.3.3.

Errors as a result of sampling of the compost are likely to be relatively small given the method of substrate preparation in mixed sub-batches and the static nature of the substrate in the incubators. The main variation was likely to have been caused by condensation dripping from the lid which can result in unbound metals leaching out of the top layer, resulting in an uneven distribution in metals. However, the samples were taken from a deeper point than the condensation would have reached. This could have caused some mixing of the layers though, by top layer substrate falling into the sampling hole.
The percentage reductions as a result of the 30% and 40% red mud addition were calculated for each metal and can be found in Table 6.5.

Table 6.5 The reduction in metal mobility, relative to the blank, for each metal as a function of red mud addition and as a function of time.

<table>
<thead>
<tr>
<th>% mud</th>
<th>Cr</th>
<th>Cu</th>
<th>Cd</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>red mud effect</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>30</td>
<td>&gt;99</td>
<td>66</td>
<td>&gt;99</td>
<td>96</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>&gt;99</td>
<td>30</td>
<td>&gt;99</td>
<td>47</td>
<td>80</td>
</tr>
<tr>
<td>plant available</td>
<td>30</td>
<td>&gt;99</td>
<td>54</td>
<td>67</td>
<td>73</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>&gt;99</td>
<td>57</td>
<td>64</td>
<td>77</td>
<td>50</td>
</tr>
<tr>
<td>acid extractable</td>
<td>30</td>
<td>- 98*</td>
<td>69</td>
<td>69</td>
<td>76</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>- 92*</td>
<td>72</td>
<td>40</td>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>time effect</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leachable</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>66</td>
<td>-100*</td>
<td>39</td>
</tr>
<tr>
<td>plant available</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*negative value indicates an increase in concentration.

6.3.2.3.2 Plant available metals

The plant available level of metals is higher than the level of leachable metals because of the capacity, though limited, of a vegetative root system to extract cations from the soil matrix. The plant availability of each metal in the compost from the experiment was much reduced as a result of red mud addition. This is demonstrated in Figures 6.22 - 6.24. Thus the metals must be complexed to red mud in such a way that they are no longer available for plant uptake. The more red mud the less metals are available. The plant available metal fraction is relatively low considering the magnitude of the initial metal spiking concentration shown in the figure captions in brackets (C_i).

The reduction in plant availability is similar to the reduction in leachable metals. The main difference is that the low plant availability as a result of red mud addition is
maintained even at 40% red mud addition for nickel and copper unlike in the case of the leachable metals which increased for some metals. This shows a very strong reduction in plant availability since the leachable metals form part of the plant available metals and the reduction appears to undo the earlier found increase in leachable metals.

Figure 6.19 The effect of red mud addition on the leachable chromium ($C_i = 50$), cadmium (10) and lead (50).

Figure 6.20 The effect of red mud addition on the leachable copper ($C_i = 100$) and nickel ($C_i = 20$).
Figure 6.21 The effect of red mud addition on the leachable zinc ($C_i = 500$).

Figure 6.22 The effect of red mud addition on the plant available chromium ($C_i = 50$), cadmium (10), nickel (20) and lead (50).
Figure 6.23 The effect of red mud addition on the plant available copper ($C_i=100$).

Figure 6.24 The effect of red mud addition on the plant available zinc ($C_i=500$).

The actual reduction, due to red mud addition, in the amount of each metal that is available to plants is greater than that for the leachable metals. However, percentage wise relative to the blank, the reduction as a result of red mud addition is higher for leachable metals. This is shown in Table 6.5. At a 40% red mud addition the plant available Cu and Ni increases suggesting releases of these metals from red mud - gypsum.
6.3.2.3.3 Acid extractable metals

The acid digestion of compost samples was designed to recover the added metals from the compost to enable a metal balance to be made. However, it appears from Figures 6.25 and 6.26 that the extent of metal recovery was a function of the amount of red mud added to the spiked organic matter. For all metals, except chromium, the relationship was negative, the more red mud added the lower the metal recovery, though metal recovery levelled out at addition of 20% red mud or more.

The amount of chromium recovered was found to be much higher than was initially added. The additional recovered chromium could only come from the red mud. Red mud is known to contain heavy metals and is particularly high in chromium (Table 6.6). In order to verify this hypothesis, 30 g of red mud was equilibrated for 24 hours with 2.5 ml of spiking solution, diluted to 100 ml, simulating the level of metal spiking in the 30% red mud amended incubator. The resulting red mud, after filtration and drying, and a blank red mud, were digested according to the procedure used for the original red mud compost samples. Both the acid digest and the supernatant of the equilibration were analysed for the relevant metals. The metal recovery could be determined by comparing the amount of metals adsorbed and the amount recovered.

![Graph showing the effect of red mud addition on the acid extractable zinc (C_t= 500) and copper (C_t= 100).](image)

Figure 6.25 The effect of red mud addition on the acid extractable zinc (C_t= 500) and copper (C_t= 100).
Figure 6.26 The effect of red mud addition on the acid extractable chromium (C$_i$= 50), cadmium (C$_i$= 10), nickel (C$_i$= 20) and lead (C$_i$= 50).

The results of this test are presented in Table 6.6. The percentage recovered is calculated from the quotient of the amount of metals recovered from the acid digest (column 5) and the amount of metal added (column 3). The metal content of red mud as determined with a HNO$_3$ - HClO$_4$ - HCl acid digest is significant compared to the metal levels used in this study, though lower than that found by Ward (1983).

The results confirmed that more chromium was recovered from red mud than was added. The recovery rate was similar to the one found in the compost sample amended with 30% and 40% red mud (factor ± 2 (Table 6.5) vs. ± 2.5 (Table 6.6). The additional 3.1 mg/30g extracted on top of what was added must have come out of the 216 mg./kg (or 6.5 mg/30g) that was extractable with the acid from the blank red mud, thus less than 50%.

Another interesting finding was that in this experiment all other metals were virtually 100% recovered except cadmium (77%). Thus, a comparison of Table 6.5 and 6.6 suggests that the interaction between organic matter and red mud reduces the acid extractable copper, nickel, lead and zinc from compost.
Table 6.6 Heavy metal content of red mud and metal recovery from red mud with acid after equilibration with the spiking solution (2.5 ml in 100 ml/30g red mud).

<table>
<thead>
<tr>
<th>metal</th>
<th>red mud mg/kg*</th>
<th>metal added to 30 g red mud (mg)</th>
<th>supernatant mg/kg</th>
<th>in red mud mg/30 g</th>
<th>recovery in % total*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 chromic</td>
<td>216 (1)</td>
<td>2</td>
<td>0</td>
<td>5.1</td>
<td>255 (36)</td>
</tr>
<tr>
<td>1 cadmium</td>
<td>0 (0)</td>
<td>0.4</td>
<td>0</td>
<td>0.31</td>
<td>77 (77)</td>
</tr>
<tr>
<td>1 copper</td>
<td>38.4 (0.04)</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>100 (29)</td>
</tr>
<tr>
<td>1 nickel</td>
<td>6.7 (0.04)</td>
<td>0.8</td>
<td>0</td>
<td>0.83</td>
<td>104 (11)</td>
</tr>
<tr>
<td>1 lead</td>
<td>21.6 (0.02)</td>
<td>2</td>
<td>0</td>
<td>2.3</td>
<td>114 (56)</td>
</tr>
<tr>
<td>1 zinc</td>
<td>22.1 (0.07)</td>
<td>20</td>
<td>0</td>
<td>19.7</td>
<td>98.5 (62)</td>
</tr>
</tbody>
</table>

* Figures in brackets are standard deviations.

6.3.2.3.4 Effect of red mud on the relative metal mobility

In order to compare the relative effect of red mud addition to compost on the level of leachable, plant available and acid extractable metals the ratios between the levels of extractable metal were determined. The level of acid extractable metal in the blank was used as a reference with an index value of 100. The ratio were calculated for the blank and the 30% red mud amended compost, since this addition appeared to have the most significant effect on the metal mobility. The ratios are indexed to the concentrations in the acid digest of the blank, set as 100. The data of the 30% red mud addition have been corrected for the dilution effect of the red mud i.e. 3 kg red mud was added to 4 kg dry matter, thus a correction factor of 7/4). The data for both treatments are the average values over time as discussed in section 6.3.2.1. The results are shown in Table 6.7.

The ratios give some insight into whether the effect of red mud addition to compost is similar in each of the three extractions. It can be that relative to the acid extractable metals in the blank, the levels of plant available and leachable metals decreases in that respective order. Red mud addition further reduces the relative levels of plant available and more so the leachable metals compared to both the acid extractable metals in the
blank and the red mud amended sample. This means that red mud has relatively more effect on the leachable metals than on the plant available and acid extractable metals. This is expected since this fraction is most reactive. The level of plant available metals decreases also relative to the acid extractable metals as a result of red mud addition. The effect of red mud on extractable metals thus decreases in the order:

leachable > plant available > acid extractable.

The addition of red mud greatly reduces the leachable metals, especially Cr, Cd, Ni and Pb. The relative plant availability is much reduced for Cr, Cd, Ni and Zn and to a lesser extent Pb and Cu. This is probably due to the presence of Pb and Cu in red mud (Table 6.6). The low extractability but high Cr content of red mud, is also shown in Table 6.7.

Table 6.7 Effect of red mud on the relative metal mobility indexed to the acid extractable metals in the blank.

<table>
<thead>
<tr>
<th>metal</th>
<th>blank</th>
<th>30 % red mud</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soil</td>
<td>plant</td>
</tr>
<tr>
<td></td>
<td>available</td>
<td>digest</td>
</tr>
<tr>
<td>chromium</td>
<td>2.5</td>
<td>6.2</td>
</tr>
<tr>
<td>cadmium</td>
<td>2.5</td>
<td>63.8</td>
</tr>
<tr>
<td>copper</td>
<td>5.7</td>
<td>22.6</td>
</tr>
<tr>
<td>nickel</td>
<td>8.3</td>
<td>46.7</td>
</tr>
<tr>
<td>lead</td>
<td>1.7</td>
<td>26</td>
</tr>
<tr>
<td>zinc</td>
<td>11.5</td>
<td>71.3</td>
</tr>
</tbody>
</table>

During composting a loss of dry matter occurs as a result of decomposition. Since the metal concentrations are expressed with reference to the dry matter, a concentrating effect of the metals occurs by the same factor as the reduction in dry matter. The extent of the reduction in dry matter is mainly dependent on the level of microbial activity i.e. decomposition rate. The amount of dry matter in the incubators could only be assessed indirectly by deducting the amount of moisture from the total weight (section 6.3.7). Due to the large variation in moisture content, no accurate independent data about
the dry matter reduction could be produced. For this reason the metal data have not been corrected for loss of dry matter.

6.3.4 Composting process parameters

6.3.4.1 pH

The pH of the substrate during the thermophilic stage of composting is an important process parameter as it affects microbiological activity and ammonia volatilisation. The pH is also an important parameter for the use of compost as a soil amender. The results of the pH measurements in each incubator are shown in Figure 6.27. The data can be found in Appendix 6.III. The graphs allows a good comparison between the incubators.

The general trend shows an initial slightly acidic pH, which increases considerably and then stabilises at slightly alkaline levels, which is characteristic for the composting process (section 2.2.2). The presence of red mud generally appears to maintain a more neutral initial pH and also appears to buffer the pH increase that follows, except for the 20% sample. The final pH is near neutral for each type of compost produced.

![Figure 6.27 The effect of red mud on the development of the pH during the thermophilic stage of the composting process.](image)

6.3.4.2 Gas respiration balance

The conversion of oxygen into carbon dioxide is the most direct indication of aerobic microbial activity. The rate of this conversion is a measure of the decomposition rate of
the organic matter and the cumulative quantity of carbon dioxide that is released is a measure of the level of decomposition in organic waste. The concentration of oxygen and carbon dioxide and the sum of both for each incubator during the composting period are shown in Figures 6.28 - 6.34. The data in the graphs are as measured by the gas analyser in percentage with a sensitivity of 1 % of full scale. Over the full composting period 265 data points were taken for each gas in each incubator.

There was a problem, however, in quantifying the gas balance. Since the aeration rate fluctuated between 1 and 3 L/min, depending on the temperature, the air retention time in the bins consequently fluctuated between 20 and 7 minutes respectively. This resulted in a problem with the synchronisation of the gas concentrations and the air flow rate since a change in the flow rate would normally take displacement of one pore volume to result in a corresponding change in gas concentration. This problem occurred only during periods when the temperature fluctuated around 55°C. The sampling rate of every 2 hours over a period of 20 days provides for averaging over the period and gives the gas balance adequate statistical significance (Table 6.8). The fluctuations in the gas concentrations are attributable to the changing flow rates, since an increase in flow rate will dilute the carbon dioxide concentration. A sudden drop in airflow following an abundant oxygen supply could result in relatively increased carbon concentrations. The reverse situation would occur for the oxygen concentration. However, generally the sum of the two remains close to 21%. The relationship between the fluctuations and the temperature is clearly shown in the graphs.

Table 6.8 Statistical analysis of sum of the oxygen and carbon dioxide concentration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mean</th>
<th>std. deviation</th>
<th>std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>21.2</td>
<td>1.1</td>
<td>.07</td>
</tr>
<tr>
<td>blank</td>
<td>21.4</td>
<td>1.6</td>
<td>.10</td>
</tr>
<tr>
<td>10 %</td>
<td>20.8</td>
<td>2.0</td>
<td>.12</td>
</tr>
<tr>
<td>20 %</td>
<td>21.2</td>
<td>1.6</td>
<td>.10</td>
</tr>
<tr>
<td>25 %</td>
<td>21.6</td>
<td>1.4</td>
<td>.09</td>
</tr>
<tr>
<td>30 %</td>
<td>21.2</td>
<td>1.4</td>
<td>.09</td>
</tr>
<tr>
<td>40 %</td>
<td>21.2</td>
<td>1.6</td>
<td>.10</td>
</tr>
</tbody>
</table>
The mean sum of the oxygen and carbon dioxide concentrations, except 10% red mud, are consistently slightly above the combined oxygen and carbon dioxide concentration in air, i.e. 20.95 ± 0.03 = 20.98%. However, the difference between the mean concentration from the concentration in air is well within the standard errors of the mean values. The fact that the values are higher may have been caused by a higher sampling flow rate through the analyser than was specified due to the elevated pressure in the venting system from which gas was sampled.

Another aspect to be considered in the oxygen balance is its uptake in the formation of water as a process by-product. From the mass balance data in Appendix 6.VII, the following increases in total water can be calculated, its oxygen content in brackets: control 270 (240), blank 270 (240), 10% 310 (275), 20% 230 (204), 25% 340 (302); all expressed in grams. There was no increase in water mass in the 30 and 40% samples. Thus oxygen should be higher than is accounted for in the released carbon dioxide.

The total quantity of carbon dioxide released, expressed as carbon, was determined by multiplying the average concentration of two consecutive analysis with the air flow rate and conversion from carbon dioxide to carbon, calculated according to the formula,

\[
\text{Amount of carbon (g)} = \frac{C_1 + C_2}{2} \cdot 24 \cdot 60 \cdot \frac{T_1 + T_2}{2} \cdot \frac{1}{22.4 \cdot 100} \cdot Q \cdot 12 \ (g)
\]

where \( C_1 \) = the last reading of carbon dioxide concentration (%),

\( C_2 \) = the new reading of carbon dioxide concentration (%),

\( T_1 \) = time of reading \( C_1 \) since \( T = 0 \) (hours)

\( T_2 \) = time of reading \( C_2 \) since \( T = 0 \) (hours)

\( Q \) = air flow rate: 1 L/min if \( T \leq 55^\circ C \),

3 L/min if \( T > 55^\circ C \).

The factor 2 is to obtain the average time between two readings, 22.4 litres is the volume of 1 mol of gas and the factor 100 is to eliminate the percentage of concentration. The factor 12 converts from moles carbon dioxide to grams carbon. The results of this calculation for each incubator are given in Table 6.10 where an attempt was made to demonstrate a relationship with the increase in carbonate content in the compost.
The results show that approximately 20% of the dry matter (0.8 out of 4 kg) was lost through carbon volatilisation as carbon dioxide. This is remarkably high considering that the average carbon content in the dry matter is approximately 35%, so more than half the total carbon content in the dry matter was volatilised as carbon dioxide.

6.3.4.3 Temperature

The temperature is an important process indicator since heat production and release is a direct result of meso- and thermophilic bacterial activity. A high temperature indicates a correct nutrient balance, presence of easily digestible organic compounds with a high enthalpy and adequate supply of oxygen. The temperature patterns during composting in each bin are shown in Figures 6.28 - 6.34, superimposed onto the gas graphs. The graphs show the close relationship between oxygen respiration, carbon dioxide production, the associated heat release and the resulting temperature in the compost. The temperature follows a similar pattern in each incubator. This pattern shows a steep increase, within hours of the start of incubation, to a thermophilic level, as high as 65°C, until the easily digestible substrate with a high enthalpy starts to diminish. The bacteria then move on to organic compounds with a lower enthalpy, releasing less heat which is insufficient to maintain the high temperature. At this point the temperature starts to fall and the so-called 'cooling down' phase commences (see section 2.2.2.2). Each of the graphs follows this pattern.

The temperature drop in the blank incubator at day 6 was caused by a connection failure in the air supply. The lack of oxygen caused a temporary anaerobic condition under which microbial heat production is known to be much lower. This resulted in a sudden drop in temperature. The temperature recovered soon after reconnection of the air supply. The graph shows that oxygen levels rapidly increased after reconnection but the temperature only increased around 1 day later due to the time required to reverse the anaerobiosis and re-establish the appropriate aerobic microbial population.

The temperature did not reach its potential maximum level of 65 - 70°C, since the temperature was set to be maintained at around 55°C. However, it can be seen that in several incubators the temperature could not be maintained at the preset temperature,
particularly in the beginning. The time that the temperature in these incubators did come down to the set temperature of 55°C coincided with the failure of the humidifier. The drier air had a greater cooling capacity since it could absorb more moisture. As a consequence the lower part of the substrate dried out and ceased to take part in the decomposition process. When using humidified air, which is to be recommended, a higher air flow rate than 3 L/min. is required to control the temperature.

![Graph showing changes in gas composition and temperature over time.](image)

**Figure 6.28** The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting in the control incubator.

![Graph showing changes in gas composition and temperature over time.](image)

**Figure 6.29** The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting in the blank incubator.
Figure 6.30  The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 10% red mud.

Figure 6.31  The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 20% red mud.
Figure 6.32 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 25% red mud.

Figure 6.33 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 30% red mud.
Figure 6.34 The oxygen and carbon dioxide concentrations in the effluent gas and the temperature during composting with 40% red mud.

6.3.5 Compost maturity

The maturity of compost is an indication of the state of decomposition of the organic matter. The decomposition of organic matter takes place in different stages. First microorganisms, mainly heterotrophic, thermophilic bacteria, will metabolise and mineralise simple carbon compounds such as soluble sugars, organic acids, etc. The decomposition of natural long-chain polymers takes place later, principally by fungi and actinomycetes. However, this stage was not completed in the experiment due to the lengthy time requirement for complete compost maturation. Progress in the microbial decomposition of organic waste is associated with an increase in soluble humic substances, the humic and fulvic acids. The level of maturity of a compost can be quantified by measuring the chemical oxygen demand of a compost water extract.

It appears that during compost stabilisation a change occurs in the soluble organic matter as a result of further decomposition and oxidation. Generally humic acids are formed first before further decomposition to fulvic acids which have a lower molecular weight but contain a higher percentage of functional groups (Jackson et al., 1978). Measuring
the $E_4/E_6$ ratio is a way of assessing a change in the molecular weight of soluble organic matter. The $E_4/E_6$ ratio increases during composting (section 2.3.6.5).

6.3.5.1 Soluble organic matter

The results of the COD analysis of a water extract from compost samples from each incubator over time are shown in Figure 6.35. The data can be found in Appendix 6.IV.

The COD of the samples all follow a similar pattern. The COD increases in the first nine days, then at day 14 all samples appear to have a reduced level of soluble organic matter, before increasing steeply to various levels. The decrease in COD around day 14 agrees with results of a similar previous experiment where the COD in all samples taken at day 15 showed a similar reduction. All samples were analysed simultaneously thus a random analytical error is unlikely.

![Figure 6.35 Solubilisation of organic matter during the thermophilic stage of composting measured as the chemical oxygen demand of a water extract.](image)

The elevated levels found at day 9 are hard to explain, but cannot be dismissed, since the higher levels were measured in each of the bins except the blank. It may be a particular phase in which cell walls are broken and cell contents appear in water extracts. Another
explanation may be that after the thermophilic phase lignin degrading microorganisms
become active, releasing soluble cellulose for degradation.

The mud addition clearly decreases the amount of soluble organic matter. This may be
caused by the formation of stable complexes between humic and fulvic acids and red
mud, through bridges between the organic matter and the mineral clay particles and
adsorption. The ability of red mud to reduce the level of soluble organic matter was also
shown in Chapter 4.

Red mud addition causes a dilution of the organic matter fraction. Since samples of
equal weight are taken, there will be proportionally less organic matter in the samples
with red mud. This will reduce the COD in a water extract. However, the reduction in
soluble organic matter is much higher than can be attributed to the dilution effect,
particularly for the samples with 25, 30 and 40% red mud added, but also the samples
with 10 and 20% red mud.

6.3.5.2 E4/E6 ratio

The E4/E6 ratio was determined separately for the fulvic and the humic acids. The
results are shown in Table 6.9. The sample taken on day nine was lost as a result of
glassware breakage, hence the absence of the results. The measured E4/E6 ratios for the
samples of this study are within the ranges quoted for humic and fulvic acids in soil
organic matter (section 2.3.6.5).

The E4/E6 ratio in the spiked blank appears to be higher than that in the control. This
suggest a lower degree of condensation of the organic acids and is likely to be the result
of metals adsorbed to the functional groups of the fulvic acids which subsequently block
potential sites for condensation of fulvic acids with other organic compounds. This was
also observed in three out of the five samples of the humic acids. However, humic acids
have a considerably lower functional group content and are more highly condensed.

The E4/E6 ratio is concentration dependent if the concentration of humic or fulvic acids
is below 0.5 gram/l (Choudry, 1984b), though this is not in agreement with Chen et al.,
(1977). This helps explain the increase in E4/E6 as a function of time since the organic
acids are formed as composting progresses, since the $E_4/E_6$ was expected to increase due to further decomposition of large humic acids into lower molecular weight fulvic acids. The increase in concentration appears not so much the case at 30 and 40% red mud addition, where the organic acids, mainly humic acids as shown in chapter 4, are more likely to react with clay particles, thus maintaining a low concentration of fulvic and humic acids in solution, as demonstrated by the low COD levels in the water extracts (Figure 6.35).

The $E_4/E_6$ ratio in the fulvic acid solution in the extracts of the compost with 10, 20 and 25% red mud shows a very sharp increase by the third day and remains fairly constant thereafter. This increase is less profound in the compost with respectively 30 and 40% red mud. This could be due to the higher rates of decomposition and thus organic acid formation in the samples with 10, 20, and 25% red mud. This hypothesis is supported by the temperature and carbon dioxide release data (section 6.3.4.2 and 6.3.4.3).

Table 6.9 The $E_4/E_6$ ratio in the separate fulvic and humic acid fractions during composting.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Control</th>
<th>Blank</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>30%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fulvic acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.61</td>
<td>5.69</td>
<td>5.18</td>
<td>4.71</td>
<td>4.43</td>
<td>4.63</td>
<td>4.62</td>
</tr>
<tr>
<td>3</td>
<td>5.81</td>
<td>6.86</td>
<td>6.47</td>
<td>6.43</td>
<td>6.96</td>
<td>5.67</td>
<td>4.89</td>
</tr>
<tr>
<td>6</td>
<td>5.63</td>
<td>7.20</td>
<td>6.23</td>
<td>6.26</td>
<td>6.49</td>
<td>5.00</td>
<td>3.97</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>6.60</td>
<td>6.76</td>
<td>6.69</td>
<td>6.18</td>
<td>6.48</td>
<td>5.69</td>
<td>4.77</td>
</tr>
<tr>
<td>20</td>
<td>5.75</td>
<td>6.37</td>
<td>7.32</td>
<td>7.38</td>
<td>6.07</td>
<td>4.67</td>
<td>4.12</td>
</tr>
<tr>
<td><strong>Humic acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.41</td>
<td>3.22</td>
<td>3.46</td>
<td>2.86</td>
<td>2.78</td>
<td>2.82</td>
<td>2.48</td>
</tr>
<tr>
<td>3</td>
<td>2.95</td>
<td>3.22</td>
<td>3.38</td>
<td>3.43</td>
<td>4.00</td>
<td>3.19</td>
<td>3.07</td>
</tr>
<tr>
<td>6</td>
<td>3.14</td>
<td>3.76</td>
<td>3.67</td>
<td>3.68</td>
<td>4.06</td>
<td>3.23</td>
<td>2.85</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>3.41</td>
<td>3.31</td>
<td>3.93</td>
<td>4.13</td>
<td>3.46</td>
<td>3.76</td>
<td>3.49</td>
</tr>
<tr>
<td>20</td>
<td>3.03</td>
<td>3.40</td>
<td>3.76</td>
<td>3.67</td>
<td>3.37</td>
<td>2.95</td>
<td>2.95</td>
</tr>
</tbody>
</table>
In the same way that metal spiking appeared to increase the \( E_4/E_6 \) ratio, the addition of mud clearly decreases the \( E_4/E_6 \) ratio. This is possibly the result of adsorption of the organic acids onto red mud particles using metal ions as bridges. Ions that form this type of bonding are termed ligands (section 2.3.3.1).

The use of the \( E_4/E_6 \) ratio as an indication of the level of compost maturity may not strictly be appropriate here since a composting time of 20 days only is generally insufficient to produce a mature compost. There were also fluctuations in the pH of the extracts which would have affected the \( E_4/E_6 \) ratio due to its pH dependence. The concentration of humic and fulvic acids would have varied considerably between samples, as indicated by Figure 6.35, due to varying rates of organic acid production combined with selective adsorption by red mud, and may have been too low in some cases, resulting in data of low relevance to compost maturity indication.

6.3.6 Compost quality

6.3.6.1 Buffer capacity

The buffer capacity was measured as the carbonate content in each sample. The results are given in column 2 of Table 6.10. Red mud was found to contain 7.4% carbonate.

Table 6.10 Effect of red mud on the pH buffer capacity of the final compost, expressed in % \( CaCO_3 \) and the relation to loss of carbon as \( CO_2 \).

| sample | \( CaCO_3 \) in
\( \text{bin} \) (g) | g red mud in
\( \text{final sample} \) | g \( CaCO_3 \) | \( \Delta CaCO_3 \) (g) | nett g C | C lost as \( CO_2 \) (g) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>8.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>851</td>
<td></td>
</tr>
<tr>
<td>blank</td>
<td>5.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>699</td>
<td></td>
</tr>
<tr>
<td>10 %</td>
<td>60.7</td>
<td>1000</td>
<td>74</td>
<td>-13.3</td>
<td>-1.6</td>
<td>816</td>
</tr>
<tr>
<td>20 %</td>
<td>124.3</td>
<td>2000</td>
<td>148</td>
<td>-23.7</td>
<td>-2.8</td>
<td>794</td>
</tr>
<tr>
<td>25 %</td>
<td>192.0</td>
<td>2500</td>
<td>185</td>
<td>+7.0</td>
<td>.84</td>
<td>799</td>
</tr>
<tr>
<td>30 %</td>
<td>306.1</td>
<td>3000</td>
<td>222</td>
<td>+84.1</td>
<td>10.1</td>
<td>768</td>
</tr>
<tr>
<td>40 %</td>
<td>371.9</td>
<td>4000</td>
<td>296</td>
<td>+75.9</td>
<td>9.1</td>
<td>699</td>
</tr>
</tbody>
</table>
Thus the buffer capacity of the samples was expected to be a function of the level of red mud addition. In order to determine the net effect of red mud on the buffer capacity in red mud - compost, the amount of carbonate originating from the red mud added, shown in column 4, was deducted from the total amount of carbonate in the final red mud - compost mass.

This showed that in the higher red mud additions, namely 25, 30 and 40%, there was a net increase in buffer capacity (column 5). This is most likely the result of the formation of bicarbonates through the reaction of hydroxide in red mud with, during composting abundantly produced, carbon dioxide.

This could form part of an explanation for the lower carbon dioxide release from the incubators with compost amended with 30 and 40% red mud (column 7), since there is a high correlation between the reduction in loss of carbon as carbon dioxide and the increase in carbonate as a function of red mud addition. The covariance and correlation between the buffer capacity in the final compost and the red mud addition and loss carbon as carbon dioxide was determined by calculating the covariance between the respective data listed in Table6.10. The results are shown in Table 6.11.

The lower release of carbon dioxide from the blank compared to the control could be because of spiked metal toxicity to the microbes and/or the initial lower pH (Figure 6.27) due to the acidity of the spiking solutions, though several red mud samples had a lower pH for much of the process.

Table 6.11 The correlation between the loss of carbon during composting and red mud addition as well as the buffer capacity after 20 days.

<table>
<thead>
<tr>
<th></th>
<th>loss of carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>covariance</td>
</tr>
<tr>
<td>red mud addition</td>
<td>-89.9</td>
</tr>
<tr>
<td>buffer capacity</td>
<td>-16</td>
</tr>
</tbody>
</table>
6.3.6.2 Carbon to nitrogen ratio

The C/N ratio is calculated by taking the quotient of total organic carbon (TOC) and the total nitrogen content (TN). It is an important indicator for the nutrient balance in the substrate which needs to be correct for the micro-organisms to ensure complete decomposition (section 2.2.2.3). The C/N ratios are shown in Table 6.12. The TOC and TN data are tabled in Appendix 6.V as the average of a duplicate analysis.

Table 6.12 The effect of red mud on the carbon to nitrogen ratio in the substrate during the thermophilic stage of composting.

<table>
<thead>
<tr>
<th>Days</th>
<th>Control</th>
<th>Blank</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>30%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>20</td>
<td>25</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>22</td>
<td>29</td>
<td>28</td>
<td>38</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>22</td>
<td>20</td>
<td>23</td>
<td>28</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>9</td>
<td>19</td>
<td>23</td>
<td>27</td>
<td>29</td>
<td>37</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td>14</td>
<td>24</td>
<td>25</td>
<td>23</td>
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<td>24</td>
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<tr>
<td>21</td>
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<td>25</td>
<td>24</td>
<td>32</td>
<td>28</td>
<td>38</td>
<td>25</td>
</tr>
</tbody>
</table>

The C/N ratio was determined in each sample as a process parameter and as an indicator of compost maturity. An increase would indicate a excessive loss of ammonia. This results in an odour problem, the loss of nitrogen available to the microbes and a reduced nutrient value in the end product. The C/N initial ratio in each incubator was within the optimum range of 20 - 30 in each incubator. By the end of the experiment the ratios had stabilised in each substrate except for those in the control and the 30 % red mud sample. The ratios are generally higher in the red mud samples. It appears that the C/N ratios were too variable to allow more definite conclusions to be drawn.

6.3.6.3 Salinity

The salinity was measured as the electrical conductivity (EC) in mS/cm in a water extract. The results are given in Table 6.13. Naturally, red mud addition increased the salinity of the compost due to its high salt content. In order to demonstrate the effect of
red mud and the spiking solution on the salinity of the final red mud compost, separate conductivity measurements were done as well as a measurement in a red mud extract with the spiking solution, in the same ratio as in the experiment. The conductivity of a red mud only water extract was 3.12 mS/cm and the diluted spiking solution had a conductivity of 0.12 mS/cm. The conductivity of the red mud spiking solution extract was 3.25 mS/cm, slightly higher than the red mud only extract and equal to the cumulative separate conductivities of red mud and the spiking solution (3.24 mS/cm). Based on these figures it can be shown that the EC in the blank agreed with the combined EC value of the control sample and spiking solution i.e. 1.48 versus 1.56 measured. The addition of 10% red mud did not increase the EC in the extract compared to the blank, except in the final sample, and in some samples the EC was lower than the EC in the blank. The insignificant effect of 10% red mud addition on the salinity may have been a result of ion exchange of metals with sodium in the red mud, as sodium has a relatively lower EC value in solution. However the variability of samples is the most likely explanation. Further red mud additions only moderately increase the EC in the extract due to ion exchange and an increase in the equilibrium concentration due to sodium release. The EC in the red mud - compost after 20 days is on average approximately 3 mS/cm. Due to the 10 fold dilution of the dry compost in the extractant this equates 30 mS/cm in the solids. For sodium, which would have been the main cation in solution, 1000 mg/l is equivalent to around 2 mS/cm. Thus the salinity in the red mud - compost is about 1500 mg/l. This is well within the compost salinity guideline of 2 g/l (section 6.2).

<p>| Table 6.13 Electrical conductivity (mS/cm) in compost - red mud extracts. |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>Blank</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>30%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.36</td>
<td>1.56</td>
<td>1.29</td>
<td>1.99</td>
<td>2.27</td>
<td>2.24</td>
<td>2.44</td>
</tr>
<tr>
<td>3</td>
<td>1.38</td>
<td>1.71</td>
<td>1.75</td>
<td>2.23</td>
<td>2.70</td>
<td>2.22</td>
<td>2.56</td>
</tr>
<tr>
<td>6</td>
<td>1.01</td>
<td>1.71</td>
<td>1.00</td>
<td>1.32</td>
<td>2.07</td>
<td>2.31</td>
<td>1.76</td>
</tr>
<tr>
<td>9</td>
<td>1.98</td>
<td>2.40</td>
<td>1.59</td>
<td>2.33</td>
<td>2.84</td>
<td>2.48</td>
<td>3.01</td>
</tr>
<tr>
<td>14</td>
<td>2.55</td>
<td>2.80</td>
<td>2.55</td>
<td>3.00</td>
<td>3.38</td>
<td>3.33</td>
<td>3.41</td>
</tr>
<tr>
<td>20</td>
<td>1.77</td>
<td>2.47</td>
<td>2.83</td>
<td>3.05</td>
<td>3.29</td>
<td>2.93</td>
<td>2.88</td>
</tr>
</tbody>
</table>
The loss of organic matter as a result of the time dependent decomposition has a concentrating effect on the salt. That this effect appears to be smaller at high mud additions is probably mainly due to the relatively lower organic fraction in these batches, but also a possible reduction in decomposition rate, limiting the loss of organic matter and the contribution to salinity of red mud. The extent of the salt concentrating effect can be a measure for the loss of organic matter through decomposition since no further salts were introduced and little left the system. Furthermore, it is likely that sampling errors resulted in varying amounts of dry matter in each sample from a particular bin. The trends over time are not clear however and often the data spread exceeds the trend.

6.3.6.4 Macro elements

Macro elements are required at high concentrations to support plant growth and thus their content in compost is an important quality aspect. The compost blank had high levels of potassium, magnesium and calcium (Table 6.14).

Table 6.14 Macro elements and total nitrogen content of the blank and the 20% red mud amended compost; concentrations expressed in % dry matter.

<table>
<thead>
<tr>
<th>Element</th>
<th>Blank</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.26</td>
<td>0.85</td>
</tr>
<tr>
<td>K</td>
<td>0.35</td>
<td>0.26</td>
</tr>
<tr>
<td>Mg</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>N</td>
<td>1.5</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The higher calcium content of the red mud - compost originates from the 4% gypsum added to red mud to neutralise the alkalinity. The other macro elements are lower in the red mud compost as a result of the dilution effect of red mud addition and possibly a lower extractability. The nitrogen content was analysed as total Kjeldahl nitrogen. The nitrogen level of 1.5% in the blank is common in compost. The red mud-compost nitrogen content is 0.93%. This is lower than can be explained by the dilution effect of
the red mud addition (18%). The higher pH in the compost in the beginning of the process may have increased the loss of N as ammonia through volatilisation, resulting in a lower nitrogen content.

6.3.7 Mass balances

The use of mass balances to describe and analyse a process such as composting is of high value as it gives insight into the fate of the solids involved in the process and it is a tool to scrutinise the validity of the measurements during the process. The composting process converts solid organic waste into a modified product, compost. A mass balance can assist, through insight into the process, in optimising the output of compost.

A properly monitored process should be able to produce an accurate mass balance. During the composting process the dry organic matter fraction decomposes and is converted into humus with water and carbon dioxide as by-products. The moisture that is initially present and the produced moisture will partly evaporate as a result of aeration and high temperatures. In order to make mass balances for each incubator, the following was measured, in kg, at each sampling time:

- moisture loss from the process through evaporation;
- carbon loss from the process as carbon dioxide;
- mass of the dry matter in the incubator; and
- mass of the moisture in the incubator.

The moisture loss was measured by collecting the condensate from each condenser through which the effluent air was led prior to ventilation and gas analysis. The loss of carbon was calculated from the data of the continuous carbon dioxide analyser (refer to section 6.3.4.2 and Table 6.10). The data of the components that were lost to the process were accumulated in the mass balances in order to balance the cumulative loss of solids from the incubators. The moisture in the incubators was determined by measuring the moisture content in a representative sample and the total weight of the substrate (Appendix 6.VI). The dry weight was calculated as the difference between the total mass and the mass of the moisture in each incubator. This forms a weakness in the mass balance, since the validity of a mass balance and scrutiny of the accuracy of the data requires independent measurement of each component of the mass balance. In addition,
the moisture entering the incubator in the influent air and the moisture exiting the incubator as well as the temperature of these air flows was not monitored. Thus the effect of these flows on the moisture content of the mass balance could not be quantified.

The mass of the samples, 6 x 0.1 kg, that were taken during the process are not part of the mass balance since that loss of mass to the process is not the result of decomposition. However, the dry matter and moisture content in the incubators were compensated for the loss through sampling by the appropriate mass of the fraction of moisture and dry matter in the samples. The results are shown in Figures 6.36 - 6.42. The quantity of carbon lost as carbon dioxide can be found in Table 6.10.

A decrease in the amount of dry matter is a prominent feature during composting, so it can be used an indicator for the accuracy of the mass balances. In all incubators, except in the 40% red mud incubator, a decrease in dry matter can be observed, most rapidly in the first 6 days when the level of microbial activity and the temperature were highest.

There appears to be a relationship between the presence of red mud (except 20%) and reduced moisture evaporation. This is probably the result of the ability of red mud to retain moisture strongly, due to capillary forces and its salinity, since the moisture content in these incubators remained higher than the ones without red mud.

![Graph showing mass balance of composting process](image)

**Figure 6.36** The mass balance of the composting process in the control incubator.
Figure 6.37  The mass balance of the composting process in the blank incubator.

Figure 6.38  The mass balance of the composting process in the incubator with 10% red mud amendment.
Figure 6.39 The mass balance of the composting process in the incubator with 20% red mud amendment.

Figure 6.40 The mass balance of the composting process in the incubator with 25% red mud amendment.
Figure 6.41 The mass balance of the composting process in the incubator with 30% red mud amendment.

Figure 6.42 The mass balance of the composting process in the incubator with 40% red mud amendment.

The mass balance over the compost with 40% red mud shows a 30% increase in dry matter while the moisture content is halved. This is an impossible development during the process, and it demonstrates the error in the indirect dry matter determination and the error introduced due to unrepresentative samples.
6.4 Discussion

6.4.1 Effect of metal spiking on the composting process.

Heavy metals can have an adverse effect on microbial activity as a result of metal toxicity or increased salinity. Since during this experiment the microbial activity was measured in organic substrate with and without metal contamination, a comparison can be made between these two treatments to assess the effect of metals on microbial activity.

The temperature profiles of the control and the blank during the composting process are quite different. The aeration system had more difficulty to control the temperature at 55°C in the control and this temperature was exceeded on several occasions. The cooling phase was also much longer, indicating greater microbial activity since the substrates are the same. The amount of carbon lost as carbon dioxide was also approximately 20% higher in the control (Table 6.10). Nevertheless the effect of the accidental anaerobic period in the blank must be considered since this would have reduced carbon emission as carbon dioxide and possibly resulting in release of carbon as methane which was not analysed for.

The acidic nature of the spiking solution resulted in a lower pH of the substrate in the blank at the start of the composting experiment (Figure 6.25 and Appendix 6.III). However, this difference disappeared after 3 days. The pH levels remained fairly even, except at the end at day 20 the pH in the control had dropped from 7.72 to 7.10 while the blank only dropped from 7.72 to 7.45. Thus the acidic effect of the spiking solution was neutralised.

The control had a higher buffer capacity at day 20 (Table 6.10). The loss of carbon as carbon dioxide was also higher. This seems to invalidate the relationship between buffer capacity and carbon dioxide release. However the release of carbon dioxide in the blank was interrupted when the oxygen supply failed and the temperature dropped (Figure 6.27) during the highly active thermophilic stage. This interference invalidates a meaningful comparison between the release of carbon dioxide in the control and the blank. The higher buffer capacity of the control might be explained by the combination
of the temporarily (0 - 6 days) higher pH in the control and the higher total production of carbon dioxide creating better conditions for carbonate formation.

The electrical conductivity in the blank is on average approximately 30% higher, due to the salinity of the metal salts (Table 6.13). The increase in salinity with time is caused by the loss of organic solids during the decomposition, which concentrates the salts.

The solubilisation rate of organic matter can be used as a measure of decomposition rate, since soluble organic acids such as humic and fulvic acids are formed during decomposition. It appears that the blank has almost 50% more solubilised organic matter, measured as the COD in a water extract. This seems remarkable considering that 6 days earlier, at day 14, the blank had a lower soluble organic fraction. At this point a 30 hour period without aeration occurred in the blank due to technical failure in the air supply, resulting in temporary anaerobiosis. The high level of soluble organic matter seemed too high to be acceptable without a clear explanation.

The available data for comparing the effect of metal spiking on the composting process seems insufficient to make a meaningful comparison. The level of metal spiking of the organic substrate in this experiment could have some detrimental effect on the composting process but seems insufficient to have a significant effect on the investigated compost quality parameters.

6.4.2 Effect of time on the mobility of heavy metals.

Heavy metals are adsorbed in compost by organic compounds that are produced as a result of the degradation of organic matter. This makes the adsorption of metals time dependent. This was confirmed by the observations on metal mobility in the blank. The leachable and plant available metals were reduced over time due to adsorption on to soluble organic acids and to adsorption sites on the insoluble humin fraction.

In the red mud amended samples, the metal mobility did not change over time but remained the same as it was from the start of the incubation. This shows that the metals in the substrate were immobilised by the red mud right from the beginning when the first sample was taken.
The mobility of metals, over the 20 day period, in the mud amended samples was lower than in the blank, though the mobility in the blank reduced as a function of time. For some metals the time dependent reduction in metal mobility achieved through adsorption onto the organic fraction after 20 days was the same as the mobility that was obtained instantly in the red mud amended compost. However due to the organic fraction being subject to further and relatively rapid biological degradation it is desirable for the metals to be adsorbed to an inorganic fraction which is subject only to chemical degradation and weathering. These processes take place over a much longer period.

6.4.3 Effect of red mud on the mobility of heavy metals.

According to the hypothesis, red mud can reduce the mobility of heavy metals in compost through adsorption onto cation exchange sites, precipitation of metal hydroxides and carbonates and adsorption of organic acids containing metals. In this regard it must be borne in mind that the substrate was spiked with metals in soluble form as salts prior to composting. The ionic metals in salt form could be more reactive with surrounding compounds than the metals in actual waste, due to higher solubility.

Precipitation of metals in the form of hydroxides or carbonates is mainly governed by pH and ionic strength of the soil solution. At the pH levels measured in the red mud amended compost some precipitation of metal hydroxides is likely to have taken place during the occurrence of higher pH levels (Appendix III, Table 6.15).

Copper and chromium in particular have a very low solubility product with their hydroxide. The same situation exists for the presence of a high percentage of carbonates in the red mud - compost that are available to complex and precipitate heavy metals (Table 6.10).

The overall effect of red mud addition to compost on the concentration and mobility of heavy metals is given in Table 6.5. It can be seen that red mud has an overall effect of reducing the availability of the metals to the soil solution, i.e. leachable and plant available metals. Red mud also affected the recovery of metals in the acid digest.
The soil solution soluble and plant available fractions of the total metal content in the blank were low for chromium (2.5%, 6.2%), copper (5.6%, 22.5%) and lead (1.7%, 26.1%), (refer to Appendix 6.II). This indicates the affinity of these metals to organic matter. Cadmium, zinc and nickel have low soil solution soluble fractions, respectively 2.5%, 11.5% and 8.3%, but a relatively high plant availability of respectively 64%, 71% and 43%. This suggests either adsorption to microbial cells or a low stability constant of the metal - organic matter complex.

The overall effect of red mud on the plant available and leachable metals appears to be most pronounced with the addition of 30% red mud. However the reduction is similar at 25% and 40% red mud. At 40%, however it appears that some of the metals that naturally occur in red mud are released, particularly chromium and nickel. This is an important aspect that demonstrates the need for restricted red mud amendment and defines the upper limit of red mud amendment. The metal release is mainly an issue during the composting process. Repeated red mud application to the soil in this manner should thus be restricted to levels that prevent increased metal concentration in the soil solution. The metal release in soil however is controlled by the soil pH and to a limited extend the equilibrium of the red mud - metal complex with the soil solution.
In most cases the percentage reduction in leachable metals with addition of red mud, as shown in Table 6.5, is slightly higher than the reduction in plant available metals. There appears no trend that suggests that this is due to metal precipitation, in accordance with Table 6.15. The addition of 30% red mud resulted in the lowest soil and plant extractability of each metal in comparison with the blank and other additions.

Over the relatively short time of 20 days of decomposition of the organic matter and red mud interaction, a clear reduction in metal mobility was demonstrated for all metals. Red mud reduced the mobility of lead to less than was found in the non-spiked control. Lead is known to have strong affinity to soluble humic acids, which are formed firstly during organic matter degradation. Copper is strongly bound by fulvic acids which are a product of humic acid degradation. They are of lower molecular weight but have a high functional group content (see Chapter 3).

It is important to consider the pH when comparing the mobility of metals in the differently amended substrates. The final pH of the blank and the 20, 25, 30 and 40% mixtures were all around 7.4 (Appendix 6.III). The pH in the control was slightly lower (7.1). This could have contributed to a higher heavy metal mobility in the control resulting in relatively lower mobility in the blank and the red mud samples as a result of the deduction of the control data. The 10% mixture had a pH of 7.02 which is lower than the control. This would cause a higher metal mobility compared to the other samples. This pH level is however a realistic value under soil conditions.

Red mud had an effect on the level of recovery of metals with an acid digest. None of the metals could be 100% recovered with the HNO₃-HClO₄-HCl digest, except chromium, which was 'over' recovered. This must be due to the high chromium content in red mud. There could also be a reducing effect of the organic acids on red mud particles, i.e. Fe- and Al- oxides, that could result in additional chromium release.

6.4.4 Compost maturity

Two parameters were measured specifically to provide information on compost maturity, the formation of soluble organic matter and the $E_4/E_6$ ratio. The C/N ratio and carbon dioxide emission rates can also be used to give an indication of the level of
compost maturity. An increasingly stable value for both of these parameters is positively correlated to compost maturity.

It was shown that an increase in solubilised organic matter takes place during the course of the thermophilic stage of the composting process, particularly after an initial two week period. The general increase in soluble organic matter is as expected. The effect of increasing red mud additions appears to be to strongly reduce the solubilised organic matter. It is unlikely that this is solely the result of a detrimental effect of red mud on the decomposition rate, as temperature and CO₂ production do not indicate this, except in the case of the 40% red mud addition (Table 6.10). The dilution effect of red mud for 40% was 4/14*100% = 32%. The reduction in COD is 80 - 90%, thus the COD reduction cannot be attributed to red mud dilution effect only (Figure 6.35).

In research described in chapter 4, on the effect of red mud on solubilised organic matter, it was found that red mud could adsorb considerable amounts of soluble organic matter. This was demonstrated by a strong reduction in COD in solution after shaking with red mud. Red mud is thus able to adsorb metals directly and also adsorb soluble organic matter - metal complexes.

The adsorption of soluble organic matter by red mud reduces the potential leaching of organic compounds and metals complexed to them to groundwater. Thus the use of soluble COD does not appear to be a good indication of the state of compost maturity when red mud is used as an amendment.

When comparing the results of the concentration of soluble organic matter and the \( \frac{E_4}{E_6} \) ratio measurement, there appears no correlation, though the loss of the \( \frac{E_4}{E_6} \) samples at day 9 made the comparison incomplete.

There are three aspects in this research that influenced the \( \frac{E_4}{E_6} \) ratio; time because of the time dependence of soluble organic acids formation, metal adsorption onto the organic acids, and the effect of red mud addition. The \( \frac{E_4}{E_6} \) ratio is concentration and thus time dependent, due to the organic acid formation, until a concentration of 0.5 mg/ml has been reached. The ratio did not change significantly in the control or blank,
though the concentration would have been below 0.5 mg/ml. The red mud amended samples showed a more positive correlation between time and E₄/E₆ ratio.

In the fulvic acids, the ratio increased with addition up to 25% and then sharply decreased. It cannot be ruled out that red mud selectively adsorbs the aliphatic chains over the condensed aromatic rings, resulting in a relatively increased level of condensed aromatic rings. This is however a speculation that requires more evidence. This could be obtained by determining their ratio before and after red mud addition.

The increase in E₄/E₆ from the control to the blank is a result of metal adsorption onto functional groups. This increases the molecular weight of the organic acids and more importantly, enables them to become ligands and form high molecular weight complexes with other such ligands (section 2.3.3.1).

The E₄/E₆ ratio increases during composting in extracts with comparable humic substance concentrations (section 2.3.6.5), as was observed in this research. However the time dependence of the E₄/E₆ ratio in the early stages of the composting process and the interaction of the organic acids with the red mud interfered with the E₄/E₆ ratio, thus making this parameter unsuitable as measure for compost maturity.

The C/N ratio had stabilised within 21 days in most substrates, except the control and the compost amended with 30% red mud, and the carbon dioxide respiration had reduced significantly indicating progression towards maturity.

In general the determination of maturity indicators showed some expected results. However the results were incomplete due to the inadequate time allowed for maturation and the interference of red mud with the COD, E₄/E₆ ratio and carbon dioxide emission.

6.4.5 Compost quality

Red mud addition has a typical effect on the development of the pH at the start of the thermophilic stage. A slight increase can be observed in the samples with more red mud. Over time the pH in the different samples shows a greater fluctuation with lower
red mud addition (Figure 6.27). It shows that red mud buffers the compost with its high bicarbonate content (Table 6.10).

The pH value of the composts after 20 days stabilised at around pH 7.4. This is a desirable pH for a soil conditioner, particularly since this is a highly buffered value and the local sandy soils suffer from a low pH (4.5 - 6.5). At a pH value of 7.4 most metals are strongly bound by red mud. Some trace elements may have a slightly reduced plant availability at this pH. The local sandy soils are however deficient in trace elements due to leaching at low pH.

The development and stabilisation of the pH in each of the composts follows a similar pattern which is in accordance with a conventional compost process; an initial low pH as a result of acidic sap release, followed by an increase in pH due to formation of ammonia and carboxylic and phenolic functional groups through oxidation. After 8 days the pH decreased slightly and stabilised at around 7.4.

The buffer capacities of 20, 25, 30 and 40% red mud can be easily compared as their pH levels were all around 7.4. The lower pH of 10% red mud does not seem to have had a profound effect on the carbonate content, as the increase in carbonate content in the 10% sample is similar to the increase in the 20 and 25% sample. The addition of 40% red mud did not increase the buffer capacity significantly higher than the addition of 30% red mud. The addition of 30% red mud to organic matter appeared most effective in achieving a high buffer capacity in this batch experiment.

The carbon to nitrogen ratio is an important process parameter, as it determines the extent of carbon decomposition and indicates possible excessive loss of nitrogen. The C/N ratio for the blank and control were in the range of 18 - 25 and remained quite stable during the process (Table 6.12). The red mud - compost samples had a slightly higher ratio particularly at day 3 when the pH also peaked, despite a considerable loss of carbon as carbon dioxide. This can be explained by a high loss of ammonia as a result of a relatively high pH. This increases the C/N ratio, up to 38 and 40 for 25% and 30% respectively. The C/N ratios remained higher in these samples. The relatively low C/N ratios in the 40% red mud sample over time were most likely due to reduced loss of nitrogen as a result of reduced composting activity and ammonia formation. Any
carbon that was adsorbed to red mud during the process would have been recovered during the total organic carbon analysis.

Red mud was expected to increase the salinity of the product. This occurred in each incremental addition except the first addition of 10% which had a consistently lower salinity than the blank. The only feasible explanation for this would be the adsorption of the di- and trivalent metal ions and desorption of monovalent sodium from red mud. This would theoretically reduce the electrical conductivity of the solute. However no other evidence is available in the data to support this, thus the reason is most likely the difficulty in obtaining truly representative samples.

The salinity of the red mud - compost is within compost quality guidelines and is thus not an obstacle for its use as a soil amender (Zucconi and de Bertoldi, 1987).

In general, it was found that addition of red mud to organic waste prior to composting to reduce metal mobility has no adverse effect on the quality of the final compost. It has in fact improved several compost quality parameters. Repeated application of the compost to a soil should not increase metal mobility as each application will have sufficient red mud to control the solubilisation of heavy metals. In a conventional soil the release of these metals is a function of soil pH and the stability of the adsorption complexes.

6.5 Conclusions

Red mud addition to organic waste has the effect of reducing the mobility of heavy metals in the end product. The study indicates that this effect is evident as early as 20 days after the commencement of the composting process. The addition of 30% red mud to the organic waste was found to give the lowest metal mobility, instantly as soon as red mud is added.

The mobility of heavy metals in organic matter only is time dependent and reduces over time. However the metals are adsorbed onto organic matter which further decomposes rapidly which results in re - mobilisation of the metals. This is not the case when metals are adsorbed to the inorganic red mud fraction.
The use of carbon dioxide release as a parameter for measuring degradation rate is not entirely valid due to adsorption of this gas by red mud alkalinity. Red mud compost has a very high pH buffer capacity due to its high carbonate content. A separate assessment of carbon dioxide adsorption by red mud during composting is required before carbon dioxide release can be used as a parameter for characterising biodegradation.

Red mud appears to have a slightly detrimental effect on the composting process as shown by reduced carbon dioxide release and lower solubilisation of organic matter at high additions. These components could, at least in part, be adsorbed by the red mud instead of released to the gas or liquid phase. This interferes with their use as parameters for measuring the rate of biodegradation. It was apparent however that the degradation rate of the organic fraction was reduced at a red mud addition of 40%. Red mud addition at the lower rates was not shown to reduce the biodegradation rate of organic matter.

Red mud improves several quality parameters of the final compost for use as a soil conditioner.
Chapter 7

Municipal refuse composting

7.1 Introduction

The approach to reducing metal mobility and concentration in compost was examined in Chapter 6 in relation to organic matter spiked with metal salts. In order to validate the results of those laboratory experiments in an applied situation the process of adding red mud to organic waste prior to composting needed to be applied to the organic fraction of actual municipal waste.

It was hypothesised that the reduction in metal mobility that was achieved in the laboratory experiments could to a certain extent also be achieved in a pilot plant situation, using sorted domestic waste as a substrate for composting.

This contaminated organic waste fraction differs markedly from the substrate used in the laboratory experiments, in that the organic matter in domestic waste is of more diverse origin, more heterogeneous and the metal contaminants are not in such a reactive form as the metal salts used in the laboratory experiments. A fraction of the metals present in the waste is in metallic form, e. g. lead (wine caps, lead shot) and copper (electrical wire). Metals in their metallic form are not reactive with red mud until ionised through oxidation. However the metals in metallic form will be solubilised in an acid digest when analysing for total metal of the compost.

In order to obtain a compostable waste fraction that is likely to be contaminated with metals so the effect of red mud can be demonstrated and to optimise the economics of the resource recovery from the municipal waste, it was decided to separate the fractions that are economically recyclable i. e. the plastics, glass and metal fractions. These fractions are easily recyclable due to existing demand and are visual and/or chemical contaminants for compost. Paper was not removed, since paper is compostable and the Council from which the waste was derived has a separate collection scheme in place for paper recycling. A double paper recovery system was considered unnecessary. The rest
of the waste was to be composted and the compost tested for levels of metal contamination and quality.

The objectives of the pilot plant study were, in order of priority.

1. to field test the process described in chapter 6 for reducing metal mobility in municipal compost;

2. to produce municipal compost of acceptable quality in relation to metal contamination and its application as a soil conditioner when red mud was incorporated; and

3. to collect data on the composition of domestic waste.

7.2 Materials and methods

In order to ensure that a statistically significant amount of domestic waste was processed a pilot plant was designed with a capacity to handle 5 m$^3$ sorted municipal waste. Domestic waste from a residential area was delivered to the pilot plant by random redirection of a half filled municipal garbage collection truck. The incoming waste was hand sorted to remove plastics, glass and metals. The residue was composted in the compost pilot plant, with daily monitoring of moisture content, pH and temperature. Samples were taken daily. On a weekly basis samples were analysed for soluble COD, organic matter content, the carbon to nitrogen ratio and for the following heavy metals, cadmium, copper, chromium, lead, nickel and zinc.

7.2.1 Pilot plant

The compost pilot plant consisted of a 5 m$^3$ rotating open ended reactor and a conveyor belt used for hand sorting the waste and filling the reactor. A diagram of the reactor is given in Figure 7.1 and a photograph in Plate 7.1. The reactor consisted of a redundant concrete mixer including worm shaped agitators running along the inside wall of the reactor. The agitators enhanced the aeration of the waste and improved the physical breakdown of the waste into smaller particles during rotation.
The reactor could be operated at two rotation speeds. During filling and initial physical breakdown, the reactor rotated at 6 revolutions per minute (rpm). The power for this speed was provided by a 4 pole 5.5 kWh (415 V) electrical motor at 1450 rpm with a gear reduction of 20 \cdot 1 and a chain reduction of 50 \cdot 9. The gearbox allowed this same speed in reverse mode for emptying the reactor.

The second speed was 1 revolution per day (rpd) and could be used for aeration and mixing of the waste later during the composting process when the demand for oxygen would start to drop. At this speed the reactor was driven by a 8 pole 0.15 kWh (415 V) electrical motor at 650 rpm. The required gear ratio for the reduction was 936,951:1. This was achieved by adding an epicyclic double reduction gearbox with a ratio of 8,441:1 in addition to the existing gearbox. Both electrical motors were enclosed, fan cooled and required a three phase power supply.

Figure 7.1 Diagram of the composting pilot plant.

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A timer was fitted in the circuit board to enable intermittent rotations at 6 rpm, between static periods without rotation. This switching relay system could be altered to accommodate rotation on demand, either temperature or oxygen concentration driven or for emptying the compost from the reactor on completion of the thermophilic and cooling down phase (section 2.2.2.2).
A gearbox between the 5.5 kWh electrical motor and the reactor allowed rotations in reverse mode. A ten metre long conveyor belt was placed in such a way that the top end was above the flight of the reactor to guide the refuse into the reactor. The bottom end of the conveyor belt had a hopper fitted to dump refuse in before transportation up the conveyor belt. During transport of the refuse by the conveyor belt into the reactor, the refuse was hand sorted by three pickers standing on each side of the belt, removing glass, metals and plastics.

Plate 7.1 Pilot plant set up with conveyor belt, reactor, control, motor and gear box and sorting bins.

7.2.2 Pilot plant operation

7.2.2.1 Waste preparation

A refuse collection compaction truck (10 m$^3$) was filled to approximately half its capacity (5 m$^3$) by collecting domestic refuse from 240 L mobile garbage bins (Sulo) in a nominated residential area within the Perth City Council area. The truck was weighed on a weighbridge before and after unloading the refuse in order to measure the weight of the refuse. The refuse was unloaded near the hopper of the conveyor belt on a heap.
Alongside the conveyor belt, six bulk bins were placed to for storing the individually sorted fractions of glass, metals and plastics. Three 240 L bins were placed near the hopper, also for receiving sorted recyclables.

The filling and sorting was done by four persons. Two persons picked up refuse from the heap, placed it in the hopper or on the conveyor belt and opened the plastic bags in order to expose the individual waste fractions. Some sorting was carried out here, depending on the load of the other sorters. The other two persons stood halfway along each side of the conveyor belt and thoroughly removed the glass, metals and plastics from the refuse on the belt, including synthetic clothing, shoe ware, rubber etc. The residual waste travelled further up the conveyor belt and entered the compost reactor (see Plate 7.2).

Plate 7.2 Mixed domestic waste on the conveyor belt prior to sorting and discharge of the organic fraction into the reactor.
The reactor was rotated at a speed of 6 rpm during filling in order to homogenise and pulverise the waste. This rotation speed was maintained for 48 hours to ensure a completely homogenised and pulverised composting substrate.

After some initial trial runs with the pilot plant, it was decided to do 3 runs of which in the first run the substrate consisted of refuse amended with 30% w/w (dry weight) red mud — gypsum (4%) at the beginning of the 48 hrs mixing period; the substrate of the second run consisted of plain unamended refuse, and finally, a third run where 25% w/w (dry weight) red mud was added to the refuse after 24 hours mixing and circa 20 mins before the end of the mixing period (6 rpm). In earlier trials it was found that an early addition of the mud had a granulating effect on the substrate, and it seemed to impair the composting process, because the inner core of the granules, that were formed, was not sufficiently aerated. The plain substrate run was necessary to demonstrate the effect of the mud addition.

The amount of red mud added was 30% or 25% respectively of the total weight of the refuse in the reactor. The latter was determined by subtracting the combined weight of the glass, metals and plastic fraction from the total incoming weight of the refuse. The addition of 30% w/w red mud was based on the laboratory experiments, where this percentage of addition did not affect the composting process while achieving a high degree of reduction in heavy metal mobility. The 25% red mud addition in the third run was based on experience gained in the first run which indicated that the dosage was too high.

7.2.2.2 Composting runs

After the 48 hour mixing period the rotation speed was reduced to 1 revolution per day. This speed made it possible for the substrate to develop a heat core, based on the theory that heat loss is less at a lower rotation speed. A consequence of this, however, was also reduced ventilation and thus oxygen supply. In the case of an oxygen deficiency developing in the substrate as indicated by a drop in temperature and development of odours, we switched to a mode where the reactor would turn at a speed of 6 rpm for 5 minutes in every hour as an intermediate aeration period between the 6 rpm and the 1 rpd speeds.
7.2.2.3 Process monitoring

The recyclables, glass, metals and plastics, were weighed in order to collect data on the composition of the incoming waste. The weights of these fractions are also included in a material - mass balance.

In order to achieve the objective of producing a good quality compost from the sorted municipal waste, it was essential to monitor and control the composting process. The relevant process and compost quality parameters monitored are described below.

The temperature in the substrate is a symptomatic parameter and gives an overall indication of the quality or the progress of the process. A high temperature e. g. > 55°C can only be achieved under favourable process conditions. The temperature was measured daily, except over some weekends, during each of the three runs. After the period in the reactor, i. e. during the windrowing stage, the temperature was measured occasionally since it was not expected to increase. However, this was not the case, particularly for run 3, where difficulty was experienced in obtaining thermophilic conditions in the substrate. The highest temperature achieved in the reactor was 39°C. This is too low for proper composting. However, during windrowing the temperature increased to 55 - 60°C, well into thermophilic conditions (section 2.2.2.2).

The moisture content is very important since it is the medium in which the microbes can develop and thrive using the dry matter as a source of energy and nutrients. Moisture content was measured daily and maintained or adjusted to a level of between 50 and 60% if required.

Oxygen is required during composting as a hydrogen acceptor to oxidise the carbon in the substrate. Oxygen uptake can be very high during the thermophilic phase and thus, in order to prevent anoxic conditions, abundant supply is necessary. Oxygen concentration in the gas phase was measured daily. The rate of oxygen uptake has a positive relationship with the rate of heat production by the microorganisms. Increased oxygen uptake thus is reflected by an increased temperature in the substrate.
On a daily basis, a 1 kg sample was taken from the reactor. This was prepared by compositing various samples from different sections of the reactor. This composite sample was thoroughly mixed and 100g was oven dried, at 105°C, until stable weight was obtained, to determine the moisture content.

The dried sample was analysed for total ash content, total organic carbon (TOC), total Kjeldahl nitrogen (TN), pH and leachable, plant available and total metal content. The methods are listed in Table 6.3.

The pH is an important process parameter as it influences the level of activity of the microorganisms, and the pH causes loss of nitrogen from the substrate as ammonia (NH₃) if it rises to above mildly alkaline levels (pH > 8.5). The pH also appears to have an effect on the formation of volatile organic compounds that are responsible for odour. Particularly an elevated pH level which is promoted in presence of red mud, combined with the presence of clay constitutes an effective odour control since there is no formation of free carbonic acids and the malodorous Maillard - products (Krauß et al., 1992). The pH was measured in a 1:10 sample to water extract of a fresh compost sample.

The ash content of the compost was determined to obtain an indication of the organic matter content of the load. This is important in determining its suitability as a substrate for composting and the eventual use of compost as a soil conditioner.

The total organic carbon and total nitrogen content were analysed to enable calculation of the carbon to nitrogen (C:N) ratio. The C:N ratio is an important process parameter, since it is an indication for the nutrient balance in the substrate, which the microbes require for complete decomposition of the organic matter. Due to the volatilisation, and thus loss, of carbon as carbon dioxide during composting, a reduction in the C:N ratio results during the process. The C:N ratio should be 25 - 30 at the start of the process reducing to only 10 - 15 in the final mature compost.

The increase in soluble organic matter during composting was monitored by analysing a water extract, prepared as for pH measurement, for its chemical oxygen demand (COD).
Finally the compost was analysed for the level of heavy metals. The compost was analysed for the leachable, plant available (DTPA) and total metal content in the compost as described in Chapter 6. The level of extractable metals assessed relative to the total content in each compost sample. This enabled a comparison of the effect of red mud on the mobility of the heavy metals in the municipal compost, despite the use of different wastes between the runs. The compost was analysed for cadmium, copper, chromium, lead, nickel and zinc.

After the temperature in the reactor had dropped back to ambient levels the reactor was emptied by reversing the rotation direction and placing a trailer underneath the output flight.

The immature compost was windrowed to allow further maturation. The temperature continued to be measured, since in some cases the temperature increased again after windrowing.

7.3 Results

7.3.1 General pilot plant operation

The pilot plant functioned well for the purpose of the experiment. The filling procedure worked very efficiently. It generally took about 8 hours to fill the reactor. This time was split up over two days. The bulk of the reactor volume was filled in 6 hours on the first day. The high rotation speed of the reactor reduced the waste volume in the reactor overnight due to the pulverisation and subsequent decrease in bulk density. On day two, another two hours of filling ensured a maximum load of waste in the reactor. Water was added to the waste to bring the moisture content up to 50 - 60%.

The 6 rpm initial speed was sufficient to pulverise and homogenise the substrate into a mulch type substance. This increased the specific surface area and thus the access for microbes to the substrate.

The 1 rpd rotation speed during composting appeared insufficient to supply enough oxygen to prevent the process from becoming anoxic, during the thermophilic phase.
Since the gearing did not allow intermediate speeds, a timer was installed in the power circuit board to allow intermittent rotations at 6 rpm in between static periods. This option was available only during the third run. Until then, if an anoxic situation occurred in the reactor the speed was manually changed to 6 rpm by changing gears, for a period of 10-20 minutes, or until any odour that was present had disappeared.

7.3.2 Operational matters for each run

Particular operational problems and experiences that are relevant to the management of the pilot plant are discussed separately for each run.

7.3.2.1 Run 1

The waste came from West - Perth which is a suburb with a mixture of the following activities, small business, professional services and some residential housing. As a consequence the waste was relatively low in food and garden waste though high in paper content from the offices in the area. Of particular interest was the regular occurrence of photographic and printing waste e. g. paper, toner and ink.

Composting process did not commence naturally, due to the low moisture content, until 9 days after filling, when enough water was added to achieve a 60% moisture content.

Red mud, neutralised with gypsum by dry mixing, was added early during filling of the pilot plant to ensure thorough mixing. During mixing the mass granulated as a result of the dry red mud forming a coating around small bits of substrate. This became a problem for the aeration of the waste, since inside the granules anaerobic conditions occurred.

Because of the high paper content of the substrate the carbon to nitrogen ratio was too high. In order to reduce the ratio, 10 kg of urea (46% N) was added dissolved in 240 litres of water at day 24 of the run.
The compost was discharged from the reactor after 77 days and windrowed under a tarpaulin cover for further maturation. The temperature and pH were monitored up to day 150. The organic matter content was measured up to day 134.

7.3.2.2 Run 2

The refuse for the second run was collected in a mainly residential area in Wembley. Some commercial waste particularly from the medical sector was present, e.g. syringes, ampoules, medicines, etc. The garbage had a high content of garden waste, which was not surprising since the suburb is well known for its well trimmed gardens and the garbage was collected following a fine weekend. An amount of water of 810 litres in total was added to achieve a moisture content of 52.8%. The plant was left turning continuously at 6 rpm to break up and mix the waste until day 3.

- On day 3 the pilot plant was set to composting mode, which meant rotating the reactor for 5 minutes per hour at 6 rpm. The next day it appeared the plant had not turned because the setting of the timer was not correct.
- On days 7 and 8 the reactor did not turn either, because a flange in the transmission had shifted. This flange has to be regularly checked and if necessary pushed back. These periods of standstill caused anaerobic microbial activity, resulting in an ammonia smell.
- On day 15, 200 litres of water were added to the composting mass because the moisture content had decreased to 44.2%. The water was added while the plant was turning to ensure good mixing.
- On day 22 a larger sample (about 2 kg) was taken for measuring heavy metal contents. The sample consisted of 20 sub-samples, taken in series of 5. After each series the pilot plant was turned for about 1.5 minutes. The sub-samples were put together in one bag and dried at 105°C. After drying, the sample was ground and analysed for heavy metals. The organic matter content was also measured.
- On day 24, the pilot plant was emptied. The compost was stored under black plastic sheets to prevent drying out and compost being blown away. Eight days later, the temperature was measured and appeared to be about 62°C. In the outer layer, 10 cm, white fungus was growing. The inner core was dark in colour and showed no visible changes.
7.3.2.3 Run 3

The waste was collected in Perth, from the St Georges Terrace and Mill Street area, and consisted for a large part of paper and wrapping materials (plastics). Very little garden and kitchen waste was present. During filling, 800 litres of water was added to increase the moisture content and reduce the resistance in breaking up the waste. Filling was completed on day 2 at noon. The waste had a very fibrous texture after breaking up and mixing, due to the high paper content

- After five days, 10 kg urea in solution was added to increase the nitrogen content and reduce the C/N ratio. The urea addition resulted in an increase in pH to above 9. This was not considered a favourable pH level for composting. The increase was caused by the release of hydroxide as a result of the microbial decomposition of urea.

- On day 8, rotation was set to 1 revolution per day (rpд), because it was suspected that continuous fast rotation resulted in a too high heat loss. The reactor was turned at 6 rpm for some minutes after each temperature measurement. Temperature started to rise after this modification. On day 13 rotation timer was set to 5 min in every 2 hours at 6 rpm. On day 14, 300 kg red mud was added, with a moisture content of 16%, so effectively 250 kg dry red mud was added.

- On day 19, 350 litres of water were added to adjust the moisture content. The next day, rotation mode was set to 1 rpд. On day 21 another 250 litres water were added because moisture content was still only around 50%. No obvious granulation of the compost occurred. On day 23 granulation of the compost appeared to occur. Possibly the moisture content of the compost had an influence on the granulation process.

- On day 28 an anaerobic smell was emitted from the compost, indicating insufficient aeration. To alleviate the anoxic state the turning mode was set to 5 minutes of 6 rpm every two hours. On day 30 the turning mode was returned to 1 rpд, because the compost was cooling down rapidly while the anaerobic smell was still there. The pilot plant appeared not to be turning. On day 35 the gearbox overload mechanism which had cut off the power because of overheating of the gearbox was reset. After this the drum still was not turning when the low speed was set. It appeared that the 1 rpд turning gear was disconnected, which was rectified. On day 49 the turning speed was set to 1 rpд.

- On day 59 approximately 250 litres of water were added as the moisture content had dropped below 50%. It was anticipated that the increased moisture content
might have an effect on granulation of the compost. The compost had not
granulated. On day 65 the reactor was set to fast turning mode, 10 minutes per hour
in order to granulate the compost. However, the compost only granulated to a
minor extent.
- On day 66 the pilot plant was emptied. The weight of the compost was 1820 kg.
The compost was taken to a plot of land on Murdoch University grounds for further
maturation. The composts from the previous two runs were collected and taken to
the same plot for storage.

7.3.3 Waste fractionation

The composition of the waste processed during the three experimental runs is given in
Table 7.1. The waste of the first run contained a lot of paper, which is shown by the high
organic matter fraction (51.5%), yet a low moisture content (12.8).

At the beginning of this run 415 kg of red mud (dry weight) was added, equivalent to
30% of the dry weight of the waste at the start of the 48 hour mixing period. This meant
that 23% of the total dry weight consisted of red mud.

Table 7.1 Composition of the domestic waste used in the experiments, including
moisture content, compared to results of a local waste survey (Mindarie

<table>
<thead>
<tr>
<th>Fraction</th>
<th>West Perth</th>
<th>Wembley</th>
<th>Perth</th>
<th>Mindarie</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg</td>
<td>%</td>
<td>kg</td>
<td>%</td>
</tr>
<tr>
<td>Composted*</td>
<td>1375</td>
<td>51.5</td>
<td>1310</td>
<td>45</td>
</tr>
<tr>
<td>Glass</td>
<td>170</td>
<td>6.4</td>
<td>130</td>
<td>4.5</td>
</tr>
<tr>
<td>Metals</td>
<td>240</td>
<td>8.8</td>
<td>125</td>
<td>4.3</td>
</tr>
<tr>
<td>Plastics</td>
<td>550</td>
<td>20.5</td>
<td>305</td>
<td>10.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>345</td>
<td>12.8</td>
<td>1040</td>
<td>35.7</td>
</tr>
<tr>
<td>Total (kg)</td>
<td>2670</td>
<td>100</td>
<td>2910</td>
<td>100</td>
</tr>
</tbody>
</table>

*on a dry weight basis and may contain an inorganic fraction not sorted for ie. stones,
#organic fraction (food, garden and paper)
The waste of the second run came from households in Wembley. This run was used to produce plain domestic waste compost i.e. without red mud addition. The waste appeared to be relatively low in compostable matter in comparison with the previous run. However, the high moisture content indicated that most of the compostable fraction consisted of food and garden waste rather than paper which resulted in a low moisture content in the waste in run I. A combination of food and garden waste form a better substrates for composting due to their higher nutrient and moisture content.

The third run waste was very high in paper content due to the high concentration of offices in the collection area. This is shown by the high organic matter content and very low moisture content.

7.3.4 Composting process

Due to the heterogeneous nature of the waste, the different red mud treatments employed, the considerable differences between the wastes and also process operating conditions, the results of the process parameters and compost quality, in relation to heavy metal contamination and particle size distribution, will first be given separately for each run. The combined results will then be discussed in the discussion section.

7.3.4.1 Red mud amended municipal waste composting I (run 1)

7.3.4.1.1 Process parameters

Temperature

The results of the changes in temperature during composting are shown in Figure 7.2-A. The temperature only started to increase after adding water to the waste to increase the moisture content to within the 50 - 60% range. Due to a technical problem with the oxygen probe, the moisture addition was delayed until 8 days after filling. Oxygen measurement was abandoned. The initial moisture content was too low to allow sufficient bacterial activity to raise the temperature above ambient. The temperature fluctuated for 10 days between 35° and 40°C. This is a mesophilic level. The sudden temperature drop after 21 days was caused by a lack of oxygen for microbial metabolism. Subsequently a timer was installed in the circuit board to increase aeration by rotating
the reactor for 5 min per hour at a rotation speed of 6 rpm. The temperature briefly increased after that before cooling down. The absence of a thermophilic stage was probably caused by granulation of the substrate early in the process. The red mud appeared to form a thin coating around waste particles, mainly consisting of paper. Though this created larger pores and easier air flow between the granules, the organic material in the interior of the granules turned anoxic. This was demonstrated by the low redox potential (-90 mV) of a compost extract.

During windrowing the temperature slowly increased to 55° - 60°C and remained in this range for 10 weeks. This suggested that perhaps the type of substrate and the aeration method prevented the thermophilic micro-organisms from establishing themselves in the reactor.

**Moisture content**

The initial moisture content of the waste was 20%. This was increased to 58 - 60% after 8 days by adding water from a nearby groundwater bore. This moisture content was maintained throughout the reactor period. The moisture content during composting is given in Figure 7.2-B.

**Organic matter content**

During composting a reduction in organic matter content takes place as a result of decomposition. In Figure 7.2-C the organic matter content during composting is plotted. A slow decrease in organic matter content can be observed of from 66% to 62%. The organic matter content is an important quality parameter for compost as a soil conditioner.

**Carbon to nitrogen ratio.**

Due to the loss of carbon as carbon dioxide, the C/N ratio usually reduces during composting. However, this can be countered by a high pH (7.5 - 9) in the substrate when loss of nitrogen as ammonia can occur. The C/N ratios are given in Table 7.2.
The C/N ratio in the initial substrate was too high for good composting due to a high paper content. In order to reduce the C/N ratio 10 kg of urea was added during day 24. This addition did not show up in the total nitrogen result, possibly due to volatisation as a result of the pH increase the urea degradation caused combined with the elevated temperature, and nitrates formed during nitrification are not included in Kjeldahl method of total nitrogen analysis. However nitrate normally only appears during the maturation phase. A strong ammonia smell was observed shortly after urea addition.

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>Total Organic Carbon</th>
<th>Total Nitrogen</th>
<th>C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>279</td>
<td>6.10</td>
<td>46</td>
</tr>
<tr>
<td>16</td>
<td>260</td>
<td>6.70</td>
<td>39</td>
</tr>
<tr>
<td>28</td>
<td>281</td>
<td>5.58</td>
<td>50</td>
</tr>
<tr>
<td>29</td>
<td>271</td>
<td>5.28</td>
<td>51</td>
</tr>
</tbody>
</table>

**Table 7.2 The total organic carbon, total nitrogen (g/kg) and the C/N ratio of the waste during composting.**

**pH**

The initial pH slowly increased before stabilising at between 8 and 8.5 (Figure 7.2-D). A further increase was observed after addition of nitrogen in the form of urea. Urea, (CO(NH₂)₂), is decomposed bacterially into ammonium, carbon dioxide and hydroxide, hence the pH rose. The formation of ammonia under the high pH resulted in volatilisation of ammonia (NH₃), indicated by the distinctive odour.

However, after maturation in a windrow, the pH came down to 7.4. This drop in pH was probably the result of neutralisation of hydroxide by carbon dioxide formed during composting. The bicarbonate (HCO₃⁻) formed acts as a pH buffer.

**Soluble organic matter**

The level of soluble organic matter was relatively low during this run and fluctuated strongly (Figure 7.2-E). The low level of soluble organic matter is likely to have been
caused by adsorption to red mud, which was observed in laboratory experiments as well (chapter 4). In addition, there was a low level of microbial activity (indicated by the absence of a thermophilic phase) which would have resulted in reduced organic matter solubilisation.

Figure 7.2 Temperature (A), moisture content (B), organic matter content (C), pH (D) and soluble organic matter (E) during composting (run 1).
7.3.4.1.2 Heavy metal content and mobility

A composited compost sample was analysed for leachable, plant available and total heavy metal content. The results are given in Table 7.3.

The analysis for leachable and plant available metals was repeated twice as a function of time after the initial complete analysis. The repeat analyses were done at the 12 and 20 week points respectively.

Table 7.3 Total metal content in municipal red mud-compost and the plant available and leachable fractions (run 1); in mg/kg dry matter.

<table>
<thead>
<tr>
<th>Metal</th>
<th>leachable</th>
<th>plant available</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Age (d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>60</td>
<td>150*</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Copper</td>
<td>0.8</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Chromium</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nickel</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Lead</td>
<td>0</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.5</td>
<td>2.8</td>
<td>2</td>
</tr>
</tbody>
</table>

* matured compost of run I.

It appears that a concentration effect occurred during the first part of the process as a result of loss of dry matter. During the maturation phase the metals appeared to be bound in a less mobile form as shown by a reduced extractability.

The total metal content is very low compared with the data found by other researchers shown in Table 1.2.

7.3.4.1.3 Particle size distribution

After complete maturation, 555 kg of the compost was sieved using a 6.35 mm and a 12.7 mm sieve. The major part of the compost (72.6%) consisted of a fine fraction with particles smaller than 6.35 mm, 8.9% was in the range 6.35 - 12.7 mm and 18.5% was
larger than 12.7 mm. The results of sieving the compost are shown in Table 7.4. The high fines content is due to the 24 hours of intensive mixing and agitation in the drum.

The largest size fraction consisted mainly of plastics, metal pieces and large paper balls.

Table 7.4 Compost particle size distribution on the basis of weight (run 1).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Size (mm)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>fine</td>
<td>&lt; 6.35</td>
<td>72.6</td>
</tr>
<tr>
<td>medium</td>
<td>6.35 - 12.7</td>
<td>8.9</td>
</tr>
<tr>
<td>coarse</td>
<td>&gt; 12.7</td>
<td>18.5</td>
</tr>
</tbody>
</table>

7.3.4.2 Plain municipal waste composting (run 2)

7.3.4.2.1 Process parameters

Temperature

The temperature in the reactor rose to 62.5°C on day 7 and then decreased to a low point of 22.4°C on day 15 (Figure 7.3-A). On day 15 water was added, and the following day the temperature rose again to 27.5°C. Moisture content was likely the limiting factor for microbial growth. The temperature in the substrate did not change much from then on, for as long it was in the reactor. Only after the compost was taken out of the reactor at day 24 did the temperature in the pile of compost start to go up again.

On day 48 the temperature was 42 - 43°C in the outer layer and near ground level. Here white fungus growth was visible. The whitish layer was considerably thicker than on day 31, about 20 cm. In the core of the pile temperatures were as high as 58°C and no fungus growth was visible. Fungus growth was probably limited there by the high temperature.

On day 56 the temperature in the outer layer (5 cm depth) was in the range 42 - 43°C, in the core (30 - 40 cm depth) it was 56 - 59°C and at ground level it was 50°C. The white fungus growth was visible throughout the heap, but the core was somewhat darker (i.e. less fungus growth) than the outer layer and at ground level. The compost had a
mouldy smell  On day 63 the temperatures were; in the outer layer, 34°C; 44 - 50°C in the core; 46°C at ground level  The white fungus was not as obvious as the week before

On day 71 the temperature was 38 - 39°C at 5 cm depth, 40 - 42°C at 15 cm depth, 45 - 46°C at 25 cm depth, 46 - 47°C at 35 cm depth, while at 45 cm depth it was 43 - 44°C and at the bottom it was 38°C.  On day 80 the highest temperature was 40°C in the core of the pile.

*Moisture content*

The moisture content of the composting material was brought up to 58.6% by adding water during the filling of the reactor.  This assisted in shredding the waste by reducing the tearing resistance of paper products.  However, the water content dropped again down to 44.2% after 18 days during composting.  The moisture content dropped consistently of composting (Figure 7.3-B).  Water was added again at day 19 to bring the moisture content within the 50 - 60% range and make conditions for the microorganisms closer to optimum.

After the compost was taken out of the reactor and stockpiled in a heap covered with sheet plastic, the moisture content dropped below 25% though the compost maintained elevated temperatures.  During storage in a stockpile the moisture content dropped, probably due to evaporative losses of moisture as a result of relatively high temperatures in the stockpile and prevailing dry and windy weather.

The moisture content in the outer layer was 32.8% after 48 days.  After 56 days the moisture content in the top layer was 28.4% and in the core of the heap the moisture content was 22.4%.  The higher moisture content in the top layer was probably caused by water vapour condensing on the black plastic at night, since the inside of the plastic was wet.  After 63 days the moisture content in the top layer was 22.0% and in the core it was 19.8%.  At day 71 the moisture content had fallen to 21.7%.  At the final measurement at day 80 the moisture content was 32.8%.  The increase was due to wet weather.

*Carbon to nitrogen ratio*

In the initial raw organic matter the C/N ratio was rather high for optimum composting.  Nitrogen was the limiting factor.  However, the C/N ratio gradually
reduced to a more favourable value during composting as organic carbon was oxidised and lost as carbon dioxide (Table 7.5). After day 4 the C/N ratio decreased slowly.

Figure 7.3 Temperature (A), moisture content (B), organic matter content (C), pH (D) and soluble organic matter (E) during composting (run 2).
The decrease in C/N ratio after the compost had been taken out of the reactor indicated that there still was a lot of microbial activity. This was also indicated by the high temperatures. The final C/N ratio in the mature compost after 73 days was of adequate value for use of compost as a soil conditioner, without causing nitrogen drawdown.

Table 7.5 The carbon to nitrogen ratio in plain municipal waste during composting.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>34</td>
</tr>
<tr>
<td>12</td>
<td>31</td>
</tr>
<tr>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>73</td>
<td>22</td>
</tr>
</tbody>
</table>

*Organic matter content*

The organic matter content of the material decreased from 88% to 68% as the organic matter was oxidised to carbon dioxide and water (Figure 7.3-C). Carbon dioxide and water are lost to the process through evaporation and ventilation.

The non-organic fraction is not decomposed microbially and remains. The organic matter content reduced quickest in the early stages of the process during the thermophilic phase when the bacterial activity and thus decomposition rate was highest. The organic matter content of the compost would be expected to reduce further, but slower, after taking the compost out of the reactor for further maturation.

*pH*

The pH value of the compost water extracts did not change much during the process. The pH was slightly alkaline all through the process which is an optimum level for the microbes active in the composting process (Figure 7.3-D).

After the compost had been taken out of the reactor and stockpiled for further maturing, there was virtually no change in the pH. Although fungi prefer a slightly acidic
environment the compost was visibly invaded by a white fungal growth. The pH of a compost water extract was 8.1 after 52 days and 8.0 after 79 days.

*Soluble organic matter*

The soluble organic matter, measured as COD, of the water extract decreased throughout the period that the compost was in the reactor. In the first 9 days it decreased more rapidly than later on in the process (Figure 7.3-E).

After the compost had been taken out of the reactor the COD increased again, from 920 mg/l at 48 days to 1380 at 56 days, 1520 at 67 days before stabilising at 1510 mg/l at 73 and 80 days respectively. A value of 1500 mg/l is used as a standard for maturity (DHV, 1990). The circa 5 times higher COD in this compost compared with the red mud compost of run I (Figure 7.2 - E) is mainly due to adsorption of soluble organic matter by red mud.

7.3.4.2.2 Heavy metal content and mobility

The total metal content was very low in the compost and this is reflected in relatively low concentrations of mobile metals in this compost (Table 7.6). The total level of contamination in the compost for each metal was lower than the levels quoted in Table 1.2 and complies with the maximum permissible concentrations of heavy metals for land application quoted in Table 1.1.

The only metal that raises some concern in this compost batch appears to be lead particularly its plant availability, though the lead level has not been found to be causing toxicity according to the literature. Permissible concentrations are usually based on total concentrations rather than the metal mobility in the soil matrix.

The results obtained from metal analysis of this plain compost can be compared with the corresponding results for the red mud - compost of run 1 (Table 7.3). It can be seen that the mobility of metals in the plain compost relative to its total metal content is higher than that in the red mud - compost. A comparison between the metal mobility in plain and red mud amended compost will be made in section 7.4.
Table 7.6 Heavy metal content in mature (100 days) plain municipal compost and the plant available and leachable fractions (run 2); in mg/kg dry matter.

<table>
<thead>
<tr>
<th>metal</th>
<th>leachable</th>
<th>plant available</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0</td>
<td>0.77</td>
<td>1.4</td>
</tr>
<tr>
<td>Copper</td>
<td>1.5</td>
<td>6.9</td>
<td>58</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.5</td>
<td>0.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.3</td>
<td>1.2</td>
<td>12.2</td>
</tr>
<tr>
<td>Lead</td>
<td>0.12</td>
<td>20.4</td>
<td>105</td>
</tr>
<tr>
<td>Zinc</td>
<td>3.5</td>
<td>113</td>
<td>255</td>
</tr>
</tbody>
</table>

7.3.4.2.3 Particle size distribution

After the maturation stage was complete, the compost was separated into 3 fractions using sieves. A high percentage, 70%, of the compost ended up in the fine fraction. The results of the particle size classification are given in Table 7.7.

The coarse fraction consisted mainly of inorganic contaminants such as plastics as well as pieces of wood and paper balls, usually from thick magazines or telephone books. This fraction has a relatively higher density and this contributes to the compost consisting of 20.8% of this fraction by weight.

Table 7.7 The particle size distribution in plain municipal compost (run 2).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Size (mm)</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>fine</td>
<td>&lt; 6.35</td>
<td>69.9</td>
</tr>
<tr>
<td>medium</td>
<td>6.35 - 12.7</td>
<td>9.3</td>
</tr>
<tr>
<td>coarse</td>
<td>&gt; 12.7</td>
<td>20.8</td>
</tr>
</tbody>
</table>
7.3.4.3 Red mud amended municipal waste composting II (run 3)

7.3.4.3.1 Process parameters

Temperature

The development of the temperature in the red mud amended waste during composting is shown in Figure 7.4-A. The temperature of the waste in the reactor remained low until day 8, then rose quickly, reaching 64°C on day 11. The moisture content became limiting after that, probably caused by the addition of dry red mud and as a result the temperature dropped to 32°C. The drop in temperature could have had causes other than red mud addition. However this hypothesis was abandoned when it was observed that the temperature rose again after the moisture content was adjusted, by addition of water, to be within the 50 - 60 % range.

Because of technical problems, described in section 7.3.2.3, the process was at least partially anaerobic during some periods between day 28 and 52. This had an effect on the temperature, as it dropped down to 39°C. This indicated a decreased level of aerobic microbial activity. However, after the aeration problems were corrected, the temperature rose again to 52.9°C. The temperature remained at thermophilic levels for about 20 days before decreasing slowly towards the end of the run.

Moisture content

Since the waste came from an area which had a high concentration of offices, the waste was marked by a high paper content and a low moisture content of about 20%. The moisture content in the waste during composting is shown in Figure 7.4-B.

During the filling of the reactor 800 litres of water were added to increase the moisture content to 54.8%. This also assisted in breaking up and reducing the volume of the waste. The moisture content slowly decreased from then on until it fell to just below 50%. The large drop in moisture content, from 48.8 to 41.9, between day 13 and 16 was mainly caused by the red mud addition to the waste on day 14. Water was added at days 19 and 22 to bring the moisture content up to about 55%. After the red mud and
moisture was added, the moisture content remained more stable though it decreased slowly. The higher moisture content stability could possibly be attributed to the hygroscopic nature of red mud.

Figure 7.4 Temperature (A), moisture content (B), organic matter content (C), pH (D) and soluble organic matter (E) during composting (run 3).
The increase in moisture content from 49.2% on day 51 to 51.2% on day 53 was caused by very heavy rainfall. On day 59 water was added again to increase the moisture content from 49.5% to 54%. It then slowly dropped again to 53% until it was windrowed.

Carbon to nitrogen ratio

The carbon to nitrogen ratio in the initial material was 88, caused by the large paper fraction. This is well above the optimal C/N ratio of 20 - 30 for composting.

In order to adjust the C/N ratio to a more favourable level, 4.5 kg of nitrogen in the form of urea was added on day 5. As an undesired side effect of the urea addition, the pH increased from 8.4 to 9.5 because of release of hydroxyl during the bacterial decomposition of urea. The nitrogen addition was expected to lower the C/N ratio to 42. However, the C/N ratio was still 80 on day 13. Some nitrogen would have been lost through evaporation of ammonia due to the prevailing high pH of 9.5. Theoretically however, the C/N ratio of 80 means approximately 4.3 kg of nitrogen was lost. This seems rather high though a strong ammonia smell was observed during the 8 days between urea addition and the C/N analysis. Nitrification is likely to have played a minor role (section 7.3.4.1.1). The growth of micro-organisms decomposing the material was thus limited by the nitrogen content of the substrate, so it took a longer time before this run was completed.

A reduction in C/N ratio occurred however during the process as a result of loss of carbon as carbon dioxide. The results of the C/N ratio analysis during the process are shown in Table 7.8.

Table 7.8 The C/N ratio during red mud amended municipal waste composting (run 3).

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>88</td>
</tr>
<tr>
<td>13</td>
<td>80</td>
</tr>
<tr>
<td>20</td>
<td>71</td>
</tr>
<tr>
<td>33</td>
<td>55</td>
</tr>
<tr>
<td>58</td>
<td>57</td>
</tr>
</tbody>
</table>
Organic matter content

The initial large drop in organic matter content coincided with a period of intense microbiological activity during which the temperature was very high (Figure 7.4-A). The organic matter content slowly dropped further during the composting process as the organic fraction was decomposed in compost, forming carbon dioxide and water (Figure 7.4-C). There was quite a large variation in the results, which can probably be explained by sampling errors and varying degrees of inorganic contamination.

As 250 kg red mud was added on day 14 a decrease in organic matter content of around 10% was expected between the measurements on day 13 and day 20. This was not however shown by the data and reflects inaccuracy in the sampling and measurements.

Due to the method used to determine the organic matter content, samples could have included some inorganic contaminants, such as plastics, causing a slightly overestimated organic matter content.

pH

The pH of the water extract in the original raw material was 8.4. After addition of urea, the pH went up to 9.4 (Figure 7.4-D). The pH decreased very slowly after that. The high pH level caused loss of nitrogen through ammonia evaporation. This had an acidifying effect on the pH. Also the formation of carbon dioxide had an acidifying effect through the reaction of carbon dioxide with free hydroxides to form buffering bicarbonates. Decomposition of organic matter progressively produces soluble organic acids which during maturation will further neutralise the pH.

The final pH level after maturing in a stockpile was 8.2, which is still rather high for use as a soil conditioner though suitable for application on acidic sandy soils.

Chemical oxygen demand

The chemical oxygen demand of the water extract rose to 970 mg/l during the first eight days. The COD remained around that value until day 14, when red mud was added to
the substrate (Figure 7.4-E). The COD then dropped and fluctuated between 200 and 600 mg/l. This is considerably lower than observed in the plain compost (Figure 7.3-E). It shows again the effect of red mud on reducing the soluble organic matter level. The increase in COD during maturation, that was observed in the plain compost did not occur with the red mud-compost due to likely adsorption of the soluble organic matter.

7.3.4.3.2 Heavy metal content and mobility

The total content of heavy metals in this compost was very low (Table 7.9). This can be explained by the origin of the raw material, which consisted mainly of waste paper from offices (Table 7.1). The relatively high total chromium concentration is probably a result of the natural chromium content of red mud. The leachable and plant available levels of the metals were also very low. This was the result of a combination of the low total levels and the addition of red mud.

Table 7.9 Heavy metal content in mature (100 days) municipal red mud-compost and the plant available and leachable fractions (run 3); in mg/kg dry matter.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Leachable</th>
<th>Plant available</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.7</td>
<td>5.4</td>
<td>40</td>
</tr>
<tr>
<td>Cr</td>
<td>0.4</td>
<td>0.45</td>
<td>16.8</td>
</tr>
<tr>
<td>Ni</td>
<td>0.12</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.12</td>
<td>2.2</td>
<td>21</td>
</tr>
<tr>
<td>Zn</td>
<td>1.82</td>
<td>19.5</td>
<td>61.8</td>
</tr>
</tbody>
</table>

7.3.4.3.3 Particle size distribution

The results of the determination of the fraction size distribution are given in Table 7.10. The table shows a very high fraction of fine compost and relatively low percentages of the coarse and medium size fractions. This indicates a low level of contamination by plastics and other large inorganic particles, but also a low level of the 'balling' effect.
Table 7.10 Compost particle size distribution (run 3).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Size (mm)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>fine</td>
<td>&lt; 6.35</td>
<td>80.3</td>
</tr>
<tr>
<td>medium</td>
<td>6.35 - 12.7</td>
<td>6.6</td>
</tr>
<tr>
<td>coarse</td>
<td>&gt; 12.7</td>
<td>13.1</td>
</tr>
</tbody>
</table>

7.3.5 Mass balances

The data collected on dry mass and moisture content of the waste before and after composting allowed a mass balance for each run to be developed. The mass balance gives some insight into the loss of dry matter during composting and the release of moisture and carbon dioxide. The accuracy of the balance is subject to errors in weighing the wet waste on the weigh bridge (± 10 kg) and sampling errors as a result of the less than homogeneous nature of the material. The mass balance for each run is given in Table 7.11.

Table 7.11 A comparison of the mass balances for each run (kg).

<table>
<thead>
<tr>
<th>Fraction (kg)</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>input</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry matter</td>
<td>1375</td>
<td>1310</td>
<td>980</td>
</tr>
<tr>
<td>total moisture</td>
<td>2380 (345)*</td>
<td>2050 (1040)*</td>
<td>2000 (350)*</td>
</tr>
<tr>
<td>red mud</td>
<td>425</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td><strong>output</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry matter</td>
<td>575</td>
<td>940</td>
<td>605</td>
</tr>
<tr>
<td>moisture</td>
<td>1210</td>
<td>830</td>
<td>960</td>
</tr>
<tr>
<td>red mud</td>
<td>425</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td><strong>lost</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry matter</td>
<td>800 (58%)</td>
<td>370 (28%)</td>
<td>375 (38%)</td>
</tr>
<tr>
<td>moisture</td>
<td>1170 (51%)</td>
<td>1220 (60%)</td>
<td>1040 (48%)</td>
</tr>
</tbody>
</table>

*Amount of moisture in the waste is given in brackets; the rest was added as water.

A remarkable result is the lower dry matter reduction in the substrate of run 2 which contained a high percentage of garden and food waste and no red mud, as opposed to the substrate of runs 1 and 3 which had a high paper content and had red mud added.
The high reduction in dry matter content during the first run tie up with the observed change in the organic matter content. The organic matter content hardly reduced during composting (Figure 7.2-C) while, according to Table 7.11, 800 kg of dry matter was lost. The loss in dry matter is likely to be the result of a weighing error in the total in- and output weight. Loss of dry matter in run 1 was expected to be lower than the loss during runs 2 and 3 due to the high paper content in that particular run, which generally takes longer to decompose than food and garden waste.

7.4 Discussion

7.4.1 Waste composition

The manual sorting of the waste prior to the organic fraction being composted in the pilot plant contributed valuable data on municipal waste composition.

The compostable fraction ranged from 45 - 70% (Table 7.1). The higher value is linked to a high paper content. Most of the paper in the waste appeared to be of commercial origin. The high percentage of compostable material definitely makes composting of this fraction an attractive alternative to landfilling.

Paper content is also linked to the moisture content. A high content of paper resulted in a low moisture content of the overall waste. Both the waste from West Perth and that from Perth City contained a high percentage of paper resulting in a low moisture content of respectively 12.8 and 20%.

In all three experimental runs, the moisture content of the waste was too low for optimum composting to take place, so water had to be added to bring the moisture content into the favourable range of 50 - 60%.

The high paper content in the waste from commercially zoned areas is remarkable since a paper recycling program had been in operation throughout Perth City Council for more than a year. This suggests that residential areas have a higher participation rate in the paper recycling scheme.
The glass fraction ranged from 4.5 to 9.5%. The 45% glass in the waste from Wembley consisted mainly of large soft drink and beer bottles and glass food containers. The 9.5% glass in the waste from Perth however, consisted mainly of small soft drink bottles.

The percentage of metals was in a similar range to that for the glass, 4.3 - 8.8%. Dry cell batteries, car parts and hardware, e.g. nuts, bolts, etc., contributed mostly to this fraction.

The plastic fraction was higher than the glass and metal fractions, despite plastic being much lighter in weight. This indicates the large volume of plastics in the waste. The fraction ranged from 8 to 20.5%, mainly consisting of packaging material and synthetic or rubber products, e.g. sport shoes, toys, clothing, etc.

Since the waste was only three fractions were removed from the waste and the residue composted, some inorganic contaminants, not included in the three fractions removed, remained in the substrate. Some contamination of the three fractions removed, remained due to imperfect sorting. Of this contamination pieces of glass are the main threat to the commercial value of the compost, due to visual pollution and safety aspects. The metals that remained in the residue would contribute to the level of metal pollution in the compost which may restrict compost application to soils.

The measured waste compositions compare well with that determined in a local waste survey conducted in 1991 (Mindarie Regional Council), (Table 7.1). The organic fraction in that survey was lower than found in this survey and the levels of the three fractions separated in this survey were higher. The three fractions are present in the same reducing order of presence, by weight fraction, in each waste: plastic > glass > metal.

The percentages of the three sorted recyclables seem high enough to warrant a resource recovery program, for example through source separated collection or processing mixed municipal waste in a resource recovery plant.

7.4.2 Compost process and the effect of red mud addition

The organic waste lends itself well as a substrate for the composting process. There were, however, a number of adjustments to be made. Firstly the moisture content was
too low in each case. This problem was easily solved by addition of water. Secondly, the waste contained inadequate amounts of nitrogen which resulted in a carbon to nitrogen ratio of well above the optimum range of 20 - 30.

The lack of nitrogen during runs 1 and 3 was compensated for by addition of organic nitrogen in the form of urea. The addition of urea did not produce the expected effect since the decomposition of urea resulted in the release of hydroxyl ions. This caused an increase in pH of up to about 9. This was followed by the loss of nitrogen through ammonia evaporation, thereby greatly reducing the availability of the added nitrogen to the process. It is suggested to use in future operation an acidic nitrogen salt, such as ammonium sulfate, since the compost process is slightly alkaline and well buffered.

The problem of a high C/N ratio was associated with the high paper content. During the composting process, under slightly alkaline conditions, a decrease in C/N ratio occurs as a result of the loss of carbon through the release of carbon dioxide. This was observed clearly in run 2. The fluctuation in C/N ratio in runs 1 and 3 is the result of a combination of release of carbon dioxide and the addition of nitrogen, followed by loss of ammonia through evaporation and nitrification.

The pattern that the temperature follows during composting is a good indication of the quality of the process. There were some problems in this area.

During run 1, the temperature development was inadequate to achieve thermophilic levels. The two reasons for this are firstly the high C/N ratio. Secondly, as a result of adding red mud immediately after filling the plant, the mixture of organic waste and red mud granulated into small particles, consisting of organic matter coated with red mud particles. Despite efforts to aerate the substrate, the core of the granules became anaerobic. This inhibited the composting process and thus the release of heat.

However, when this compost was stockpiled, the temperature rose to thermophilic levels which were maintained for over two months. Possibly a reduction in moisture content due to drying, thus improving access of air into the granules, created better composting conditions. The chemical properties of red mud thus did not appear to interfere with the composting process, during this run.
The organic matter content was reduced by only a few per cent in run 1 and was reduced by approximately 30% in runs 2 and 3. This also suggests that red mud did not directly cause the low reduction in organic matter content during run 1.

The parameter on which red mud addition had a significant effect was the soluble organic matter fraction in a water extract. The chemical oxygen demand of water extracts from red mud amended compost was approximately 90% lower than that in extracts from the plain compost. The effect of red mud on soluble organic matter was established previously in the laboratory experiment (See Chapter 4).

Red mud particles appear to adsorb humic and fulvic acids as was found in previous laboratory experiments (Chapter 4 and 6). These organic acids can function as carriers of heavy metals in soils during leaching. From this it follows that red mud reduces the leaching of organic acids, which should be valuable to the soil, and of heavy metals to the groundwater aquifer.

7.4.3 Effect of red mud addition on heavy metal mobility

The addition of red mud to organic waste prior to composting has a dilution effect on the total heavy metal concentration, the extent of which is dependent on the amount of dry matter in the waste and the amount of red mud added.

One of the objectives of this pilot plant study was to verify whether red mud reduces the mobility of heavy metals in the compost. Since the three compost batches cannot be compared on the basis of total metal content, due to the variation in composition of the raw material, any change in the mobility of the metals in each compost has to be related to that compost's total metal content. However, in order to assess the environmental effects in relation to groundwater leaching and plant toxicity the actual leachable and plant available concentrations have to be considered.

In Table 7.12 the mobile fraction of heavy metals is expressed as a percentage of the total content for each compost. The total content of metals for runs 1 and 2 is similar, which allows for a more meaningful comparison of their metal mobility. A very low total
metal content such as in run 3 has the effect of relatively increasing the metal mobility when expressed as a percentage of the total content.

Table 7.12 shows that the mobility of metals relative to the total content is significantly lower in the red mud amended compost from run 1 than in the plain municipal compost, except for the leachable lead. The compost of run 3 shows a strong reduction in plant availability of chromium, lead and zinc compared to that of run 2; copper seems unaffected while the plant availability of nickel increased. The lower total metal concentration in run 3 compost must be taken into consideration in this comparison. The higher relative mobility values for some metals cannot be translated into increased metal exposure to plants since the absolute levels are extremely low. The metal concentrations in each compost were well within recent standards for municipal waste compost.

Table 7.12 The leachable (L) and plant available (PA) heavy metals as a percentage of the total metal concentration in the compost.

<table>
<thead>
<tr>
<th>Metal</th>
<th>red mud - compost I</th>
<th>plain compost</th>
<th>red mud - compost II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>PA</td>
<td>L</td>
</tr>
<tr>
<td>cadmium</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>chromium</td>
<td>0.6</td>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>copper</td>
<td>0.4</td>
<td>1</td>
<td>2.2</td>
</tr>
<tr>
<td>nickel</td>
<td>1.2</td>
<td>12.3</td>
<td>5.0</td>
</tr>
<tr>
<td>lead</td>
<td>0.3</td>
<td>5.2</td>
<td>0.2</td>
</tr>
<tr>
<td>zinc</td>
<td>0.8</td>
<td>22</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The results of the effect of red mud on the municipal waste compost can be compared to the results obtained from the laboratory composting experiments described in Chapter 6 (Table 6.7). When comparing the tables it has to be considered that the results in Table 6.7 are indexed to the total metal concentration in the blank, while the results of Table 7.12 are relative to the total concentration in each sample. In addition the metal levels in the municipal waste are much lower than the metals levels that the laboratory compost was spiked with, which favours the municipal compost in a comparison.
blank can be compared to the plain compost, and shows that for all metals except lead the relative mobility is lower in the municipal waste compost. This could be expected since the metals in the laboratory were in a much more mobile state, as salts, at the start of the experiment as opposed to the metals in the refuse which is bound in many different materials (Chapter 1) The figures of the red mud amended samples can be compared on a fairly even basis, as the incomplete total metal recovery in the laboratory experiment was likely to be consistent in the municipal red mud - compost samples. These results also show that generally the relative mobility was lower in the municipal compost samples. It is clear though that red mud addition resulted in a reduced relative metal mobility for most metals.

7.4.4 Compost quality

The quality of the compost was assessed on the basis of appearance, smell, particle size distribution, C/N ratio and heavy metal content. The compost had to be screened after discharge from the reactor and maturation to remove inorganic contaminants such as glass and plastics which had escaped the sorting process. The contamination is clearly shown in Plates 7.3 and 7.4 depicting compost of runs 1 and 2 respectively.

The plain compost was black in colour and had a typical fresh sweet soil smell, virtually a typical compost. The red mud amended compost initially had a red-brown (ferrous oxide) colour which after maturation turned to dark brown. The red mud compost from run 1 had granulated, which improves the materials handling property of the compost, since it improves rate of sieving and materials flow.

The finer, mulch type compost of the third run was slightly lighter in colour than the run 1 red mud-compost. Both the red mud-composts had very little smell. This was probably the result of red mud adsorption of the odorous compounds or suppression of formation due to the slightly higher process pH.

The particle size distribution showed a high fraction of fine compost in each run. The percentages were respectively 73%, 69% and 80% for runs 1 to 3. The fine compost fraction has the highest commercial value.
Plate 7.3 The red mud compost of run 1 after discharge from the reactor and prior to maturation.

Plate 7.4 The plain municipal compost of run 2 after discharge from the reactor and prior to maturation.
The C/N ratio is a good measure of the nutrient balance in the compost. An optimum ratio for a mature compost is 10 - 20. The plain compost can be considered to have an optimum C/N ratio for use as a soil conditioner. The red mud amended composts both had nitrogen added to reduce the C/N ratio. This was necessary due to the high C/N ratio in the raw organic material. The C/N ratio did not decrease to reach an optimum level during composting. Some nitrogen was lost as ammonia due to an elevated pH level.

The total heavy metal contents of the composts produced were within the heavy metal guidelines for composts, stated in Table 1.1. The addition of red mud appears to reduce the availability of the metals for leaching and plant uptake relative to the total content. The heavy metal content of all three composts are low enough to allow for unlimited application to soils. However, further research into the effect of red mud on the composting process as well as the heavy metal mobility is required. Also, the effect of red mud on waste with much higher metal levels compared to those in this relatively clean compost requires further investigation.

7.5 Conclusions

The pilot plant functioned well enough to enable the production of three batches of municipal compost. Further maturation of the compost after the pilot plant stage was essential for producing good compost. The addition of red mud did not directly interfere with the microbial activity that is the basis of composting. Red mud can interfere indirectly with the composting process by changing the texture of the compost such aeration of the organic fractions is interfered with. This could be overcome by using a static pile composting system, where aeration is supplied by means other than tumbling the substrate, reducing the 'balling' effect and thus granulation.

The addition of red mud significantly reduced the concentration of heavy metals which municipal compost can contain due to dilution, and the levels of metals available for leaching into groundwater or for plant uptake.

The mixed municipal waste that was received at the pilot plant had a high compostable fraction. This fraction proved suitable as a composting substrate when the moisture content was increased to the optimum level. In some cases, it may be necessary to adjust the C/N ratio by addition of a nitrogen source.
Chapter 8

General discussion, conclusions and recommendations.

8.1 General discussion

Red mud was shown to be a suitable amendment to municipal compost since it was shown to have a very high adsorption capacity for heavy metals in solution. Metal concentrations in solution at toxic levels were reduced to levels that would pose no threat to environmental health. A number of metals could not be recovered from solution. The adsorption complexes were very stable as indicated by the fact that only 40 - 70% of spiked metals, except chromium, could be recovered even with an acid digest (Table 6.5).

The adsorption of heavy metals by red mud from a mature municipal compost from Auckland, New Zealand, proved more difficult. It appeared that more than 90% of the total metal content was strongly complexed to the insoluble humus fraction of the compost. The remaining metal content was complexed to the soluble organic matter fraction and/or in free ionic form. Red mud amendment with this compost showed that red mud could reduce the soluble metal content for some metals i.e. copper and zinc, but for others it increased the soluble metal content, due to increased solubilisation of organic matter caused by the high alkalinity and sodicity in red mud. Even though red mud was shown to be capable of forming complexes with soluble organic matter during equilibration experiments, this organic matter removal process from solution did not match the increased solubilisation of otherwise insoluble organic matter.

From the experiments described in chapters 3 and 4, it is clear that heavy metals remain largely in the organic matter fraction in municipal compost. Red mud did not fix the majority of heavy metals and possibly does not bind the metals that are released as a result of solubilisation, since even these metals are complexed to soluble organic matter.

The laboratory composting system that was designed and built to test the hypothesis that red mud would be more effective in reducing metal mobility when added to organic matter prior to composting performed very closely to its design objectives. The system -239-
was able to simulate, control and monitor the composting process for the required parameters, independently in the separate incubators. The facility was able to produce a good fresh compost in accordance to composting process requirements. The computer recorded for each incubator the temperature, carbon dioxide and oxygen levels in effluent air on a real time basis and the airflow rate and timing of boosted air. Improvements on the initial design were the installation of an air humidifier to avoid excessive drying of the substrate and the installation of condensers to cool and dry the effluent air. This allowed measurement of the moisture loss from the incubators. An accurate mass balance could be produced from the collected data.

The main limitations of the system were that the installation of the humidifier reduced the cooling capacity of the incoming air considerably, resulting in the temperature in several incubators exceeding the control temperature of 55°C, though for relatively short periods of time; Due to the sampling of the incubators by rotation, a varying air flow rate and the air retention time in the incubators, the gas concentrations (O₂, CO₂) were not always matched with the correct flow rate at the time of measurement during the thermophilic phase; This was a cause for error in the amount of carbon lost as carbon dioxide. However, as discussed before, the large number of data collected statistically reduced the effect of this inaccuracy. Finally, some minor heat loss may occur through the incubator walls and lid as a result of imperfect insulation, though this would have had a very minor effect on the temperature and its control.

The composting facility proved itself suitable for use in an experiment to test the effect of red mud on the mobility of heavy metals in metal spiked organic matter after composting when red mud is added to the organic matter before the composting. The mobility of metals, expressed in leachable, plant available and acid extractable (total) metals, was greatly reduced when red mud was present. Each metal in the study behaved differently though the mobility of all metals was reduced.

The red mud did not affect the composting process itself adversely up to a level of 30% w/w addition. In regard to this it is important that red mud interfered in the parameters used for measuring the decomposition rate and maturity independent from the process.
Some carbon dioxide released during decomposition could have been adsorbed by the alkalinity in red mud to form bicarbonate. This would result in a low carbon dioxide reading, incorrectly suggesting a lower decomposition rate. This could however not conclusively be demonstrated in the calculation of a carbon balance (Table 6.10). Red mud interfered with the correct measurements of the maturity parameter, COD and \( E_4/E_6 \) by forming complexes with the soluble organic matter. This reduced the level of soluble organic matter, after it was formed as a result of composting.

The alkalinity in red mud must be neutralised using a minimum of 4% gypsum to reduce loss of ammonia and solubilisation of organic matter. The calcium in gypsum provides a divalent electrolyte which replaces sodium in the red mud matrix and functions as a flocculant for soluble organic matter thus assisting in reducing solubilisation of organic matter.

In addition to the effect of red mud on metal mobility and decomposition rate, red mud also increased the pH buffer capacity by 30% and reduced the amount of soluble organic matter by 90%. These aspects improve the value of compost as a product for end users.

The findings of this laboratory study could not be entirely repeated in the research carried out at the compost pilot plant using the organic fraction of mixed collected municipal waste. One of the difficulties is that each trial was based on a different municipal waste, thus the trials and different treatments could not be compared on an equal basis. This applies particularly to the heavy metal content and metal mobility as a function of red mud addition, thus the metal mobility was determined as the relative fractions of leachable and plant available metals of the total metal content of each compost. The relative mobility of the metals was reduced by the red mud addition for all metals (Table 7.12), to a similar extent as the reduction in laboratory experiment where the substrate was spiked with a metal salt solution. In the latter, the metals were in a more reactive soluble form when added. The majority of heavy metals present in the organic fraction of a domestic waste are present in a less reactive form such as metal oxides (paint, dye), carbonates, hydroxides (dry cell batteries), complexed in the form of medicines, cosmetics, pesticides, in lubricants or anti-corrosion coatings (ref). Several of these metal species may not be leachable or plant available, but will be recovered with an acid digestion. Metals in this category are not available for adsorption to red mud.
until the complexes decompose. This aspect interferes with obtaining a clear picture of the effect of red mud in this experiment. However, the long term release of metals from either the organic matter fractions (compost) on the previously mentioned metal forms could pose an environmental health concern for receiving soils, crops and groundwater. The results of the experiments presented in this thesis show that most of the metals released in the long term are likely to be adsorbed to red mud if present in the compost. The release of metals from organic matter is generally a function of the rate at which the compost is mineralised. This happens in a relatively short period of time, i.e. several years.

The release of heavy metal from red mud is mainly governed by the equilibrium concentration between solid and solute. Both release mechanisms are pH dependent. The experiments have shown that the stabilities of metal - red mud complexes are such that metal release will be extremely low and red mud itself is not subject to solubilisation or biological degradation. A significant amount of adsorbed metals will not be released at all, unless the complete red mud matrix is dissolved. Thus, it is desirable from an environmental health viewpoint that red mud is present to adsorb available metals prior to composting and to adsorb metals that are released from other chemical forms at a later stage. The ability of red mud to adsorb soluble organic acids reduces the mobility of the metals that are complexed to these organic acids.

The mobility of metals reaches a minimum when 20% w/w red mud is mixed with organic waste. Red mud itself contains significant levels of heavy metals although they are not mobile in the natural soil environment. Due to its high adsorption capacity for metals and phosphate, excessive application of red mud may reduce the plant availability of trace elements and nutrients to below plant requirements. It is thus recommended to amend organic waste with the minimum amount of red mud required to achieve minimum metal mobility. This amendment is 20 - 25% w/w red mud addition to fresh organic waste.

The samples produced in the pilot plant (Chapter 7) are being trialled, in conjunction with the Western Australian Department of Agriculture, in a pot plant experiment, growing carrots from seed. Results available to date show a 100% germination rate, a
greater than 50% reduction in nutrient leaching and improved plant growth compared to unamended soil.

The suitability of the technique for application to anaerobic and aerobic sewage sludges will be investigated. An important difference between this waste and municipal waste is that metals are already adsorbed by the organic matter (bacterial floc).

8.2 Conclusions

In order to reduce effectively the concentrations and the mobility of heavy metals that may contaminate municipal waste compost, red mud - gypsum must be mixed with the waste prior to the waste being composted.

Since the optimum addition of 20% red mud was found under fairly ideal laboratory conditions, and the lower metal availability in actual waste, an addition of 25% red mud may be more appropriate for a large scale municipal waste operation, inorder to allow for the less than ideal conditions. These levels of red mud were found not to interfere with the microbial activity during composting. There were, in fact, indications that at these levels, microbial activity was stimulated.

In situations where heavy metal contamination is not an issue, for example when separately collected biowaste or green waste is used as a substrate, red mud addition can be reduced to 10%, to reduce cost and still have the soil conditioning benefits of the red mud addition, mentioned before.

The resulting red mud compost (RMC) has the following improvements over conventional compost: lower metal content and mobility; much higher pH buffer capacity; increased nutrient and water retention capacity and a greater stability of the organic fractions.

This process can be easily incorporated in any of the conventional industrial composting systems currently available since only minor process engineering modifications need to be applied.
8.3 Recommendations for further research

Since the research investigated a management tool for an environmental pollution control concept that differs from the conventional approach and in fact requires a considerable change in the philosophy behind it, more towards ecological integration to provide long term sustainability, more detailed research is required. The recommended research is restricted to the proposed environmental pollution management tool since the philosophical aspects are best developed in other disciplines.

More detailed information is required about the metal binding mechanisms in red mud and decomposing organic matter.

Further research into the metal speciation and the distribution of metals in municipal compost and in red mud - compost is needed.

The long term release rate of heavy metals from red mud - compost and the potential for metal accumulation in soils is important for long term application and environmental health.

Effect of pH on the stability of metal complexes in red mud - compost requires to be assessed to prevent metal fluxes due to pH reduction i. e. as a result of superphosphate application or acid rain.

The leaching nutrient and plant availability of nutrients in red mud-compost amended soils as well as in relation to applied fertiliser needs investigation. Red mud - compost is likely to reduce nutrient leaching from the top soil, however sufficient plant availability should be maintained.

Rate of degradation of organic matter in red mud - compost as compared to plain compost is reduced according to the research. Verification and subsequent quantification of this is needed to assess the benefits of this property.
The effect of red mud on microbial population and activity during composting was not clearly demonstrated, since no microbial analyses were conducted. This needs to be further assessed since it could have a major impact on an industrial scale operation.

Determination of water retention and wettability of red mud compost, which are important properties for soil conditioners, particularly in the arid local environment.

Assessment of the beneficial properties of red mud - compost for soil structure, tillage and as an erosion control agent, since no information is currently available on this and the product is likely to influence these soil quality parameters.

Investigation of the biochemical properties of red mud - compost, which promote seed germination and are beneficial to plant (vegetable) growth, such as the presence of natural antibiotics and trace element availability would be useful.
References


Choudry G. G., 1984b. Current topics in environmental and toxicological chemistry vol. 7: *Humic substances, structural, photophysical, photo-chemical and free radical aspects and interactions with environmental chemicals,* University of Amsterdam, Gordon.


Wageningen, Netherlands.


Golueke, C. G., 1982. When is compost 'safe'?. Biocycle, 23(2); 28.


Kron I, 1986. Gel chromatography of some amino acid complexes with $^{65}$Zn, PhD thesis, Czech Technical University, Prague, Czech Republic.


