THE UNIVERSITY OF ADELAIDE

THE EFFECTS OF WEATHERING AND DIAGENETIC PROCESSES ON THE GEOCHEMICAL STABILITY OF URANIUM MILL TAILINGS

Greg Sinclair

B.App.Sc (Chemistry)

A thesis submitted in fulfilment of the requirements for the Degree of

Doctor of Philosophy

The University of Adelaide

School of Earth and Environmental Sciences

2004

| TABLE OF CONTENTS | |
|---|----------|
| Abstract | viii |
| Declaration | ix |
| Acknowledgements | X |
| 1. Introduction | 1 |
| 1.1. Overview of Mine Tailings and Management Issues | 1 |
| 1.2. Uranium Mining and Milling in Australia | 3 |
| 1.3. Review of Applicable Case Studies | 6 |
| 1.4. Hypothesis and Research Program | 11 |
| 2. The Ranger Mine Environment | 13 |
| 2.1. The Alligator Rivers Region | 13 |
| 2.2. Regional Overview | 17 |
| 2.3. The Ranger Mine Project | 18 |
| 2.4. Tailings Management | 20 |
| 3. Experimental Methodology and Materials | 23 |
| 3.1. Field Sampling Program and Measurements | 23 |
| 3.2. Solid State Speciation Test Work | 26 |
| 3.3. Kinetic Column Leach Studies | 27 |
| 3.3.1. Columns 3.3.2 Leachant Quality | 27 |
| 3.3.3. Sample Collection, Preparation and Analysis | 32 |
| 3.4. Geochemical Modelling | 33 |
| 4. Field Investigations and Summary of Key Observations | 34 |
| 4.1. Field Sampling Campaign | 34 |
| 4.2. Core Profiles | 36 |
| 4.3. Piezometer Installations | 39 |
| 5. Tailings Solids and Porewaters | 42 |
| 5.1. Processes Affecting the Geochemical Evolution and Diagenesis of the Tailings | 42 |
| 5.1.1. Geochemical Processes | 42 15 |
| 5.1.2. Effect of Redox Potential on Uranium and Trace Metal Distribution within | 43 |
| the Tailings Pile | 49 |
| 5.1.4. Autnigenic Phases | 50 |

| 5.2. Tailings Texture, Mineralogy and Geochemistry5.2.1. Tailings Texture5.2.2. Tailings Mineralogy and Morphology | 53 53 57 |
|---|--|
| 5.3. Solid State Speciation5.3.1. Phase Selectivity and Mass Recovery5.3.2. Uranium and Radium Trends in Geochemically Defined Phases | 76 78 84 |
| 5.4. Chemical Manifestations of Dissolved Radionuclides and Metals in the Tailings Pond and Underlying Porewaters 5.4.1. Chemistry of the Tailings Pond Water 5.4.2. Major Ion Chemistry of Tailings Porewaters 5.4.3. Porewater Redox Chemistry 5.4.4. Uranium and Radium Mobility | 88 88 92 102 111 |
| 6. Kinetic Column Leach Studies | 121 |
| 6.1. Overview and Experimental Design | 121 |
| 6.2. Tailings Texture, Mineralogy and Geochemistry Prior to Leaching | 126 |
| 6.3. Tailings Mineralogy and Geochemistry Following Column Leaching6.3.1. Bulk Phase Mineralogy and Geochemistry6.3.2. Textural Distribution of Mineral Assemblages | 130 130 135 |
| 6.4. Column Leachate Chemistry 6.4.1. Oxidative Dissolution of Metal Sulfides and Weathering of Phyllosilicates in the Unsaturated Tailings 6.4.2. Organic Matter Diagenesis | 145 146 161 |
| 7. Data Synthesis and Geochemical Modelling | 173 |
| 7.1. Equilibrium Model and Governing Equations 7.1.1. Distribution of Aqueous Species 7.1.2. Mineral Solubility 7.1.3. Redox Couples 7.1.4. Sorption 7.1.5. Source and Evaluation of Thermodynamic Data | 173 174 174 175 175 176 |
| 7.2. Overview of the Kinetic Model | 177 |
| 7.3. Conceptual Geochemical Model7.3.1. Steady State Dissolution Reactions in Unsaturated Tailings7.3.2. Equilibrium Trends for Saturated Tailings | 179 182 185 |
| 8. Conclusions and Implications | 198 |
| 8.1. Conclusions8.1.1. Formation of Authigenic Minerals8.1.2. Processes Governing Radionuclide and Metal Solubility | 198 199 200 |
| 8.2. Implications and Recommendations for Further Research | 202 |
| Appendix 1: Physical and Analytical Methodology | 204 |
| Appendix 2: Tailings Core Mineralogy, Geochemistry and Porewater Chemistry | 212 |

| Appendix 3: Mineralogy and Geochemistry of Tailings Prior To and After Kinetic | |
|--|-----|
| Column Leaching | 225 |
| Bibliography | 229 |

LIST OF FIGURES

| Figure 1.1: | Acid leach flow diagram for Ranger ores. (Ring et.al., 1982) | 4 |
|---------------|---|----|
| Figure 1.2: | Uranium mill tailings hazards. (Waggitt, 1994; Uranium Institute, 1991 | 6 |
| Fig. 2.1(a): | Relative sizes and location of Kakadu National Park, Jabiluka and Ranger | |
| - | Mine leases | 13 |
| Fig. 2.1(b): | Map of Kakadu National Park and Uranium mining areas | 14 |
| Figure 2.2: | Cultural and natural heritage values of Kakadu National Park | 15 |
| Figure 2.3: | Kakadu Wetland-Magela Floodplain | 15 |
| Figure 2.4: | Mt Brockman - Site of cultural significance | 15 |
| Figure 2.5: | Aerial view of Jabiluka and Ranger Mine sites | 18 |
| Figure 3.1: | Sampling pontoon on the Ranger Dam 1998 | 23 |
| Figure 3.2: | Pontoon and piston core sampler | 23 |
| Figure 3.3: | UPVC sampling tube | 23 |
| Fig. 3.4(a): | Schematic of soft sediment sampling rig | 24 |
| Fig. 3.4(b): | Schematic of piston core sampler | 24 |
| Figure 3.5: | Composite sample taken from split core | 25 |
| Figure 3.6: | General arrangement of leach column | 27 |
| Figure 4.1: | Tailings dam sample profile locations | 34 |
| Figure 4.2: | Cross section A-A' tailings core profiles January, 1998 | 35 |
| Figure 4.3: | Cross section A-A', piezometer profiles June, 1999 | 35 |
| Figure 4.4: | Original ground contours -Pre-tailings dam | 36 |
| Figure 4.5: | Artesian pore pressures at Site 9, $8 - 8.5$ m | 38 |
| Figure 4.6: | Comparison of 1990 and 1999 piezometric levels | 40 |
| Figure 5.1: | Schematic of microbially mediated redox processes | 45 |
| Figure 5.2: | Theoretical redox zonation and dissolved species distribution of submerged | |
| | sediments | 48 |
| Figure 5.3: | Tailings texture and phase descriptions | 53 |
| Figure 5.4: | Tailings size distribution | 57 |
| Figure 5.5: | Gypsum distribution for (a) sites 4 & 6 and (b) site 5 | 59 |
| Figure 5.6: | Iron oxide distribution for (a) sites 4 & 6 and (b) site 5 | 60 |
| Figure 5.7: | Manganese oxide distribution for (a) sites 4 & 6 and (b) site 5 | 61 |
| Figure 5.8: | Magnesium distribution for (a) sites 4 & 6 and (b) site 5 | 62 |
| Figure 5.9: | Uranium phase distribution for (a) sites 4 & 6 and (b) site 5 | 63 |
| Figure 5.10: | Pyrite distribution for (a) sites 4 & 6 and (b) site 5 | 64 |
| Fig. 5.11(a): | Chlorite distribution for (a) sites 4 & 6 and (b) site 5 | 65 |
| Fig. 5.11(b): | Mica distribution for (a) sites 4 & 6 and (b) site 5 | 66 |
| Figure 5.12: | Quartz distribution phases for (a) sites 4 & 6 and (b) site 5 | 67 |
| Figure 5.13: | Al-Silicate distribution for (a) sites 4 & 6 and (b) site 5 | 68 |
| Figure 5.14: | SEM field view of coarse grain tailings site 6 (5.45 m) | 71 |
| Figure 5.15: | SEM field view of silt size tailings Site 4 (11.38 m) | 71 |
| Figure 5.16: | Groundmass of fine grained chlorite in the presence of gypsum laths Site 4 | |
| | (11.38 m) | 72 |
| Figure 5.17: | Micro-crystalline barite in the presence of ferrous sulfate and gypsum Site 4 | |
| | (11.38 m) | 73 |

| Figure 5.18: | SEM field view of primary and authigenic phases, Site 5 (7.11m) | 74 |
|--------------|---|-----|
| Figure 5.19: | Magnified view showing uraninite superimposed on gypsum, Site 5 (7.11m) | 74 |
| Figure 5.20: | Weathered uraninite within a groundmass of amorphous Fe and Mn oxides | 75 |
| Figure 5.21: | Differential XRD scan of fine tailings (Site 5 at 10.3 m) following water, | |
| | exchangeable and acid soluble extractants | 78 |
| Figure 5.22: | Differential XRD scan of fine tailings (Site 5 at 10.3 m) following crystalline | |
| | Fe, alkaline earth and residue extractants | 79 |
| Figure 5.23: | Elemental fractionation Site 5 (7.11 m) – gel fraction | 81 |
| Figure 5.24: | Elemental fractionation Site 5 (10.34 m) – fine grain tailings | 81 |
| Figure 5.25: | Elemental fractionation Site 6 (5.45 m) – coarse grain tailings | 82 |
| Figure 5.26: | Uranium partitioning among geochemical phases | 84 |
| Figure 5.27: | SEM image of coarse grain tailings showing refractory brannerite in | |
| | Association with Mg – chlorite | 85 |
| Figure 5.28: | Radium partitioning among geochemical phases | 86 |
| Figure 5.29: | Tailings pond water pH trends | 89 |
| Figure 5.30: | Tailings pond water electrical conductivity trends | 89 |
| Figure 5.31: | Dominant dissolved ions in tailings pond water | 90 |
| Figure 5.32: | Tailings pond water calcium trends | 90 |
| Figure 5.33: | Tailings pond water trace metal trends | 91 |
| Figure 5.34: | Porewater pH profiles (all stations) | 93 |
| Figure 5.35: | Porewater electrical conductivity profiles (all stations) | 94 |
| Figure 5.36: | Porewater magnesium profiles (all stations) | 95 |
| Figure 5.37: | Porewater sulfate profiles (all stations) | 96 |
| Figure 5.38: | Porewater calcium profiles (all stations) | 97 |
| Figure 5.39: | Porewater manganese profiles (all stations) | 98 |
| Figure 5.40: | SEM field view of a MnO_x phase sampled at Site 5 (11.1m) or RL 32 | 99 |
| Figure 5.41: | Porewater ammonium profiles (all stations) | 100 |
| Figure 5.42: | Porewater chloride profiles (all stations | 101 |
| Figure 5.43: | Depth distributions of pH, dissolved Fe, Mn, SO_4^{2-} , NO ₃ and Eh in tailings | |
| C | porewaters at Site 5 | 103 |
| Figure 5.44: | Porewater iron profiles (all stations) | 104 |
| Figure 5.45: | Porewater cobalt profiles (all stations) | 106 |
| Figure 5.46: | Porewater nickel profiles (all stations) | 107 |
| Figure 5.47: | Porewater copper profiles (all stations) | 108 |
| Figure 5.48: | Porewater molybdenum profiles (all stations) | 109 |
| Figure 5.49: | Depth distributions of dissolved NO_3 in tailings porewaters | 110 |
| Figure 5.50: | Porewater uranium profiles (all stations) | 113 |
| Figure 5.51: | Schematic representation of data from Cochran et al. (1986) illustrating the | |
| 8 | behaviour of uranium in anoxic marine sediments | 115 |
| Figure 5.52: | Porewater radium profiles (all stations) | 116 |
| Figure 5.53: | Porewater barium profiles (all stations) | 117 |
| Figure 5.54: | Porewater strontium profiles (all stations) | 118 |
| Figure 6.1: | Annual recurrence interval for the Alligator Rivers Region based on Oenpelli | |
| 8 | rainfall records (Moliere, unpublished data 2004) | 124 |
| Figure 6.2: | Column arrangement (a) interconnection between the unsaturated & saturated | |
| | columns and (b) fresh unsaturated column image showing fresh tailings | 125 |
| Figure 6.3: | Saturated columns | 126 |
| Figure 6.4: | Particle size distribution of aged and fresh tailings | 127 |
| Figure 6.5: | Major element composition of bulk fresh & aged tailings prior to leaching | 129 |
| Figure 6.6: | Trace element composition of bulk fresh & aged tailings prior to leaching | 129 |

| Figure 67. | VPD patterns of frash tailings sampled from the saturated column | 122 |
|-----------------|--|------------|
| Figure 6.8: | XRD patterns of aged tailings sampled from the saturated column | 132 |
| Figure 6.0: | Major element composition of bulk fresh & aged tailings post leaching | 132 |
| Figure 6.10. | Trace element composition of bulk fresh & aged tailings post leaching | 133 |
| Figure 0.10 . | Silicate mineral distribution for (a) fresh and (b) aged saturated tailing | 134 |
| Figure 6.11. | Sulfide minoral distribution for (a) fresh and (b) aged saturated tailings | 120 |
| Figure 0.12 . | SEM field view showing (a) a subje porticle of primery purity and (b) | 130 |
| rigule 0.15. | tetragonal chalconvrite (Fordham 1993) | 139 |
| Figure 6 14 · | Gynsum distribution for fresh and aged saturated tailings | 140 |
| Figure 6 15: | Uranium phase distribution for fresh and aged saturated tailings | 140 |
| Figure 6 16 | Manganese oxide phase distributions for fresh and aged saturated tailings | 141 |
| Figure 6 17: | Iron oxide phase distributions for fresh and aged saturated tailings | 142 |
| Figure 6 18: | Calcium carbonate distribution for fresh and aged saturated tailings | 144 |
| Figure 6 10 | nH trends for (a) fresh and (b) aged tailings leachates | 147 1/7 |
| Figure 6 20: | Alkalinity trends for (a) fresh and (b) aged tailings leachates | 1/18 |
| Figure 6.21: | Electrical conductivity trends for (a) fresh and (b) aged tailings leachates | 150 |
| Figure 6.21. | Major ion trends for (a) fresh and (b) aged unsaturated tailings leachates | 150 |
| Figure 6 23: | Calcium trands for (a) fresh and (b) aged tailings leachates | 151 |
| Figure 6.23 . | Nitrite and Nitrate trands for aged unseturated tailings leachates | 152 |
| Figure 6.24. | Al and Si trands for (a) frash and (b) aged tailings leachates | 155 |
| Figure 6.25. | A and Si tiends for (a) fresh and (b) aged tailings leachates | 155 |
| Figure 6.20. | Conner trends for (a) fresh and (b) aged tailings leachates | 157 |
| Figure 0.27 . | Copper trends for (a) fresh and (b) aged tailings leachates | 150 |
| Figure 0.20 . | Unanium trends for (a) fresh and (b) aged tailings leachates | 139 |
| Figure 0.29 : | Vision in a far (a) fresh and (b) aged astructed tailings leachates | 160 |
| Figure 0.30 : | Major ions for (a) fresh and (b) aged saturated tailings leachates | 102 |
| Figure 0.31 : | Total iron trands for (a) frach and (b) aged saturated tailings leachates | 103 |
| Figure 0.52 : | Total from trends for (a) fresh and (b) aged saturated tailings feachates | 104 |
| Figure 0.55. | Leachates L_{1} | 165 |
| Figure 6.34: | Fe and U trends for (a) fresh and (b) aged saturated tailings leachates | 166 |
| Figure 6.35: | Fe and Mo trends for the (a) fresh and (b) aged saturated tailings leachates | 168 |
| Figure 6.36: | Radium-226, Ba and Sr trends for (a) fresh and (b) aged saturated tailings | |
| | Leachates | 170 |
| Figure 6.37: | Barite and celestite saturation indices for (a) fresh and (b) aged saturated | |
| | tailings leachates | 172 |
| Figure 7.1: | Schematic representation of kinetic model | 179 |
| Figure 7.2: | Depth distribution of saturation indices with respect to alunite at sites 5&6 | 186 |
| Figure 7.3: | Depth distribution of saturation indices with respect to barite at sites 5&6 | 187 |
| Figure 7.4: | Depth distribution of saturation indices with respect to strontianite at sites 5&6 | 188 |
| Figure 7.5: | Depth distribution of saturation indices with respect to gypsum at sites 5&6 | 189 |
| Figure 7.6: | Depth distribution of saturation indices with respect to graphical at sites | 107 |
| 1.1801.0 1.01 | 5&6 | 190 |
| Figure 7.7: | Depth distribution of saturation indices with respect to K-jarosite at sites | |
| | 5&6 | 191 |
| Figure 7.8: | Depth distribution of saturation indices with respect to rhodochrosite at sites | |
| | 5&6 | 192 |
| Figure 7.9: | Depth distribution of saturation indices with respect to schoepite at sites | 100 |
| | 3&0 | 193 |

LIST OF TABLES

| Table 1.1: | Tailings production from historic uranium mines | 8 |
|------------|---|-----|
| Table 2.1: | Mineralogy of Ranger #1 (Savory, 1994) | 19 |
| Table 3.1: | Sample preparation procedures | 25 |
| Table 3.2: | Sequential extraction scheme | 26 |
| Table 3.3: | Climatic data for Jabiru Airport (Australian Bureau of Meteorology) | 29 |
| Table 3.4: | Column design parameters and material specifications | 30 |
| Table 3.5: | Chemical composition of Jabiru East rainwater (1983-84) | 31 |
| Table 3.6: | Quantities of salts and acids for the preparation of artificial rainwater | 32 |
| Table 4.1: | Summary of sample depths and relative level (RL) for each core profile | 37 |
| Table 4.2: | Summary of porewater field measurements | 40 |
| Table 5.1: | Half cell reactions of oxidants present in the tailings pile and their associated | |
| | free energies and electron activities | 47 |
| Table 5.2: | Mineralogical composition of composite samples obtained from 0.5m tailings | |
| | Cores | 58 |
| Table 5.3: | Energy dispersive X-Ray analyses of chlorite in various tailings samples | 71 |
| Table 5.4: | Energy dispersive X-Ray analyses of muscovite, Site 4 (11.38 m) | 72 |
| Table 5.5: | Trace metal composition of selected tailings | 76 |
| Table 5.6: | Sequential extraction samples | 77 |
| Table 5.7: | Mass recovery of elements constituting key geochemical phases | 83 |
| Table 5.8: | Porewater saturation indices for gypsum, celestite and barite Sites 4 and 9 | 119 |
| Table 6.1: | Comparison of actual columns leach parameters and original design criteria | 122 |
| Table 6.2: | Mineralogical composition of fresh and aged tailings prior to leaching | 128 |
| Table 6.3: | Mineralogical composition of fresh and aged tailings sampled from the | |
| | unsaturated column following the 520-day leach experiment | 131 |
| Table 7.1: | Mass action reactions to describe the geochemical model of the tailings pile | 182 |
| Table 7.2: | Kinetic model input data | 185 |
| Table 7.3: | Summary of predicted and actual leachate chemistry for unsaturated tailings | 186 |
| Table 7.4: | Saturation indices determined for fresh saturated tailings leachates | 195 |
| Table 7.5: | Saturation indices determined for aged saturation tailings leachates | 196 |

Abstract

Uranium mill tailings from the Ranger mine, located in the Alligator Rivers Region of the Northern Territory, Australia, were examined to assess the effects of weathering and diagenesis on their long-term geochemical stability. Run of mill uranium tailings are a complex heterogeneous mixture of lithogenic (primary gangue minerals and weathering products) and secondary (components that form during milling) minerals, residual process chemicals and biogenic (products of biological activity) phases. Following transfer to the tailings storage facility, post depositional reactions alter the mineralogical and hydrochemical characteristics of the tailings solids and pore waters in accordance with weathering and diagenetic processes.

In this thesis, a detailed examination of tailings cores and pore waters, kinetic column test work and geochemical modelling was combined with results from earlier studies to examine the key processes governing the geochemical stability of the Ranger tailings. Conclusions drawn from the work clearly demonstrates that the solid state speciation and mobility of metals and radionuclides in the tailings pile are governed by the processes of oxidative dissolution of sulfide minerals, weathering of phyllosilicates and organic matter diagenesis. The processes are spatially dependent, evolve over time and are influenced by the following key factors:

- Tailings water content or degree of saturation;
- The nature and content of organic matter in the tailings;
- Redox potential of the tailings solid-pore water interface; and
- The specific reactivity of precursor minerals (primary/secondary) from the milling process and pore water solutes.

Combined, these processes lead to the formation of authigenic minerals, which control the solubility of pore water constituents. These mechanisms will also have a profound impact on the long-term geochemical stability of the tailings pile and, as such, will need to be taken into account in the design, management and closure of the final tailings repositories at the Ranger site.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

Greg Sinclair

Acknowledgments

This thesis is dedicated to my family, Wendy, Michael and Matthew, who have made a number of personal sacrifices in my pursuit of this PhD. Without their unconditional support I would not have been able to complete this project and for that I am eternally grateful. Wendy's computer skills and keen eye for detail were also invaluable in formatting and proof reading the final document.

Gaining new insights into Mother Nature and how her natural laws govern the geochemical stability of anthropogenic waste has been one of the most rewarding aspects of this project. This new found knowledge was only possible through the oversight and guidance of my supervisors and friends, Dr Graham Taylor and Dr Paul Brown. Their dedication and enthusiasm for the discipline of environmental geochemistry made this a truly pleasurable learning experience.

Similarly I would also like to express my gratitude to the professional engineers and scientists at ERA, ANSTO and CSIRO for their assistance in both the field and laboratory aspects of the project. Their practical suggestions, based on years of experience, were value added and greatly appreciated. A special thanks goes to ERA for allowing me to conduct this research and for their significant contribution to the geosciences and development of best practice.