http://researchspace.auckland.ac.nz

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author’s right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.
http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.
An Interdisciplinary Approach to the Prediction of Pit Lake Water Quality, Martha Mine Pit Lake, New Zealand

Devin N. Castendyk

12 July 2005

ABSTRACT

Lakes resulting from open pit mining may be potential water resources or potential environmental problems, depending on their water quality. As the global abundance of pit mines and pit lakes increases, there is increasing pressure on the mining industry to create pit lakes that have environmental, social, and/or economical utility. This thesis uses an interdisciplinary approach involving mineralogy, physical limnology, and geochemistry to predict and improve the water quality of a proposed pit lake at the Martha gold mine, New Zealand.

A mineral quantification method developed for this study measured the distributions and concentrations of wall rock minerals, and identified 8 relatively homogeneous wall rock regions, called mineral associations. Acid-base accounting using calcite and pyrite quantities identified 3 associations with acid-generating potential.

Three physical limnology tools (relative depth, Wedderburn number, and numerical modeling with DYRESM), predicted that the upper 2/3 of the lake will circulate annually during the winter turnover period, whereas the lower 1/3 will remain permanently isolated. Permanent stratification resulted from density differences between groundwater and river water inputs during lake filling, plus lake morphology.

The geochemical model used the distribution of mineral associations to characterize the composition of pit wall runoff, and used the limnologic prediction to define the mixing frequency, mixing depth, and layer volumes. Initial modeling with the geochemical program PHREEQC indicated the lake will have a pH of 5, and Cu and Zn concentrations that exceed aquatic life protection guidelines. Sensitivity
analyses showed that subaqueous water-rock reactions did not have a significant affect on lake pH, suggesting these reactions are less important geochemical factors in pyrite-bearing pit lakes. Surface adsorption onto ferrihydrite reduced concentrations of As, Pb, and Cu, suggesting these reactions are important geochemical factors in pit lakes. By covering the acid-generating mineral associations, lake pH increased above 6.5, allowing for future recreational use. Concentrations of Cu complied with aquatic life protection guidelines, however, Zn concentrations remained above these guidelines.

This study demonstrates the value of interdisciplinary pit lake predictions in the design of closure plans for open pit mines. Such studies improve the ability of mining companies to sustainably develop mineral resources.
This thesis is dedicated to
Ruth Laura Harman Castendyk
1908-1988
Radcliffe graduate, chemist, physicist, aviator, occidental traveler,
mountaineer, teacher, and kind inspiration.
“A lake is the landscape’s most beautiful and expressive feature. It is Earth’s eye; looking into which the beholder measures the depth of his own nature.”

Henry David Thoreau
Walden
ACKNOWLEDGEMENTS

My PhD experience began in 1998 with a simple dream to live and work overseas. Several faculty and students in the Department of Geology and Geophysics at the University of Utah cultivated my desires, and helped me to submit an application for a U.S. Fulbright Grant to study in New Zealand. I am grateful to Paul Jewell, Kip Solomon, John Bartley, Jeff Fitzmayer, Dave Chapman, Phil Armstrong, Tony Ekdale, Dave Marchetti, and Amy Sheldon for their letters of recommendation, editorial comments, and general enthusiasm. I would also like to thank Greg Waite, Kevin Mahan, and Cassandra Fenton for their encouragement and friendship.

The grant provided me with the funds and legitimacy to study in New Zealand for 5 and a half years. I am grateful to the tax payers of the United States of America, and the Fulbright New Zealand office in Wellington, for generosity supporting for my living expenses for the first two-and-a-half years. The friendly staff at Fulbright New Zealand have been an invaluable resource. I especially appreciate the efforts of Laurie Wright, Maree Yong, Ruth Payne, and their inspirational, former managing director, Jennifer Gill - the first person to suggest that I apply this research toward a PhD. I am also grateful to the University of Auckland for providing me with two additional years of financial support, and for funding my attendance at conferences in Australia and the United States.

This research would not have been possible without the permission of Newmont Waihi Operations, formerly Waihi Gold Company, who allowed me to collect samples from their active gold mine and to publish my results. I especially thank Keith Brodie for promoting my research to the upper management and for employing staff to assist me during my field work.

Each chapter of this thesis had a group of individuals that contributed time towards its success. I would like to thank Mark Simpson, Erin Hollinger, Gustav Nortje, Peter Swedlund, and Ted Eary for field assistance, petrographic analyses, constructive reviews, and helpful discussions related to Chapter 2. I would also like to thank Craig Stevens and David Hamilton for providing helpful advice and reviews on the limnologic modeling presented in Chapter 3, as well as Paul Jewell, Elaine Fouhy, and Kimberley Dunning for supplying the climate data used in this chapter. I thank Robin Hankin and Peter Swedlund for helping me learn the geochemical program PHREEQC used in Chapter 4, and Ian Warren for his assistance compiling GIS data. Additional thanks go to the Centre for Water Research at the University of Western Australia, and the United States Geological Survey for freely distributing the DYRESM and PHREEC programs used in Chapters 3 and 4, respectively.

The people in the Department of Geography and Environmental Sciences at the University of Auckland have provided me with considerable help over the years. I thank Kharmin Sukhia, Bessy D'sa, Beryl Jack, and Margaret Lichtwark for their office assistance, and Sonya Monast and Reuben Hill for routinely fixing my computer problems. I appreciate the interest John Craig has shown in my research. I also thank the department for financially supporting my attendance at various international conferences. Most of all, I thank my friends, officemates, and fellow PhD students, Rob Jessop, Sarah Burke, Eva Vesely, Chris Denny, and Stephanie May, for making thesis life more enjoyable on a daily basis.
I have had two exemplary mentors that nurtured my interest in pit lakes, enhanced the quality of my research, and inspired me to pursue an academic career; my co-supervisor Jeff Mauk, and my main-supervisor Jenny Webster-Brown. Through weekly personal meetings and monthly group discussions, Jeff provided outstanding individual supervision, plus a supportive, thought-provoking peer network. I am grateful for the assistance Jeff has provided toward my research and my professional achievements, his constructive and timely feedback, and the funds he generously contributed towards my analytical expenses and conference expenses.

Jenny’s initial enthusiasm to work with me on the Martha mine, followed by her willingness to supervise my PhD research, allowed my professional and personal dreams to be accomplished. In short, the life-changing experience that my time in New Zealand has provided would most likely have not happened were it not for Jenny’s efforts. Beyond the insightful discussions and comprehensive reviews that shaped and greatly improved this work, I will always be grateful to Jenny for enabling this experience to occur.

In closing, I would like to thank my family for always supporting me and always encouraging me to follow my dreams - even when they took me to the opposite side of the world. I also want to thank my partner Melissa for her laughter, her patience, and her thoughtfulness, and for giving me understanding and optimism when I needed them the most.
# TABLE OF CONTENTS

ABSTRACT .............................................................................................................................. ii
ACKNOWLEDGEMENTS ........................................................................................................ vi
LIST OF TABLES .................................................................................................................... xii
LIST OF FIGURES .................................................................................................................. xiii

CHAPTER 1 - INTRODUCTION ............................................................................................. 1
1.1. INTRODUCTION .............................................................................................................. 1
  1.1.1. Potential environmental concerns associated with pit lakes ................................ 2
  1.1.2. Avoiding negative impacts and developing water resources .............................. 4
  1.1.3. References for AMD and pit lake research ............................................................. 5
  1.1.4. Research objectives ............................................................................................... 8
  1.1.5. Document outline .................................................................................................. 9

CHAPTER 2 - QUANTIFYING WALL ROCK MINERALOGY ............................................... 11
2.1. INTRODUCTION ............................................................................................................. 11
  2.1.1. Climatologic, hydrologic, and geologic controls on pit lake water chemistry .... 11
  2.1.2. Research objectives ............................................................................................... 14
  2.1.3. Martha mine: Regional and local geology ............................................................. 14
  2.1.4. Martha mine: History, production, and closure .................................................... 18
  2.2. METHODOLOGY ......................................................................................................... 19
    2.2.1. Field observations and sampling ........................................................................ 19
    2.2.2. XRD analysis ...................................................................................................... 21
    2.2.3. Selection of representative samples ..................................................................... 21
    2.2.4. Geochemical analyses ....................................................................................... 21
    2.2.5. Mineral concentration calculations ..................................................................... 23
    2.2.6. Method validation ............................................................................................... 27
  2.3. RESULTS ....................................................................................................................... 28
    2.3.1. Field observations and mineral distribution maps .............................................. 28
      2.3.1.1. Pyrite ......................................................................................................... 28
      2.3.1.2. Calcite ...................................................................................................... 30
      2.3.1.3. Silicates .................................................................................................... 30
    2.3.2. Mineral associations ............................................................................................ 30
      2.3.2.1. Weakly-altered ......................................................................................... 32
      2.3.2.2. Propylitic .................................................................................................. 32
      2.3.2.3. Argillic ..................................................................................................... 35
      2.3.2.4. Oxidized ................................................................................................... 35
      2.3.2.5. Potassic .................................................................................................... 36
      2.3.2.6. Quartz veins .............................................................................................. 36
      2.3.2.7. Post-mineralization deposits ..................................................................... 37
    2.3.3. Trace elements ..................................................................................................... 38
    2.3.4. Petrographic validation ....................................................................................... 38
    2.3.5. Calcite validation ............................................................................................... 39
  2.4. DISCUSSION .................................................................................................................. 40
    2.4.1. Acid-production and acid-neutralization ............................................................ 40
CHAPTER 4 (continued)

4.2.1. The geochemical program PHREEQC .............................................. 106
4.2.1.1. Description and capabilities ......................................................... 106
4.2.1.2. Program limitations ........................................................................ 107
4.2.1.3. PHREEQC options used in each pit lake model .......................... 109
4.2.2. Modeling scenarios ............................................................................. 110
4.2.2.1. Conceptual model of lake filling: Year -4 to 0 ......................... 110
4.2.2.2. Conceptual model of steady-state conditions: Years 1 to 50 ...... 112
4.2.3. Representative input water chemistry .............................................. 114
4.2.4. Basic model: Model I ........................................................................ 122
4.2.4.1. Basic model: Model I ............................................................... 122
4.2.4.2. Sensitivity analysis of water-rock reactions: Models 1a, 2a, 2b, 2c, 2d ........................................ 127
4.3. Sensitivity analysis for surface adsorption reactions: Models 3a, 3b .......... 133
4.2.4.4. Sensitivity analysis on unoxidized runoff: Models 4a, 4b .......... 134
4.3.1. Results of the basic model: Model 1 .................................................. 135
4.3.1.1. Acidity ......................................................................................... 135
4.3.1.2. Redox and dissolved oxygen .......................................................... 137
4.3.1.3. Metal ions .................................................................................... 139
4.3.2. Water-rock reactions sensitivity analysis: Models 2a, 2b, 2c and 2d ........ 144
4.3.3. Surface adsorption sensitivity analysis: Models 3a and 3b ............... 145
4.3.4. Unoxidized runoff sensitivity analysis: Models 4a and 4b .............. 146
4.3.4.1. Pre-filling remediation: Model 4a .................................................. 147
4.3.4.2. Post-filling remediation: Model 4b ................................................. 152
4.4. DISCUSSION .......................................................................................... 152
4.4.1. Geochemical conditions in the future Martha lake ....................... 152
4.4.2. Sensitivity analyses .......................................................................... 154
4.4.2.1. Water-rock reactions ................................................................... 154
4.4.2.2. Surface adsorption reactions .......................................................... 157
4.4.2.3. Remediation of unoxidized runoff ............................................... 158
4.4.3. Martha lake water quality and potential utility .................................. 159
4.5. CONCLUSIONS ..................................................................................... 160

CHAPTER 5 - DISCUSSION and CONCLUSIONS ....................................... 162
5.1. A MODEL for the CHEMICAL EVOLUTION of MARTHA LAKE .... 162
5.2. A RECOMMENDATION to IMPROVE WATER QUALITY .............. 165
5.3. INSIGHT GAINED from this RESEARCH ........................................... 166
5.3.1. The importance of water-rock reactions .......................................... 166
5.3.2. The importance of mineral quantification ....................................... 168
5.3.3. The importance of predicting physical limnology ............................ 169
5.3.4. The importance of climate conditions ............................................ 170
5.3.5. Improving the accuracy of geochemical predictions ...................... 171
5.4. ACHIEVING the SUSTAINABLE DEVELOPMENT of PIT LAKES .. 171
5.5. CONCLUSIONS ..................................................................................... 173

REFERENCES .............................................................................................. 175
APPENDIX A - MANUSCRIPTS ........................................ CD
INFORMATION FILE ................................................... CD
APPLIED GEOCHEMISTRY MANUSCRIPT ............................ CD
ICARD 6 MANUSCRIPT .............................................. CD

APPENDIX B - MINERALOGICAL DATA ............................... CD
INFORMATION FILE ................................................ CD
GEOCHEMICAL DATA .............................................. 192

APPENDIX C - DYRESM INPUT FILES ............................... CD
INFORMATION FILE ................................................ CD
BLOWOUT LAKE INPUT FILES .................................... CD
MARTHA LAKE INPUT FILES ...................................... CD
Model 1: Cold groundwater with low $S$ runoff .................. CD
Model 2: Cold groundwater with high $S$ runoff ................. CD
Model 3: Warm groundwater with low $S$ runoff ................. CD
Model 4: Warm groundwater with high $S$ runoff ............... CD

APPENDIX D - PHREEQC INPUT FILES ............................. CD
INFORMATION FILE ................................................ CD
GEOCHEMICAL DATA .............................................. CD
River water ................................................................ CD
Groundwater ........................................................... CD
Unoxidized runoff ....................................................... CD
Oxidized runoff ........................................................ CD
PHREEQC INPUT FILES ............................................ CD
Model 1: Basic model ............................................... CD
  Model 1: Basic model ............................................. CD
Model 2: Water-rock reactions .................................... CD
  Model 2a: Surface area $\times 1$ .................................. CD
  Model 2b: Surface area $\times 10$ ................................ CD
  Model 2c: Surface area $\times 100$ ............................. CD
  Model 2d: Surface area $\times 1000$ .......................... CD
Model 3: Surface adsorption reactions ........................... CD
  Model 3a: High ferricydrite area ............................. CD
  Model 3b: Low ferricydrite area ............................. CD
Model 4: Remediation of unoxidized runoff ....................... CD
  Model 4a: Before lake filling .................................. CD
  Model 4b: After lake filling ..................................... CD
Table 2.1. Reaction rates of common minerals identified at the Martha mine .................................................................................. 13

Table 2.2. Mineral calculation sequence ................................................................................................................................. 25

Table 2.3. Mineral association surface areas, with observed and predicted mineral concentrations .............................................. 33

Table 3.1. Physical, climate, and geologic characteristics of the existing Blowout lake and the proposed Martha lake ................. 59

Table 3.2. Water properties at the existing Blowout lake and the proposed Martha lake ......................................................... 62

Table 3.3. Relative depth, physical limnology, and chemical characteristics of some pit lakes .................................................... 68

Table 3.4. Wedderburn numbers for some existing pit lakes, and the proposed Martha lake ...................................................... 73

Table 3.5. Water balance for the Blowout lake, Utah ...................................................................................................................... 81

Table 3.6. Characteristics of inputs used in four DYRESM flooding models of the proposed Martha lake .................................. 88

Table 4.1. Representative chemical analyses for lake inputs ....................................................................................................... 119

Table 4.2. Mineral association surface areas and lake layer volumes in 2002 and projected for the conclusion of mining in 2007 .......... 124

Table 4.3. Equations, mineral surface areas, specific reaction rates, and reacted masses for water rock reactions ....................... 131

Table 4.4. Summary of compliance with various guidelines for pit lake water - Model 1 .................................................................... 160
LIST OF FIGURES

Figure 2.1. Geological map of the Coromandel Peninsula, North Island, New Zealand, showing the location of the Martha mine ........................................ 15

Figure 2.2. View of the southwest wall of the Martha mine showing the subvertical Martha Lode, hosted by hydrothermally-altered andesites .... 17

Figure 2.3. View of the northeast wall of the Martha mine showing the location of the unconformity and the overlying post-mineralization deposits.. 17

Figure 2.4. Rock sample location map for the open pit Martha mine .......... 20

Figure 2.5. Mineral distribution maps for the Martha mine .......................... 29

Figure 2.6. Mineral association map of the Martha mine ............................... 31

Figure 2.7. The average mineral concentrations (wt%) for each mineral association .......................................................................................... 34

Figure 2.8. Average concentrations (ppm) of selected trace elements in each mineral association ................................................................. 38

Figure 2.9. Calcite concentrations (wt%) measured by Sobek acid digestion verses calcite concentrations (wt%) predicted by the MQ method ...... 40

Figure 2.10A. Standard ABA where NP is calculated from Sobek acid digestion and AP is calculated from total sulfur from Leco analyses .......... 43

Figure 2.10B. ABA where NP and AP are calculated from carbonate-carbon and sulfide-sulfur results from Leco and MQ methods .......... 43

Figure 2.11. ABA using calcite and pyrite concentrations (wt%) as calculated by the MQ method. ................................................................. 45

Figure 3.1. Conceptual models of holomictic and meromictic pit lakes ........ 54

Figure 3.2A. Location map and approximate bathymetric map for the Blowout pit lake, Utah, USA ................................................................. 58

Figure 3.2B. Location map and approximate bathymetric map for the Martha mine, and proposed Martha lake, Waihi, New Zealand .......... 58

Figure 3.3. Seasonal density profiles for the Blowout lake, Utah ................. 63

Figure 3.4. Comparison of the surface areas and maximum depths of 13 holomictic crater lakes and the proposed Martha lake ...................... 65
Figure 3.5. Wedderburn numbers for Blowout lake as a function of wind speed ................................................................. 74

Figure 3.6. Wedderburn numbers for the proposed Martha lake as a function of wind speed ..................................................... 77

Figure 3.7. Modeled and observed temperature profiles for Blowout lake .... 83

Figure 3.8. Discharge rates of major inputs to the proposed Martha pit lake during 5 years of lake filling ........................................... 85

Figure 3.9. Temperature, salinity, and density profiles of four DYRESM models of the proposed Martha lake ........................................... 90

Figure 4.1A. Conceptual model for Martha lake during lake filling ................. 111

Figure 4.1B. Conceptual model of the steady-state Martha lake .................... 111

Figure 4.2. Plots of 17 river water analyses showing component concentrations versus pH .......................................................... 115

Figure 4.3. Plots of 45 groundwater analyses showing component concentrations versus pH ......................................................... 116

Figure 4.4. Plots of 13 oxidized runoff analyses showing component concentrations versus pH ...................................................... 117

Figure 4.5. Plots of 35 unoxidized runoff analyses showing component concentrations versus pH ............................................... 118

Figure 4.6. Eh-pH characteristics of mine waters ........................................ 120

Figure 4.7. Flow chart of procedures for the lake filling scenario ..................... 123

Figure 4.8. Flow chart of procedures for the steady-state scenario .................. 126

Figure 4.9. pH, pe, and DO results from Models 1, 2b, 2c, and 2d .................. 136

Figure 4.10. Fe, Mn, and SO₄ results from Models 1, 2b, 2c, and 2d ................. 140

Figure 4.11. As, Cd, and Cu results from Models 1 and 3b .......................... 142

Figure 4.12. Pb, Ni, and Zn results from Model 1 and 3b ............................. 143

Figure 4.13. Example of sorption edges of various metal cations and oxyanions onto ferrihydrite as a function of pH ........................ 146

Figure 4.14. pH, pe, and DO results from Models 1, 4a, and 4b ....................... 148

Figure 4.15. Fe, Mn, and SO₄ results from Models 1, 4a, and 4b .................... 149
Figure 4.16. As, Cd, and Cu concentrations from Models 1, 4a, and 4b .......... 150

Figure 4.17. Pb, Ni, and Zn concentrations from Models 1, 4a, and 4b .......... 151

Figure 5.1. Relationships between principle variables that influence pit lake water quality and lake utility ........................................................................................................................................... 172