TITLE PAGE

Phosphate stabilisation of partly oxidised, polymineralallic mine wastes.

Thesis submitted by

David Llewellyn HARRIS BSc(Hons) *UNE*

in August 2003

for the degree of Masters by Research

in the School of Earth Sciences

James Cook University

Cairns

STATEMENT OF ACCESS

I, the undersigned, the author of this thesis, understand that James Cook University will make this thesis available for use within the University Library and, via the Australian Digital Thesis network, for use elsewhere.

I understand that, as an unpublished work, a thesis has significant protection under the Copyright Act and;

I do not wish to place any restriction on access to this thesis.

Signature

Date

STATEMENT OF SOURCES

DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

Chapter two of this thesis is based on the scientific paper Harris, D.L., Lottermoser, B.G and Duchesne, J. 2003 Ephemeral acid mine drainage at the Montalbion silver mine, north Queensland: Australian Journal of Earth Sciences (in press). Significant contributions were made to this chapter by Dr. Bernd Lottermoser (JCU) and Dr. J Duchesne (Laval University).

Signature　　　　　　Date

ELECTRONIC COPY

I, the undersigned, the author of this thesis, declare that the electronic copy of this thesis provided to the James Cook University Library is an accurate copy of the print thesis submitted within the limits of the technology available.

Signature

Date

ACKNOWLEDGEMENTS

Over the duration of this project valuable contributions have been made by many people in a wide variety of means. The quality of the final product has been greatly enhanced by this input and if I have made any omissions in these acknowledgments it is purely by accident and I extend my humble apologies.

First and foremost, *viel danke* to my supervisor Dr. Bernd Lottermoser whose guidance and support have led to the realisation of a successful, worthwhile project. His rendering of my frequently waffly text into intelligible concise script, particularly the paper we co-authored, has improved the final document greatly. Also *merci beaucoup* to the other co-author of the paper which forms the basis for Chapter 2, Dr. Josee Duchesne (Laval University), particularly for the many hours of work sifting through the complex XRD traces.

Additional academic advice was given by Dr. Dave Craw (University of Otago) and Dr. Paul Ashley (University of New England) regarding the mineralogy of the Montalbion mining area and the behaviour of metalloids in acidic systems. Dr. Michael Liddell is thanked for his advice on the behaviour of the phosphate fertilisers in the column experiments. Darryl K. Nordstrom and David Parkhurst of the United States Geological Survey are thanked for their advice on efflorescent mineral solubilities and water chemistry modelling respectively.

Peter Whitehead is acknowledged for general geological assistance and giving me work during my time at JCU. Rod Coe of the Queensland Department of Natural Resources and Mines is thanked for providing funds for water chemistry analyses of Oakey Creek.

The staff of the Advanced Analytical Centre in Cairns and Townsville are much appreciated for their willingness to bend over backwards to help with analyses, interpretation and the inevitable problems arising with advanced technology. Heather Windsor, AAC Cairns, is especially thanked for her help with almost everything analytical! In Townsville, Kevin Blake (SEM and microprobe), Alan

Chappell (XRD), Sharon Ness (XRD and SIROQUANT), Yi Hu (ICP), Gordon Warria (XRF) and Elvy Grigolato (computing) are gratefully acknowledged for all their assistance.

The IT gurus of Cairns, Rod Armstrong and Steve Stanley are thanked immensely for keeping my poor outdated laptop grinding through until the end. Meredith Austin is to be thanked for the work of art that is Figure 2.1, her other formatting assistance and the cool T-shirts from Vietnam.

To my fellow postgraduate students I am very grateful for your support and assistance in innumerable ways and means throughout my most enjoyable time here at JCU. Specifically thanks to Manfred Thienenkamp, Scott Keeling, Chris Pratt and Cheryl Roberts. My shout at Stingers!

For all my friends and family, thanks for your support and the good times had whilst not working on my project. Thanks Jaye, Matt, Horto, Krissy, the Cleghorn family, Simon, Karen, Lisa, Peteymon, Eva, Ulrika, Francie and the Hufflepuff Volleyball Team.

Finally I would like to thank my partner in love and crime, Jodi Cleghorn (soon to be Harris!?). Without your support, enthusiasm, belief, proof-reading, formatting, grammatical advice, data recording and never-ending assistance (not to mention the morning coffees!) I doubt I would have ever finished the project. *Merci beacoup mon petiti chou.*

Abstract

The oxidation of sulphides present in mine waste may produce acidity and release dissolved metals and sulphate into local surface and ground waters. This process is known as acid mine drainage and is considered the most important environmental problem currently facing the mining industry. Phosphate induced stabilisation has been used to create passive iron phosphate coatings on pyrite and pyrrhotite. The formation of solid phosphate coatings on the sulphide grains thereby inhibits sulphide oxidation. The aims of this study were to determine whether the phosphate stabilisation technique would inhibit acid generation and attenuate metals released from partly oxidised, polymineralic mine waste (obtained from the Montalbion Silver mine, north Queensland) under laboratory conditions.

Sulphide-rich materials comprising the waste at the abandoned Montalbion silver mine have undergone extensive oxidation prior to and post mining. Weathering has led to the development of an abundant and varied secondary mineral assemblage throughout the waste material. Post-mining minerals are dominantly metal and/or alkali (hydrous) sulphates and generally occur as earthy encrustations or floury dustings on the surface of other mineral grains. The variable solubility of these efflorescences, combined with the irregular rainfall, controls the chemistry of seepage waters emanating from the waste dumps. Irregular rainfall events dissolve the soluble efflorescences which have built up during dry periods, resulting in ‘first flush’ acid (pH 2.6–3.8) waters with elevated sulphate, Fe, Cu and Zn contents. Less soluble efflorescences, such as anglesite and plumbojarosite, retain Pb in the waste dump. Metal-rich (Al, Cd, Co, Cu, Fe, Mn, Ni, Zn) acid mine drainage waters enter the local creek system. Oxygenation and hydrolysis of Fe lead to the formation of Fe-rich precipitates (schwertmannite, goethite, amorphous Fe compounds) which, through adsorption and coprecipitation, preferentially incorporate As, Sb and In. Furthermore, during dry periods evaporative precipitation of hydrous alkali and metal sulphate efflorescences occurs on the perimeter of stagnant pools. Flushing of the streambed by neutral pH waters during heavy rainfall events dissolves the efflorescences resulting in remobilisation and transportation of sulphate and metals (particularly Cd, Zn) downstream. Thus, in areas of seasonal or irregular rainfall, secondary efflorescent minerals present in waste materials or drainage channels have an important influence on the chemistry of surface waters.

Waste materials for the phosphate stabilisation experiments were sourced from the Montalbion silver mine. Three kinetic column leaching experiments were conducted using (a) polymineralic unoxidised sulphidic mine waste and liquid phosphate stabiliser, (b) partly oxidised polymineralic mine waste and liquid phosphate stabiliser, and (c) partly oxidised polymineralic mine waste using liquid and solid phosphate fertilisers. SEM observations of the treated waste material showed that phosphate coatings and precipitates formed in all experiments. Metal-alkali phosphate coatings formed on all sulphides when $KMnO_4$ and phosphate fertilisers were used in the coating solutions. Otherwise tetrahedrite was uncoated. The phosphate coatings were most abundant on chalcopyrite and were interpreted to be chemically connected with the underlying sulphide. In contrast, the metal, metal-alkali and alkali phosphate precipitates were interpreted to be physically connected to their substrates. The abundance of phosphate development appeared to be dependent on the abundance of cations in solution available for precipitation with the phosphate anions. The release of cations was predominantly dependent on oxidant strength, through sacrificial sulphide oxidation, or the dissolution of soluble sulphate minerals present in the partly oxidised waste.

Leaching of the coated material in a strongly oxidising solution showed that the phosphate coatings and precipitates inhibited acid generation and probably inhibited metal release in all experiments. Thus, the phosphate coatings prevented oxidant access to the sulphide surfaces, inhibiting sulphide oxidation. Lead and Fe phosphates were the most stable in the oxidising solution, whereas Cu and Zn phosphates were partially dissolved. Arsenic and Sb were mobilised by the coating process due to the higher mobility of these metalloids at circum-neutral pH.

The results of this study demonstrate that phosphate stabilisation can suppress sulphide oxidation and metal release in partly oxidised, polyminerallic mine wastes on a laboratory scale.

Table of contents

List of Tables

List of Figures

Page No.

List of Appendices