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Assessment of Blended Waste Rock Material at Zinifex Century Mine
Consequences for Acid Drainage Generation

Thesis submitted by
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in February 2007
for the degree of
Master of Science
in the
Department of Chemistry,
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Laura Maree McIlwaine

26 February 2007

Date

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Abstract

There is little doubt that acid rock drainage (ARD) is the largest and most testing long-term environmental issue facing the global minerals industry (Lawrence and Day, 1997, Munchenberg, 1998, Olson et al. 2006). The aim of this study was to assess leachate quality from different blends of waste rock at Zinifex Century Mine and determine consequences for acid drainage generation. This thesis describes the results of research undertaken to predict the risk of ARD associated with a possible change to waste rock disposal practices at the Zinifex Century Mine.

Zinifex Century Mine Limited (ZCML) comprises a zinc, lead and silver mining and milling operation at Lawn Hill in northwest Queensland, concentrate dewatering and shipping facilities at Karumba in the Gulf of Carpentaria, and a 304km slurry pipeline connecting the two operations. Similar to other mines where sulfide minerals are present, ARD may be generated at the ZCML mine site from exposed pit surfaces, ore stockpiles, removed waste rock and deposited tailings (Bates et al. 2000). To minimise the generation of ARD in the waste rock dumps, waste rock is classified into the following three classes based on competence and acid forming / consuming capabilities:

- **Class 1:** Competent rock, non-acid forming or acid-consuming material.
- **Class 2:** Non-competent, non-acid forming or acid-consuming material
- **Class 3:** Acid-forming material.

The generalised waste rock dump design for current operations comprises an outer zone of class 1 material and inner zone containing class 2 and 3 materials. Cambrian Limestone (CLS), a class 1 material, is used for its structural and acid neutralising capabilities in waste rock dump construction.

Current mine waste rock placement procedures specify that class 1 rock with greater than 5% contamination of class 3 material is to be placed within the inner zone of the waste rock dumps due to uncertainty surrounding the long-term acid producing capabilities of this rock. This procedure, as well as additional restrictions on waste rock dump design, has the potential to cause significant scheduling problems due to the limited reserve of class 1 rock available for waste rock dump rehabilitation. This is particularly the case in the latter stages of the mine life following movement of most of the waste rock to access the ore.

Due to finite reserves of CLS material and the need to develop strategies to maximise the beneficial use of available limestone reserves, as well as the belief by mine personnel that the abovementioned contamination percentage may be conservative, this project was commissioned to enable the leachate from different blends of waste rock to be assessed. The objectives of the study were to:

- Quantify blending levels of acid consuming (Cambrian Limestone) and acid forming (Hanging Wall Siltstone (HWD)) rock that will produce pH neutral leachate low in metal and salt concentrations;
- Determine the validity of current waste rock placement procedures;
- Investigate the influence of particle size on leachate quality; and
- Attempt to establish links between results from various ARD prediction tests.

Various static (acid base accounting, net acid generation tests, acid buffering characteristic curves and cyclic voltammetry) and kinetic (column leach tests (CLTs) and heap leach pads (HLPs)) ARD prediction tests were conducted on blended waste rock material from ZCML. Twenty CLTs, representing five lithology blends and three particle size distributions were assembled in a laboratory environment. Five replicate CLTs were established. Three HLPs representing three lithology blends were constructed from run of mine material at ZCML. The CLTs and HLPs were periodically watered to simulate rainfall events. In addition, the HLPs were exposed to wet season rainfall events. Results from the static and kinetic tests were compared to address the issue of scale-up.

Findings from the study were:

- Static tests conducted on blended CLS and HWD samples classified each sample as non acid forming (NAF). Results from kinetic testwork confirmed this finding, indicating that limestone blending may be effective in controlling the pH of leachate generated from waste rock, however elevated sulfate concentrations in leachate would ensue.
- Results obtained from the column leach tests were repeatable.
- Sulfate production rates were equivalent to neutralising potential depletion rates in most CLTs and HLPs. This confirmed neutralisation of the sulfuric acid produced by pyrite oxidation by calcium and magnesium carbonates.
- The calculated time to NP depletion exceeded the time to sulfide depletion in all CLTs and HLPs, however these times were misleading for columns containing armoured CLS material.
- Despite first flush events, total metal concentrations in CLT and HLP leachate generally complied with maximum limits specified in Environmental Authority No. MIM800020402 (Ecoaccess, 2004).
- Dissolved zinc concentrations were significantly greater in CLT samples with low pH values, however were not as high as thermodynamically predicted using the geochemical modelling program MINTEQA2. Dissolved zinc concentrations in HLP leachate were also not as high as thermodynamically predicted at pH values less than 7.8. This was due to the control of dissolved zinc concentrations by the rate of sphalerite oxidation at low pH values and the solubility of $Zn(OH)_2$ at high pH values.
- Dissolved lead concentrations in CLT and HLP samples were extremely small or undetectable (i.e. less than $4.8 \times 10^{-4} \mu\text{mol L}^{-1}$) and less than those thermodynamically predicted using MINTEQA2 due to low oxidation rates of galena resulting from surface passivation at lower pH values, and $Pb(OH)_2$ solubility controlling Pb^{2+} concentrations at neutral-alkaline pH values.
- Median dissolved zinc and copper production rates were comparable between the CLTs and HLPs, however rates were greater in the HLPs during large wet season flushes.
- Geochemical modelling confirmed the absence of gypsum precipitation in the CLT comprising the most reactive waste rock blend and smallest particle size distribution and confirmed gypsum

precipitation in HLP2 and HLP3. Sulfate production, neutralising potential depletion and oxygen consumption rates were therefore underestimated in these HLPs.

The main conclusions of the study were:

- (1) Results from CLTs comprising smaller particle size distributions were most comparable with results from the HLPs. Anomalous behaviour was observed in CLTs comprising larger particle size distributions.
- (2) There was no apparent benefit in leaving the HLPs unwatered for periods of time greater than one week.
- (3) Oxygen consumption rates for CLT samples were significantly slower and consequently not directly comparable to those for the HLPs, despite greater flushing of the CLTs.
- (4) Blending CLS and HWD material was effective in maintaining neutral pH values and regulatory-compliant total metal concentrations in drainage from CLTs and HLPs comprising blends up to 75%CLS / 25%HWD. However, sulfate concentrations in drainage from all blended samples exceeded current regulatory discharge limits.
- (5) Visual inspection of material comprising the HLPs after excavation highlighted the presence of armouring layers on HWD material.
- (6) The effectiveness of CLS in neutralising sulfuric acid increased with decreasing particle size.

Corresponding recommendations were:

- (1) Construct CLTs from particle size distributions passing 10mm as a maximum to best emulate the particle size distributions and residence times in waste rock dumps.
- (2) For future HLP testwork at ZCML, or sites of similar climatic conditions, accelerate the rate of pyrite oxidation in the HLPs by watering at weekly intervals on a continual basis in the dry season (i.e. no prolonged drought period).
- (3) For future CLT testwork for sites with distinct seasonal variations, locate the CLTs in field conditions on the site under investigation, to ensure samples are exposed to similar ambient temperatures and humidity. Alternatively, where this is not possible, site temperature and humidity conditions should be simulated in a laboratory environment.
- (4) To prevent a potential increase in sulfate concentrations in WRD discharge, the current 5% contamination limit of class 3 in class 1 material should not be reduced.
- (5) Where there is insufficient CLS material available to cover both the dump surface and batters, priority should be given to the WRD surface, with other non-acid forming competent material used on the batters.
- (6) Investigate the reduction in particle size of class 1 material placed within / on the WRDs.

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Glossary / Abbreviations

Term / Acronym	Description
AAC	Advanced Analytical Centre
ABCC	Acid Buffering Characteristic Curve
AC	Acid Consuming
ACTFR	Australian Centre for Freshwater Tropical Research
Adit	Horizontal or near horizontal passage driven from the surface into the side of a mountain or hill to access mine workings or to dewater the mine (INAP, 1999).
ANC	Acid Neutralising Capacity
AP	Acid Producing
ARD	Acid Rock Drainage
Armouring	The process where acidic solutions, highly concentrated in iron and sulfur, interact with the carbonate-mineral surface forming an insoluble amorphous ferric oxyhydroxide coating on the carbonate mineral surface (Simón et al. 2004).
CANMET	Canadian National Science and Environment Research Council
CBX	Carbonate Breccia
CLS	Cambrian Limestone
CLT	see <i>Column Leach Test</i>
Column Leach Test	A <i>kinetic test</i> designed to simulate the leaching and secondary mineral precipitation and dissolution that determine drainage chemistry (INAP, 1999).
Competent	Relative to competent bed which is defined as a rock layer which, during folding, flexes without appreciable flow or internal shear (Whitten and Brooks, 1987).
Cut-off grade	The lowest grade of mineralised material in a given deposit that qualifies as <i>ore</i> . Used in the calculation of ore reserves.
Dissolved metal concentration	Operationally defined as the metal concentration in the fraction of a water sample passing through a 0.45µm membrane.
EC	see <i>Electrical Conductivity</i>
Electrical Conductivity	A measure of the ability of a water or soil solution to conduct an electric current (ANZECC and ARMCANZ, 2000).
Equilibrium Constant (K)	The equilibrium constant expresses the point of minimum free energy for a chemical reaction (Benthke, 1996).
Fault	A <i>fracture</i> or fracture zone in <i>rock strata</i> resulting from strain and with observable displacement (INAP, 1999).
Footwall	The wall or <i>rock</i> on the lower side of a vein, <i>ore deposit</i> or <i>fault</i> structure (INAP, 1999).

Term / Acronym	Description
Fracture	1. A crack, joint, <i>fault</i> or other break in <i>rocks</i> . 2. The breaking of a <i>mineral</i> other than along planes of cleavage (INAP, 1999).
Gangue	The part of an <i>orebody</i> from which a metal or metals is not extracted. Common gangue minerals include quartz, calcite, fluorite, siderite and pyrite (Whitten and Brooks, 1987).
Geochemistry	Study of the distribution and abundance of elements in <i>minerals, rocks, soils, water</i> and the atmosphere (INAP, 1999).
Hanging Wall	The wall or <i>rock</i> on the upper side of a vein, <i>ore deposit</i> or <i>fault</i> structure (INAP, 1999).
HLP	see <i>Heap Leach Pad</i>
Heap Leach Pad	Test run to show progress of <i>weathering</i> and resulting <i>drainage chemistry</i> in <i>mine</i> materials under the actual <i>minesite</i> conditions (INAP, 1999).
HWB	<i>Hanging Wall Sandstone - Interbedded Black Shale</i> (HWB)
HWD	<i>Hanging Wall Siltstone</i>
HWS	<i>Hanging Wall Sandstone</i>
IAP	see <i>Ion Activity Product</i>
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
INAP	International Network for Acid Prevention
Intrinsic Oxidation Rate	A measure of the rate of consumption of oxygen by a material under a particular set of conditions (Fague and Mostyn, 1997).
Ion Activity Product	The product of the activities of the ions in a <i>solubility product reaction</i> .
Ion-pairs	Ions that are strongly attracted to each other and act as if they are un-ionised or of lesser or different charge than anticipated (Boyd, 2000), e.g. Ca^{2+} and SO_4^{2-} form the ion pair CaSO_4 .
IOR	see <i>Intrinsic Oxidation Rate</i>
JCU	James Cook University
Kinetic Test	A procedure for characterising the physical, chemical, or biological status of a sample through time during continued exposure to a known set of environmental conditions (Morin and Hutt, 1997). Unlike <i>static tests</i> , kinetic tests measure the performance of a <i>sample</i> over a prolonged period of time (INAP, 1999).
K_{sp}	see <i>Solubility Product</i>
Lag time	Time period to the onset of acid generation.
LBV	Lower Box Value
Leachate	Solution obtained from a leaching process (INAP, 1999).

Term / Acronym	Description
MEND	Mine Environment Neutral Drainage
Mill	A facility for milling ore in order to remove and concentrate economic metals or minerals (Morin and Hutt, 1997). Milling processes include <i>crushing, grinding, screening, concentration</i> and dewatering (INAP, 1999).
Mineral	A naturally occurring inorganic element or compound having an orderly internal structure and characteristic composition, crystal form and physical properties (INAP, 1999).
MINTEQA2	A geochemical modelling program sponsored by the US Environmental Protection Agency. Its primary purpose is speciation modelling, including redox, ion-exchange, and several surface complexation models (Zhu and Anderson, 2002).
MPA	Maximum Potential Acidity
NAF	Non Acid Forming
NAG	Net Acid Generation
NAPP	Net Acid Producing Potential
Neutralising Potential	The analytical bulk capacity of a sample for neutralising acidity, in units kg H ₂ SO ₄ t ⁻¹ (Morin and Hutt, 1997).
NP	see <i>Neutralising Potential</i>
Open Pit	A surface depression created by the excavation of near surface ore, minerals or coal. In <i>open pit</i> mining, <i>overburden</i> covering the deposit is removed, exposed <i>ore</i> is blasted and moved to a <i>mill</i> , and <i>waste rock</i> is placed in one or more <i>waste rock dumps</i> (INAP, 1999). Also known as open cut or mine void.
Ore	Rock, sediments or soil that contains economically recoverable levels of metals or minerals (Morin and Hutt, 1997).
Orebody or Ore Deposit	A continuous well-defined mass of material containing sufficient quantities of the valuable material to make extraction economical (INAP, 1999).
Overburden	A general term referring to soil and broken rock, lying above <i>ore</i> and <i>waste rock</i> , that can usually be removed without blasting (Morin and Hutt, 1997).
PAF	Potentially Acid Forming
pH	The negative logarithm to the base 10 of the hydrogen ion activity [H ⁺] in solution (INAP, 1999).
Primary mineral	A <i>mineral</i> that came into existence at the time the rock was formed and that retains its original composition and form (INAP, 1999)
Relative Standard Deviation	A measure of how precise the median is, expressed as a percentage. $\text{Relsd} = 100 * (\text{standard deviation} / \text{median})$
ROM	see <i>Run of Mine</i>

Term / Acronym	Description
Run of Mine	Particle size of mined material (i.e. ore or waste rock) prior to crushing or grinding.
Saturation Index (SI)	The logarithm of the ratio of <i>ion activity product</i> to <i>solubility product</i> (Zhu and Anderson, 2002).
Scale-up	The linkages between ARD prediction tests made at increasing scales of particle sizes.
Secondary mineral	A <i>mineral</i> formed by surface processes, usually at the expense of an earlier-formed <i>primary mineral</i> (INAP, 1999).
Secondary mineralisation	The processes whereby secondary minerals are formed. May include alteration, dissolution or precipitation.
SEM	Scanning Electron Microscopy
Solubility Product (K_{sp})	Equilibrium constant for a <i>solubility product reaction</i> (Zhu and Anderson, 2002).
Solubility Product Reaction	A reaction with a solid phase on one side and its constituent ions on the other (Zhu and Anderson, 2002), eg: $\text{CaCO}_{3(s)} = \text{Ca}^{2+} + \text{CO}_3^{2-}$
Static Tests	A procedure for characterising the physical, chemical, or biological status of a sample at one point in time (Morin and Hutt, 1997).
Strip ratio	Ratio of waste rock to ore mined.
TDS	Total Dissolved Salts
Test piles	see <i>Heap Leach Pads</i>
Total metal concentration	Operationally defined as the unfiltered metal concentration in a water sample.
UBV	Upper Box Value
Waste Rock	Rock with insufficient amounts of the economically valuable elements to warrant its extraction, but which has to be removed to allow physical access to the <i>ore</i> (INAP, 1999).
WRD	see <i>Waste Rock Dump</i>
Waste Rock Dump	A mined rock pile containing <i>waste rock</i> (Morin and Hutt, 1997).
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
ZCML	Zinifex Century Mine Limited