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Minimising AMD risk across the mining life cycle

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Table of Contents

Keynote Presentations

Technical Articles

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MINE WASTE AND
WATER MANAGEMENT

Keynote Presentations

INNOVATION IN CHARACTERIZATION STUDIES OF THE WASTE ROCK DUMPS AT THE BINGHAM CANYON MINE, UTAH, USA[1]

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ABSTRACT

The Bingham Canyon Mine is surrounded by more than 6 billion tons (5.4 Bt) of waste rock developed over the open cut mining history from 1903 to present; the surface area of the waste rock is approximately 2,000 hectares. Waste rock dumps have a thickness to in excess of 300 m from crest to sole. From 1930 to 2000, selected portions of the waste rock dumps were actively leached using a ferric-sulfate-based lixiviant to extract copper, whereas other portions have only received meteoric leaching.

From 2011 to present, Rio Tinto Kennecott has studied the evolution and geochemical controls on water quality associated with the waste rock dumps at the Bingham Canyon Mine. In this program, the waste rock dumps have been characterized in detail from field logging and instrumenting 13 paired borings; at 12 of the 13 locations, the borings penetrated the full depth of the dumps, through the pre-mine soil contact, and into bedrock. Borings were installed to depths approaching 275 m below ground surface using roto-sonic drilling methods to enable (1) core recovery and (2) measurement of near in-situ properties. Field logging of the borings included Unified Soil Classification System descriptions, clast lithology, relative oxidation, paste pH, and geophysical methods (gyroscopic, temperature, neutron, and gamma). Core from the borings was analyzed for geotechnical properties (density, grain size distribution, moisture content, plasticity index and limit, and direct and block shear), quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN), modified acid-base accounting (ABA), modified synthetic precipitation leaching procedure (SPLP), hyperspectral analysis by Corescan, and grab samples of water (if encountered). Instrumentation installed within the borings included lysimeters, thermistor nodes, direct temperature sensing (DTS) fiber optic cables, time domain reflectometry (TDR) shear cables, gas (oxygen, carbon dioxide) measurement tubes, and vibrating wire piezometers (VWPs). Additionally, each drill site had multiple measurements of oxygen consumption in the surface layer of the local waste rock.

Data acquired from the borings were linked with historical information (over a period of greater than 50 years) from extensive drilling, mineralogical and litho-geochemical evaluations, hydraulic and tracer testing, and 20 years of seepage flow and water quality data to develop a conceptual model that describes the hydraulic, geochemical, and physical behavior of the waste rock dumps. Pyrite and other sulfide minerals in the waste rock dumps are oxidized by both diffusive and convective ingress of air, producing acidic, high-total dissolved solids effluents, and jarosite that has formed within the waste rock as a secondary phase that stores additional acidity. The dominant air ingress mechanism is convection, which accounts for greater than 90% of the sulfide oxidation within the waste rock dumps. Based on temperature profiles and water balance for the dumps, moisture loss to geochemical reactions is a significant portion of the water budget.

1.0 INTRODUCTION

The existing waste rock dumps at the operating Rio Tinto Kennecott Bingham Canyon Mine occupy a footprint of about 2,000 hectares and contain more than 6 billion tons (5.4 Bt) of material. The dumps were leached for copper recovery from about 1930 until leaching was terminated in 2000.

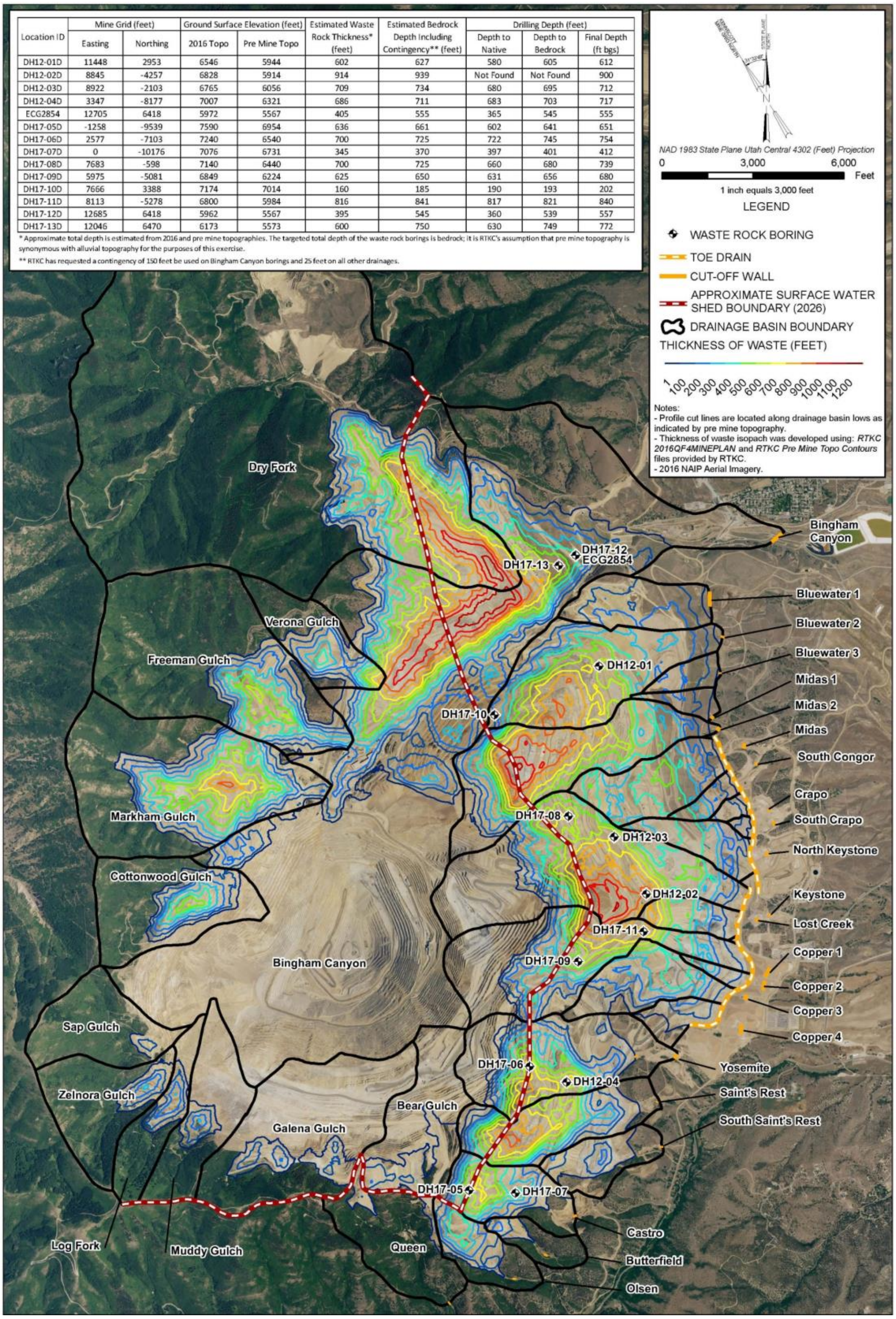
A collection system of cut-off walls keyed into bedrock and down hydraulic gradient of the waste rock dumps is used to capture acidic water flowing (or may be “draining”) from the waste rock. Acidity arises from the oxidation of sulfide minerals, principally pyrite, present in the waste rock, which is moderated by the precipitation of secondary minerals, principally jarosite, and dissolution of gangue aluminosilicate minerals. In some parts of the waste rock, there is sufficient calcite present that in situ neutralisation may be quantitatively important. During operation, the final fate of the captured acidic water is neutralisation and metal precipitation in the tailings pipeline.

The present study extends previous work [Brown et al., 2014] aimed at understanding the mechanisms and rates of geochemical and hydrogeological processes responsible for acid generation and release from the Bingham Canyon Mine waste rock. In formulating the understanding, the study has relied primarily on quantitative results obtained from investigations of the waste rock dumps that has occurred from 2011 through 2019, as well as an extensive suite of prior studies of the dumps.

2.0 CHARACTERISATION METHODOLOGY

During 2012, eight boreholes were placed in the waste rock dumps in four pairs [Brown et al., 2014]. The pairs consisted of one shallow borehole to a depth of about 30 m and one deep borehole, targeted to terminate when bedrock was encountered. Subsequently in 2017, a further 17 boreholes were placed in the waste rock dumps (giving a total of 25 boreholes). There were a further eight paired boreholes (shallow to 30 m and deep to bedrock) and a single deep (but relatively shallow – less than 65 m) borehole. Figure 1 illustrates the locations of the boreholes in the waste rock dumps and the drainages relevant for the collection system on the east-side of the dumps. As can be seen in the figure, the boreholes were paired within drainages (other than the Keystone drainage where three boreholes were installed). One borehole was installed near the valley facing dump crest and one further back in the same drainage, near the surface watershed boundary. Core from the boreholes was analyzed for mineralogy using both the QEMSCAN and CoreScan techniques.

Borehole construction logs were produced for each borehole. A typical construction log is presented in Figure 2. The construction logs convey the depth intervals for bentonite seals and filter (sand) pack media; depths of installation of suction lysimeters, vibrating wire piezometers and gas (oxygen and carbon dioxide) tubes; and the depth of 2 inch (50 mm) fiberglass casing in which direct temperature sensing fiber optic cables were installed. All other instrumentation was installed on the outside of the casing. In the 2012 program of work, thermistor strings were used to measure temperature at about 20 locations in shallow boreholes and 25 locations (below 30 m) in deep boreholes. These thermistors proved to be problematic and were found to fail in the high temperature zones within the dumps. Consequently, they were replaced by fiber optic cables in the 2017 program, which enabled temperature measurements to be made at 1 m intervals within each borehole. The complete fiber optic cable installed were much cheaper than the thermistor strings.



Location ID	Mine Grid (feet)		Ground Surface Elevation (feet)		Estimated Waste Rock Thickness* (feet)	Estimated Bedrock Depth Including Contingency** (feet)	Drilling Depth (feet)		
	Easting	Northing	2016 Topo	Pre Mine Topo			Depth to Native	Depth to Bedrock	Final Depth (ft bgs)
DH12-01D	11448	2953	6546	5944	602	627	580	605	612
DH12-02D	8845	-4257	6828	5914	914	939	Not Found	Not Found	900
DH12-03D	8922	-2103	6765	6056	709	734	680	695	712
DH12-04D	3347	-8177	7007	6321	686	711	683	703	717
ECG2854	12705	6418	5972	5567	405	555	365	545	555
DH17-05D	-1258	-9539	7590	6954	636	661	602	641	651
DH17-06D	2577	-7103	7240	6540	700	725	722	745	754
DH17-07D	0	-10176	7076	6731	345	370	397	401	412
DH17-08D	7683	-598	7140	6440	700	725	660	680	739
DH17-09D	5975	-5081	6849	6224	625	650	631	656	680
DH17-10D	7666	3388	7174	7014	160	185	190	193	202
DH17-11D	8113	-5278	6800	5984	816	841	817	821	840
DH17-12D	12685	6418	5962	5567	395	545	360	539	557
DH17-13D	12046	6470	6173	5573	600	750	630	749	772

* Approximate total depth is estimated from 2016 and pre mine topographies. The targeted total depth of the waste rock borings is bedrock; it is RTKC's assumption that pre mine topography is synonymous with alluvial topography for the purposes of this exercise.

** RTKC has requested a contingency of 150 feet be used on Bingham Canyon borings and 25 feet on all other drainages.

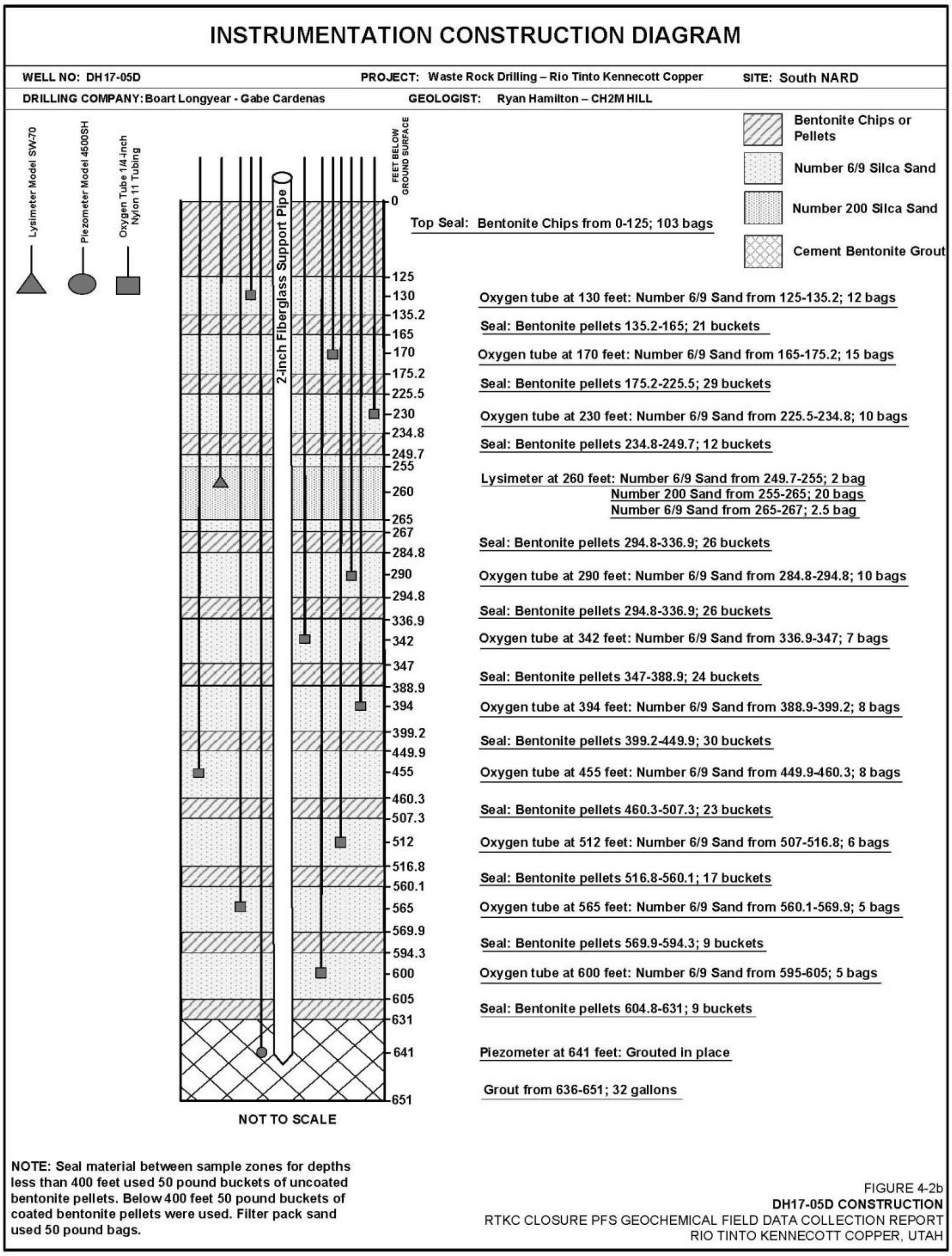
NAD 1983 State Plane Utah Central 4302 (Feet) Projection

1 inch equals 3,000 feet

LEGEND

Notes:
- Profile cut lines are located along drainage basin lows as indicated by pre mine topography.
- Thickness of waste isopach was developed using: *RTKC 2016QF4MINEPLAN* and *RTKC Pre Mine Topo Contours* files provided by RTKC.
- 2016 NAIP Aerial Imagery.

Figure 1: Bingham Canyon Mine waste rock dumps (including Isopach of dump thickness) and drainages with the locations of the thirteen boreholes as well as the collection system on the east side of the waste rock dumps



WELL NO: DH17-05D **PROJECT:** Waste Rock Drilling – Rio Tinto Kennecott Copper **SITE:** South NARD

DRILLING COMPANY: Boart Longyear - Gabe Cardenas **GEOLOGIST:** Ryan Hamilton – CH2M HILL

NOTE: Seal material between sample zones for depths less than 400 feet used 50 pound buckets of uncoated bentonite pellets. Below 400 feet 50 pound buckets of coated bentonite pellets were used. Filter pack sand used 50 pound bags.

FIGURE 4-2b
DH17-05D CONSTRUCTION
RTKC CLOSURE PFS GEOCHEMICAL FIELD DATA COLLECTION REPORT
RIO TINTO KENNECOTT COPPER, UTAH

Figure 2: Typical borehole construction log (for a deep borehole to bedrock)

3.0 OXYGEN AND TEMPERATURE

An example of the temperature and oxygen concentration profiles measured in the dumps is illustrated in Figure 3, together with the lithological log of the borehole (yellow (quartzite), pink (intrusive) and blue (limestone)). Temperature was measured using the fiber optic cables at 1 m intervals and the oxygen concentration was measured at a number of depths in both the shallow and deep boreholes.

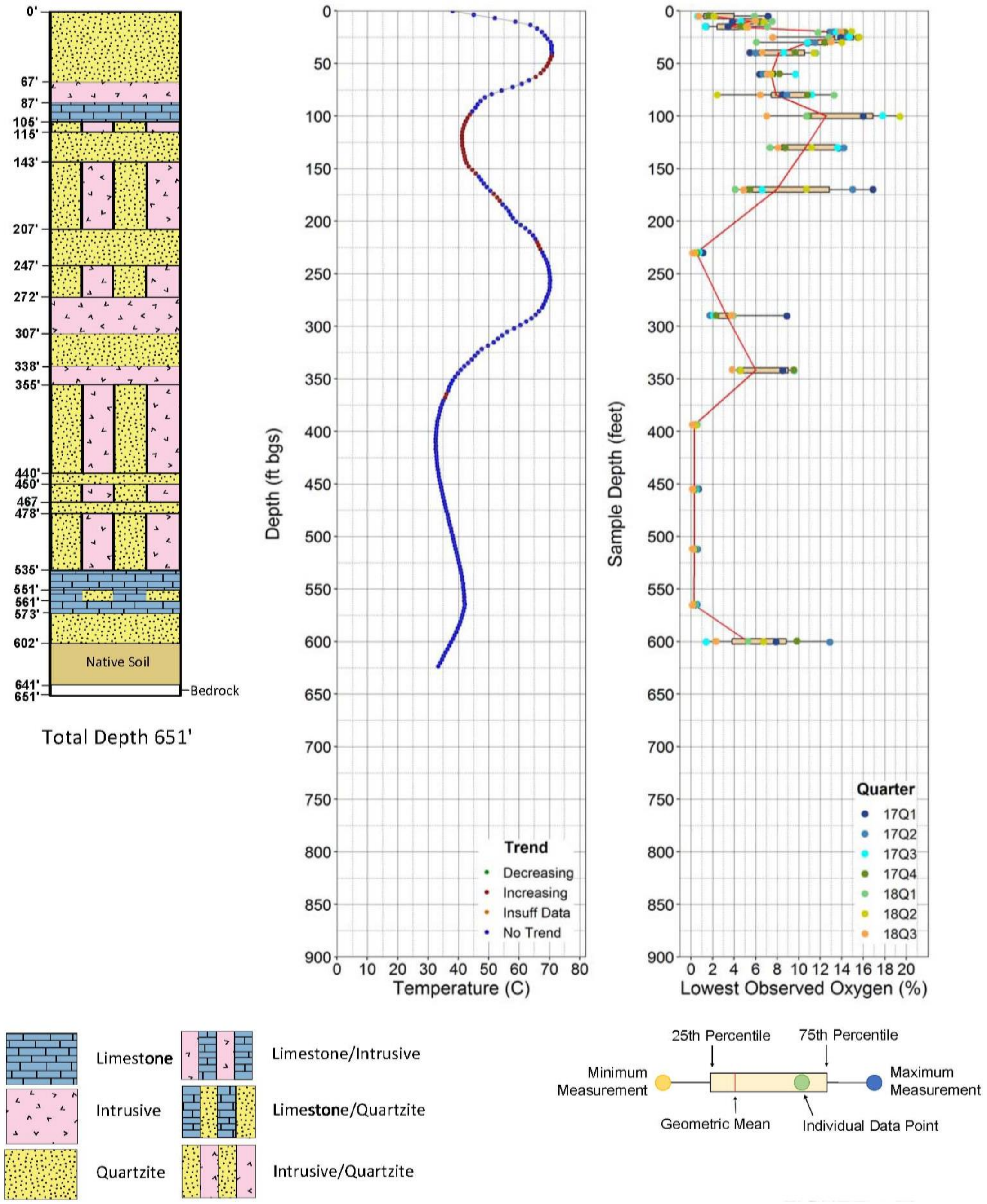


Figure 3: Example lithology log, temperature and oxygen concentration profiles

High oxygen concentrations internal to the dumps are evidence of convective air transport into the dumps. As can be seen in Figure 3, there is elevated oxygen concentrations near the base and the surface of the dump, but also there is significant oxygen concentrations deep within the interior of the dump, with peak concentrations occurring at depths of 8, 20 and 100 m below the dump surface. Diffusion of oxygen occurs near the dump surface, from which the oxidation rate can be determined, but diffusion is the smaller component of air ingress into the dumps, convection being the dominant air ingress mechanism.

At some locations within the dumps, substantial temperatures are reached, with a maximum temperature of 80 °C being recorded. In multiple dumps, the high temperatures are attained within 10 m of the dump surface less than 10 years after material placement. These elevated temperatures occur in dumps that have not been historically commercially leached. Lower temperatures occur in leached dumps as a result of the extensive leaching that occurred over many decades, removing heat from the dumps.

4.0 PYRITE OXIDATION RATE, ACTIVATION ENERGY AND HALF-LIFE

Within waste at the Bingham Canyon mine, pyrite is the dominant sulfide mineral. The oxidation rate of pyrite can be determined from laboratory based measurements or directly in the field. In the present study, a number of different techniques have been utilized to determine the pyrite oxidation rate, including fixed temperature laboratory measurements of talus samples representing all three of the main mine lithologies (quartzite, intrusive and limestone). A summary of these measurements is shown in Table 1, where measurement results from the present study have been coupled with measurement results from earlier studies.

materials from both the Bingham Canyon pit (talus) and waste rock

Table 1: Measured geometric mean pyrite oxidation rates using different methods and on different

Lithology or Waste Rock	Measurement Type	Oxidation Rate kg(O_2)/m^3/s	log(Rate)	Std Dev.	Count	Maximum	Minimum	Sulfate Release Rate mg(SO_4)/kg/a
						kg(O_2)/m^3/s		
Quartzite	Laboratory	3.98×10^{-8}	-7.40	0.40	31	2.24×10^{-7}	7.28×10^{-9}	1051
Intrusives	Laboratory	3.46×10^{-8}	-7.46	0.54	21	5.38×10^{-7}	5.43×10^{-9}	914
Limestone	Laboratory	3.25×10^{-8}	-7.49	0.85	11	1.49×10^{-6}	4.26×10^{-9}	858
Waste Rock	Laboratory	4.42×10^{-8}	-7.35	0.43	13	3.10×10^{-7}	1.39×10^{-8}	1168
Waste Rock	O_2 Concentration	5.12×10^{-8}	-7.29	0.80	13	8.59×10^{-7}	8.03×10^{-10}	1353
Waste Rock	O_2 Flux	1.23×10^{-8}	-7.91	0.49	24	5.57×10^{-8}	3.58×10^{-10}	326
Waste Rock	O_2 Flux [a]	2.66×10^{-8}	-7.57	1.07	7	4.60×10^{-7}	8.20×10^{-10}	703
Waste Rock	Natural Conv. [a]	2.37×10^{-8}	-7.63	1.04	9	4.25×10^{-7}	6.11×10^{-10}	625
All	**All**	**2.93×10^{-8}**	**-7.53**	**0.64**	**129**	**1.49×10^{-6}**	**3.58×10^{-10}**	**773**

a These data were obtained in earlier studies of RTK waste rock [RT T&I, 2009; Brown et al., 2014].

The data shown in Table 1 illustrate that regardless of the measurement technique and the material on which the measurements were made, the calculated geometric mean pyrite oxidation rates were all similar. This equivalence is surprising given the rates obtained from all measurements cover nearly four orders of magnitude. As shown in the table, the geometric mean pyrite oxidation rate for all 129 measurements is 2.93 x 10-8 kg(O2)/m3/s which is equivalent to a sulfate release rate of 773 mg(SO4)/kg(rock)/a.

Eary [2015] tabulated pyrite oxidation rate data where the measurement temperature had also been recorded. Surprisingly, there is a lack of data available in the literature where both the pyrite oxidation rate, and the temperature at which it was determined, have been reported. The data of Eary were supplemented with the datum (Table 1 – 2.93 x 10-8 kg(O2)/m3/s; determined at approximately 20 °C) from the present study. From the data tabulated by Eary (with the data reported by Linklater et al. [2006] corrected to 20 °C), an activation energy of 84 kJ/mol is determined. However, Eary recognised that the oxidation rate is also dependent on the pyrite (or sulfide sulfur) content (i.e. the rate increases as the sulfide content increases). A multiple regression on the available data, using both the inverse of temperature and the sulfide content, leads to an activation energy of 71.1 kJ/mol. Knowledge of this activation energy is critical given the very high temperatures recorded in the Bingham Canyon Mine waste rock dumps.

The pyrite oxidation rate can be described by a first-order reaction. As such, the half-life (defined as the time it takes the quantity of pyrite to decrease by half (i.e. 2% to 1% or 1% to 0.5%, etc.)) of pyrite within the dumps can be determined. The pyrite half-life determined for a characteristic Bingham Canyon mine unleached dump is 53 years whereas that for a characteristic Bingham Canyon mine leached dump is, not surprisingly, shorter at 37 years. The current pyrite content of the waste rock dumps is 3.5% to 4%.

5.0 MINERALOGY

Based on evaluation of the drilling results, models for two characteristic sets of mineralogy, for unleached dumps and leached dumps, were established. From evaluation of the details of the mineral composition ranges, it was clear that within and across dumps, mineral compositions are not approximately normally or log-normally distributed. Therefore, it was determined that the best estimator for central tendency representing characteristic conditions were median values for unleached and leached dumps. These median values are provided in Table 2.

Table 2: Characteristic median mineralogy (wt.%) of unleached and leached waste rock from QEMSCAN mineralogical analysis in the 2012 and 2017 drilling programs

Mineral	Median Observed Mineralogy of Unleached Waste Rock Dumps (wt%)	Median Observed Mineralogy of Leached Waste Rock Dumps (wt%)
K-feldspar	11.74	11.07
Anorthite	1.41	1.09
Albite	3.82	2.94
Muscovite	3.99	4.90
Kaolinite	0.78	1.24
Chlorite	1.94	2.46
Pyroxene (diopside)	0.72	1.11
Amphibole (tremolite)	1.78	0.55
Talc	1.45	1.06
Biotite (phlogopite)	2.81	1.09
Garnet (grossular)	0.30	0
Calcite	0.93	0.21
Gypsum	0.06	0.40
Pyrite	3.62	3.86
Quartz	63.1	64.8
Wollastonite	0	0
Jarosite	0.69	0.59
Iron oxides ($Fe(OH)_3$)	1.03	0.88

Inspection of the data in Table 2 shows that the two characteristic mineralogical compositions are quite similar. The main differences are the much lower calcite content, and greater gypsum content, in the leached dumps. This would be expected due to the oxidative lixiviant used in leaching. In general, the more reactive aluminosilicate minerals also have a lower content in the leached dumps.

6.0 CONCEPTUAL MODEL

A conceptual model of the dump water balance and hydraulic system has been developed, the elements of which are illustrated in Figure 4b. The model has been developed based on review of site information and consultation with Bingham Canyon mine operations personnel, calculations and numerical modelling, and development and calibration of water balance models of each waste rock dump drainage.

The climate at the Bingham Canyon Mine differs significantly from the lowest to the highest waste rock elevations. On average, mean annual precipitation varies from 18.5 inches (470 mm) at an elevation of 1,700 m to 30.5 inches (775 mm) at 2,170 m, with more precipitation during winter months falling as snow at higher elevations. The estimated average annual potential evapotranspiration is 37.1 inches (940 mm) at 1,700 m and 34.3 inches (870 mm) at 2,170 m. Waste rock dump surfaces at higher elevations will experience higher net infiltration rates than at lower elevations, and most net infiltration will occur in the winter and spring months when evapotranspiration is lowest.

Net infiltration rates from meteoric precipitation are relatively high for uncovered, unreclaimed conditions due to the nature of the mine climate and the permeability of the waste rock. Predicted net infiltration for uncovered waste rock is approximately 40% to 65% of mean annual precipitation for low and higher elevations, respectively.

Waste rock is generally mined and placed at a low moisture content of about 4 wt.%, which is below “field capacity”, the moisture content that is necessary when percolation through waste rock due to gravity becomes significant, and below the predicted moisture content in equilibrium with atmospheric conditions. As a result, some net infiltration will go toward satisfying this moisture deficit.

Some of the porewater percolating through the dumps is lost to chemical reactions between the moisture (liquid porewater and vapor) and the reactive minerals within the waste. Sulfide oxidation is the primary chemical reaction that drives a series of reactions that consume water. The amount of water lost to chemical reactions depends on the thickness of the dumps, the internal dump temperature, oxygen content, pyrite oxidation rate, and the amount of available moisture. The water lost to chemical reactions is likely limited by moisture availability in the thickest and warmest portions of the dumps, particularly below areas where new waste rock is being placed. These areas might contribute less water to the down-gradient collection system than other areas.

Given the proximity of the dumps to the pit, some portion of the dump seepage reports to underground workings, pit dewatering wells, and the pit. Percolation of distributed recharge through the dumps occurs predominantly as unsaturated flow through the fine fraction (-5 mm), which is on average 34 wt.% of the waste rock. The hydraulic response times through the dumps are much shorter than porewater residence times. The hydraulic response times are generally on the order of 6 to 18 months for most drainages, whereas the pore water residence times are of the order of multiple decades. As a result, the seepage flow rates may change seasonally, but the seepage chemistry remains relatively invariant.

The conceptual model of geochemical and physical processes (other than hydrogeological) is illustrated in Figure 4a. The figure shows that air ingress into the dumps occurs by both diffusive and convective mechanisms. The convection of air into the dumps typically occurs at the toe of dumps through coarse zones created because of material segregation by mass that occurred during the top-dumping process (often from heights of 400 to 600 ft). Similar segregation may also occur on shorter lifts in the dumps, when additional material is placed on top of existing material in a dump.

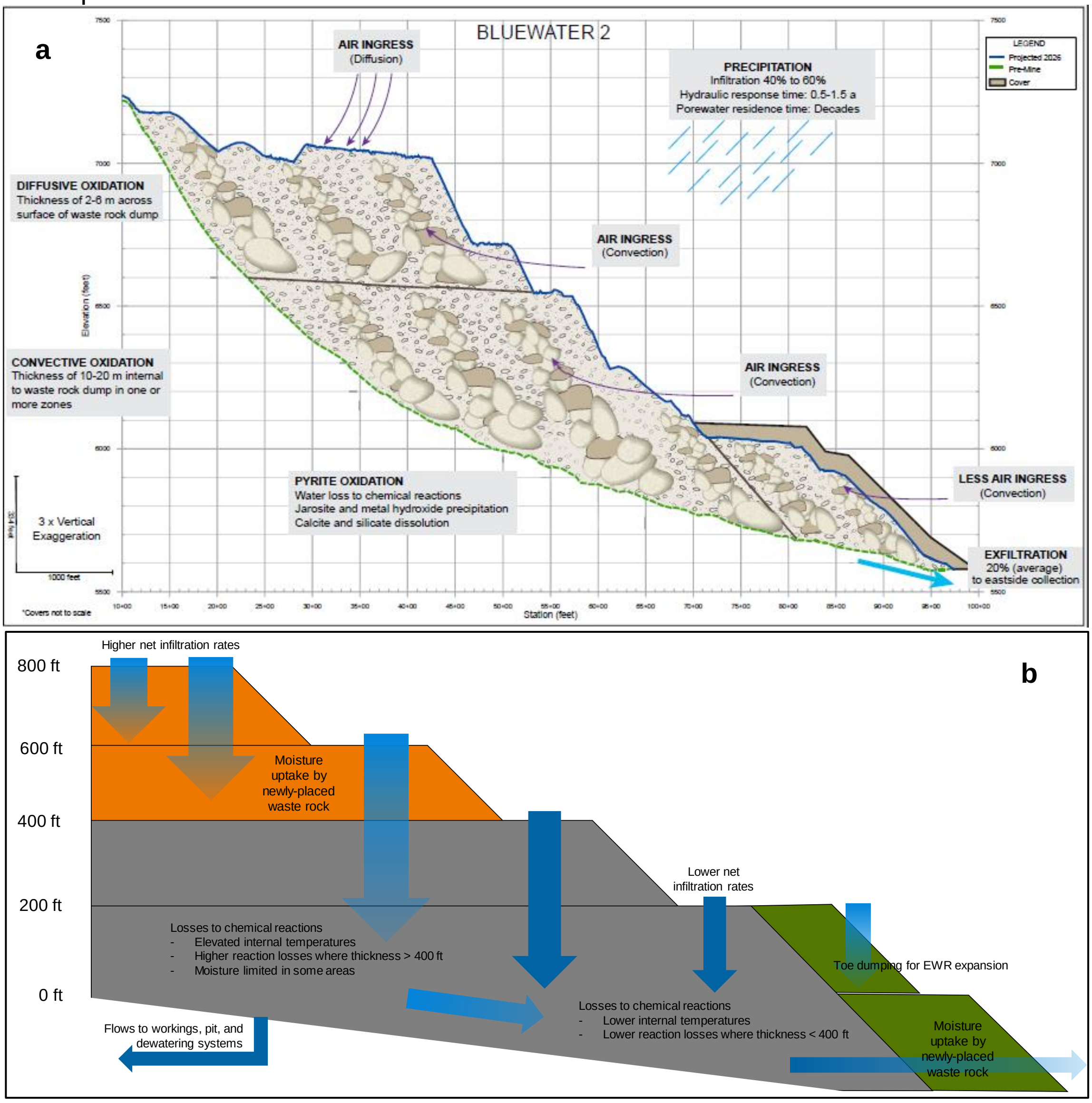


Figure 4: Conceptual model of waste rock dumps (a) air supply and (b) hydrogeology

The diffusion of air into the dumps occurs in a narrow thickness at the top and on the slopes of the dumps that is initially of the order of 2 to 6 m. The depth of diffusion is based on the measured rates of oxygen consumption, the observed oxygen concentrations in the pore space of the dumps and laboratory-based pyrite oxidation rate measurements. As indicated in Figure 4a, convective air supply occurs principally from the base, although there may be a smaller supply that occurs through the slopes of the dumps. Oxidation occurs in the diffusive zones throughout the whole thickness of oxygen diffusion, but also in deeper zones as a consequence of the convective air supply. The oxidizing layers supplied by convective air ingress may be immediately beneath the diffusive ingress zone or may occur quite deep within the dump (i.e. well away from the dump slopes). The thickness of individual convective oxidizing layers is of the order of 9 to 20 m. Outside of these oxidizing zones, oxidation may still occur, but at a much lower rate. The flux from the diffusive zones is unlikely to be greater than 10% of the flux from the oxidizing zones which, considering the thickness of the non-oxidizing zones, suggests that an oxidation rate about two orders of magnitude lower (or less) than in the oxidizing zones. Convective air supply into the dumps arises due to differences in air density (caused by temperature and/or pressure differences) within the dump as compared to ambient conditions (i.e. hotter temperatures inside the dumps resulting from heat generated from the oxidation of pyrite and/or lower pressures resulting from the consumption of oxygen in air through reaction with pyrite). Convection also redistributes heat and moisture within the dumps.

7.0 CONCLUSIONS

Paired and instrumented boreholes have been placed in the waste rock dumps at the Bingham Canyon Mine that extended the full height of the dumps (up to about 300 m). Data acquired from the boreholes and dump surface, as well as other hydrogeological data, were utilized to characterise the geochemical mechanisms occurring in the dumps that lead to generation of acidic effluent. These data have been combined with other information to demonstrate that oxidation of pyrite within the dumps occurs as a result of both diffusive and convective air supply into the dumps, with convective supply being dominant. Moreover, due to the very high temperatures (up to 80 °C) observed in the dumps, leading to high rates of pyrite oxidation, the consumption of water due to chemical reactions has been found to be a very important aspect of the water balance for the dumps.

A detailed understanding of the long-term evolution of seepage from the Bingham Canyon mine dumps is required. This information will be utilized to develop long-term plans for management of seepage from the dumps which is likely to remain at levels similar to those at present for many decades into the future. The goal of increasing the understanding of waste rock behavior at the Bingham Canyon mine, required a program of work that has involved a significant number of innovative aspects. These innovations and the magnitude of the total data collection and analysis program have enabled a substantially greater amount of understanding to be gained from the work. The work scope and its applications highlight what is needed to be undertaken at mine sites with long operational histories.

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BHP AMD MANAGEMENT STANDARD: A GLOBAL APPROACH TO REDUCING GEOCHEMICAL RISK AND MINIMISING CLOSURE UNCERTAINTIES

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ABSTRACT

Acid and Metalliferous Drainage (AMD) is one of the key risks facing the mining industry worldwide. If not properly managed and/or not identified in a timely manner, AMD has the potential to decrease environmental values for generations to come.

Ore extraction generates vast volumes of mineral waste (waste rock and tailings) which are stored in perpetuity at the mine site. Some of these materials are not inert and when in contact with air and water can react, generating poor quality water and compromising operational and closure environmental objectives. Understanding the geochemical behaviour of waste rock and tailings is therefore key to identifying risks and opportunities which support effective mineral waste management strategies across the mining value chain and progress toward an environmentally sustainable future that minimises closure liabilities.

To ensure AMD risk is recognised and managed uniformly across its portfolio, BHP developed a Global AMD Management Standard for implementation across all operations, including closed sites. The AMD Management Standard provides a management framework to support the consistent, simple and sustainable global management of AMD risks. This ensures mines are planned and operated to be environmentally smart and modern, geochemical risk management is not an afterthought but a key driver, and environmental sustainability is actively pursued to reduce closure liabilities.

The AMD Management Framework, on which the Standard is based, was adapted from industry leading practice guidance, ensuring it applies to multiple regions. The framework also comprises sequential requirements throughout the mining life-cycle. It is an iterative framework with an adaptive management approach that is designed to incorporate new data, information and management opportunities into AMD risk assessments and mine plan revisions.

Keywords: Acid and Metalliferous Drainage, AMD, AMD Management, AMD Risk

1.0 INTRODUCTION

Acid and metalliferous drainage (AMD) is recognised internationally as one of the most difficult and significant environmental issues facing miners and regulatory bodies in the pursuit of a sustainable mining industry. This is due to the ability of AMD discharge to persist for hundreds, if not thousands of years, impacting environmental values and requiring sustained financial commitments to mitigate and manage. In Australia, for example, Mt Morgan Mine in Queensland is predicted to generate AMD for up to 500 years (Gasparon et al. 2007), while the rehabilitation cost of the Rum Jungle Mine in the Northern Territory is expected to be in the hundreds of millions of dollars (DPIR, 2019).

To address current and future social licenses to operate, there is a need to develop industry leading practice approaches that adequately manage potentially AMD generating materials. As a result, a number of AMD related guidance documents (e.g. Commonwealth of Australia 2016a; Department of Mines and Petroleum 2015; Sernageomin 2015) have been developed. These documents often set minimum guidelines for AMD management. However, to achieve a sustainable mining industry which manages potentially AMD generating material, these minimum guidelines must be used in combination with other key industry standard sources including the *Global Acid Rock Drainage (GARD) Guide* (INAP, 2009) and the *Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials* (Price, 2009.

Mining generates mineral waste such as waste rock and tailings, however, if problematic materials are not properly identified and managed during operations, mine waste and exposed rock surfaces could potentially result in AMD. Once AMD processes take hold, sources of AMD and impacted waters (if any), are difficult to manage and can represent a significant portion of a site's closure liability.

Recognising the AMD risk to closure, BHP developed a global AMD Management Standard (*the Standard*) outlining the minimum requirements for consistent and practicable AMD management across all BHP's functions and operations, including closed sites. The Standard describes AMD management objectives, requirements and supporting documents upon which the Standard is based.

2.0 ACID AND METALLIFEROUS DRAINAGE IN THE BHP CONTEXT

Although AMD can have various meanings in different regions, BHP has adopted the South Pacific nomenclature (Price, 2009) for AMD which is defined as Acid and Metalliferous Drainage. AMD is a term used to describe low-quality seepage or drainage that has typically been affected by the product of sulphide oxidation. AMD can be acidic, pH circum-neutral, alkaline or saline (INAP, 2009). Whether contact water is acidic and metalliferous, neutral/alkaline and metalliferous or saline (high sulphate, plus and minus calcium and magnesium) will generally depend on the relative proportion of sulphide minerals (acid generating) and carbonate minerals (acid neutralising) in the source materials.

Several terms have been introduced to describe the different types of drainages possible: ARD (acid rock drainage), AMD (acid mine drainage), NMD (neutral and metalliferous drainage, neutral mine drainage), MD (metalliferous drainage), SD (saline drainage), and ARD-ML (acid rock drainage-metal leaching). While the chemistry of these drainages may vary, they all typically result from sulphide oxidation processes with neutralisation reactions (or lack thereof) controlling the final pH, dissolved metal concentration and speciation.

In the definition used by BHP, AMD encompasses the release of low pH drainage waters otherwise described as Acid Rock Drainage (ARD), and of high metals or salinity drainage in non-acidic waters, such as neutral metalliferous drainage (NMD) and/or saline drainage (SD).

3.0 AMD MANAGEMENT AT BHP: THE WESTERN AUSTRALIA IRON ORE JOURNEY

Each year, mine operators across the globe move significantly more mineral waste material than saleable product. BHP is no exception. This mining waste, some of which potentially contains AMD generating materials, is stored in landforms that remain on site well beyond the operating mine life. As a result, AMD risk collectively represents one of the key closure and operational environmental management liabilities.

When BHP's Western Australia Iron Ore (WAIO) reviewed how the AMD risk was managed across its' Pilbara mines, a concentrated long-term project was initiated to address the areas for improvement and implement a consistent and proactive management approach.

The beginning of WAIO's six-year journey was the development of a WAIO AMD Management Standard (the WAIO Standard). The WAIO Standard outlined AMD management requirements for the life of mine ensuring risks associated with AMD were identified and controlled. This was a multi-faceted approach that incorporated a range of activities by WAIO functions and operations to enable effective AMD management. Detailed guidelines for waste management and an AMD risk assessment procedure with associated tools were then developed. To support implementation and adoption, an ongoing WAIO-wide AMD risk education program including annual short courses provided to personnel from multiple sites and disciplines (including mine planners, production managers, environment specialists, geologists, and hydrogeologists). The AMD basics short course aimed at developing a greater awareness of AMD risk while educating those responsible for implementing various aspects of the WAIO Standard.

The outcome is a consistent and practicable AMD Management System spanning all WAIO functions and operations which has become ‘business as usual’. The AMD Management System ensures AMD risk is consistently identified, managed and controlled throughout the life of mine from exploration through mine planning, operations and closure.

WAIO’s AMD Management System now provides a management maturity comparison for other BHP assets (see Figure 1) and established BHP as an industry leader in AMD management.

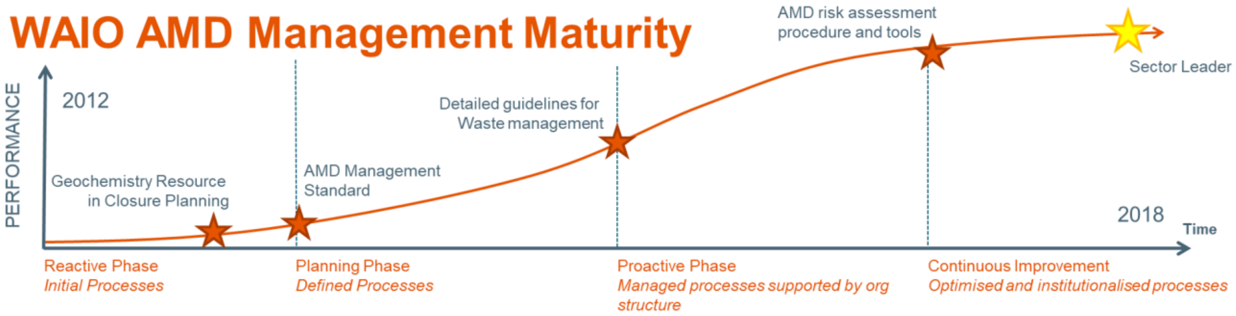

Fig. 1. An AMD management maturity curve that demonstrates WAIO’s journey. This maturity curve is used as a differentiator for assets within the company to comparatively view the various degrees of AMD management maturity

GLOBAL AMD MANAGEMENT STANDARD

With WAIO’s success in reducing AMD risk and uncertainty, BHP developed a Global AMD Management Standard. This Standard states BHP’s overall AMD Management Strategy (*the AMD Strategy*) and then details the framework for which the AMD Strategy can be executed. Compliance to the Standard informs several elements of BHP’s Closure Management Process, specifically baseline data and knowledge, risk assessment and ongoing implementation and review of Closure Management Plans.

AMD MANAGEMENT STRATEGY

Over the past 20 years, our understanding of how waste management methods control the generation and subsequent release of AMD has significantly improved (e.g., Wilson et al. 2011; Miller 2014). However, this increased understanding and awareness of AMD processes has not resulted in equal improvement in waste management across the industry. This lag between understanding of AMD processes and the implementation of effective AMD management strategy is likely due to a perceived difficulty in executing preventative AMD management methods. For example:

- there is a perception that the segregation and differential handling of high-risk waste rock (a preventative measure) will automatically result in greater haulage costs and/or potential delays to production. However, if waste rock classification systems are inbuilt into short-term mining and grade control models, waste can be moved without delay provided QA/QC processes are in place to validate the approach and the classification (performance monitoring). In some cases, optimising long-term waste haulage routes over the life of the mine can also result in lower total haulage costs compared with haulage routes optimised for the short-term.
- there are also perceived difficulties in constructing complex oxygen reducing layers within a waste rock dump to inhibit oxidation occurring (preventative measure). This can

subsequently lead to the continued selection of mitigation and control and treat methods, which may not be the best approach for a sustainable mining industry. Past designs of oxygen inhibiting structures may have been based on civil construction projects, however simple thin lift construction methods can easily be executed with available mining equipment.

Throughout WAIO's AMD Management journey, BHP has worked through these perceptions to change the way AMD management is approached. This site-based evidence of successful execution of preventive AMD management methods has been the driver for the development of the Global AMD Strategy.

BHP's overarching AMD Strategy is that prevention (source control) of AMD rather than treatment in perpetuity is the preferred lowest risk approach. While this is easier to execute at operational mines, this preferred management approach is still assessed for legacy sites where waste has already been placed and water collection and treatment systems are established. Optimising solutions for legacy landforms will drive future research and development and facilitate the movement of these sites towards source control, where possible.

AMD MANAGEMENT FRAMEWORK

BHP's AMD Management Framework (Figure 2) is adapted from industry leading practice (Commonwealth of Australia 2016a; INAP 2007; Price 2009; Sernageomin 2015) and is underpinned by six key steps of AMD Management:

- Closure Goals
- Prediction
- Prevention
- Minimisation
- Control and Treat
- Performance Monitoring.

Setting closure management plan objectives – the first step of BHP's closure management process (Our Requirements Closure) – is also the first step of AMD Management.

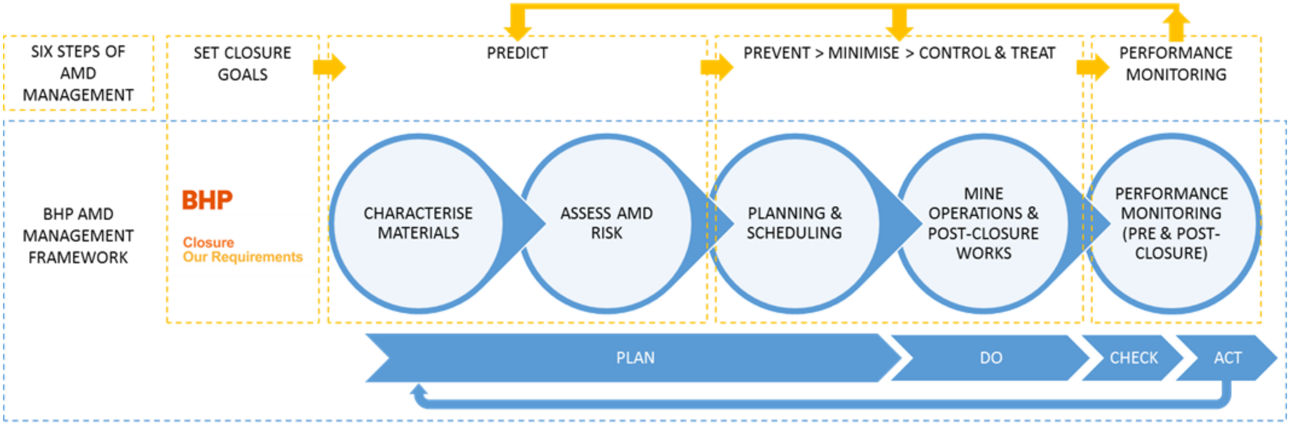

Fig. 2. How BHP's AMD Management Framework links with the Six Steps of AMD Management.

The framework uses a Plan-Do-Check-Act (PDCA) approach to facilitate continuous improvement. This consists of sequential requirements throughout the mining life cycle from early mine studies, mine planning, mine development and operations, through to closure and post-closure. Effective PDCA cycles are essential for successful AMD management. They provide a rigorous process for:

- reconciling actual performance against the plan
- identifying and implementing changes to either recover to the original plan or improve on the original plan as a continuous improvement process.

This inbuilt PDCA approach within the framework facilitates adaptive management and is designed to incorporate new information and technologies (R&D) into AMD risk assessments, mine plan revisions and closure plan updates.

Characterise Materials

Potential AMD sources include any materials such as waste rock, ore, low-grade / mineralised waste stockpiles, pit wall/floor rock, underground workings' wall rock, tailings, process residue and heap leach materials that have the potential to generate contact water of poor quality. All potential AMD sources are identified by the development of an early stage AMD Conceptual Site Model (CSM) which provides an initial fundamental view of AMD sources and AMD potential. Receptors and pathways are then identified and incorporated into the subsequent AMD Risk Assessment phase. Following the definition of the CSM, geochemical test work is required to assess the geochemical properties of the key sources and identify potential challenges and opportunities. The specific minimum requirements for materials characterisation include:

- development of an early stage AMD Conceptual Site Model (CSM) to identify all potential AMD sources and identify beneficial materials
- where ongoing drilling programs are available (operational sites), appropriate drilling programs are selected to provide samples in conjunction with other relevant BHP standards, e.g. Geoscience Activity Planning
- where ongoing drilling programs are unavailable (e.g. legacy sites or legacy landforms), a risk-based approach is used to identify appropriate sampling methods
- static and kinetic geochemical testing programs are conducted in addition to physical testing programs with parameter selections linked with other relevant BHP standards (e.g. Geoscience Data Collection, Processing and Analysis.
- maintaining an AMD data management system that interfaces with geological and assay data located on an enterprise-wide database.

BHP has also developed an AMD Management Standard Guidance Note to provide additional details for the execution of the Framework. This includes additional details such as recommended sampling frequencies and laboratory testing parameters.

Assess AMD Risk

AMD risks are assessed through source definition (characterisation of potential AMD sources), identification of pathways and potential receptors. The early stage AMD CSM developed prior to the Characterisation of Potential AMD Sources is refined at this stage within the Framework to incorporate pathways and receptors.

Specific minimum requirements include:

- refining the AMD CSM and completing a preliminary assessment of potential AMD source materials. This should be made possible by collecting data in the previous stage.
- assessing the mobilisation risk (including modelling where necessary) from potential AMD sources, that identify potential pathways for mobilisation.
- assessing potential AMD sources and mobilisation risk with respect to protecting key receptors, that is assess the risk in the context of a source-pathway-receptor model using the CSM as the template for this assessment.
- communicating the outcomes of the AMD risk assessment to all relevant stakeholders (water planning, operational management and closure planning). This ensures the AMD risk is understood and incorporated into related planning.
- Refining AMD CSM based on results of the AMD risk assessment, additional characterisation studies and geochemical modelling, water management strategies, climate change assessments and closure objectives.

Planning and Scheduling

At this stage of the AMD Framework, plans, procedures and designs for operational and post-closure works to manage AMD risks are developed. As per the hierarchy of controls and BHP's overarching AMD Strategy, preference is given to prevention strategies where achievable.

Specific requirements include:

- estimating the quantity and schedule of all potential AMD sources and beneficial materials in mine plans through the life of asset. For this to be completed, AMD classifications are developed and incorporated into mining models to facilitate AMD management planning for problematic and beneficial material alike.
- where possible, avoiding potential AMD sources through modification of pit and/or underground designs and waste scheduling. Another way to avoid disturbing potential AMD sources includes adjustment of drill and blast practices, and strategic placement of haul roads and infrastructure.
- selectively managing AMD sources that cannot be avoided. This is done by embedding AMD classification systems within mining models.
- for sites where sub-aqueous storage of AMD sources is possible, considering final storage designs and placement techniques for both AMD generation rate and the time between placement and inundation. That is, if the time to inundation is a significant period of time, due to the slow rebound of the groundwater table post mining, then some preventive oxidation management methods may be required (e.g. thin lifts) to manage oxidation of sulfides between the time of placement and the time of groundwater rebound.
- Developing final landform designs for sub-aerial storage of AMD sources based on principles that prevent or minimise AMD risk. Designs however must be achievable with the characteristics of the available materials, both temporally and spatially.

Mine Operations and Post-Closure Works

Operational and post-closure construction procedures are developed to verify that AMD risks are being properly managed to achieve the AMD Strategy. The procedures developed and implemented at an individual site also depend on the specific management methods employed at that site and are to be consistent with the AMD risk of that site.

General AMD management procedures that may be included are:

- Ongoing geochemical testing to:
    - collect geochemical data on potential AMD sources and geochemical nature of the sources to allow ongoing refinement of the AMD classifications and verification of the predictive models.
    - collect geochemical data and ensure QA/QC procedures are appropriate so that if required, a site can demonstrate, with an acceptable degree of certainty, the characteristics of materials placed in specific mine domains.
- AMD classification refinement to:
    - facilitate continuous refinement of a site's AMD classification by incorporating data collected under the ongoing geochemical testing procedure, or through other geochemical studies.
    - continuously refine AMD classifications to ensure appropriate management of high-risk material and handling of low-risk waste rock, and that beneficial material is identified and used appropriately.
- Mining model verification to:
    - provide continuous assessment of the accuracy of the mining model and the AMD classes through operational geochemical testing and refinement of the mining model.

  - check and validate the AMD classes to ensure the correct placement of potential AMD sources.
- Materials movements tracking to:
  - ensure appropriate handling of different types of potential AMD sources and beneficial materials.
  - establish appropriate material movements records for regular reporting purposes.
  - minimise the amount of re-handling.
- Materials placement and compliance to plan to:
  - ensure appropriate management of all potential AMD sources excavated during mining and construction of AMD management supporting structures within the specific landform, such as lift heights, cover thicknesses, etc.
  - minimise the exposure of sulfidic waste rock to water and oxygen (e.g. minimise the oxidation of sulfides and mobilisation of oxidation products – formation and release of AMD).

Each procedure developed should include a Trigger Action Response Plan (TARP). This defines the actions to be taken when conditions change from normality and have the potential to trigger an event. Primarily, TARPs should be developed for an AMD incident and include the key parameters that would facilitate the identification of that specific AMD incident occurring. A TARP will identify a series of hazard levels (triggers) for an operation that will range from normal to extremely abnormal. Each level will then be associated with a range of controls and actions, together with responsibilities for taking the appropriate actions. Regular reviews of the risk assessments and of research and monitoring will ensure triggers and planned action within the TARPs are appropriate.

Performance Monitoring (Pre- and Post-Closure)

A key aspect of performance evaluation, which assesses the response of a system while referencing specific criteria, is the ability to provide early warning of developing trends (triggers for change management) and facilitate the reporting of environmental performance to regulators and stakeholders (Commonwealth of Australia 2016b). Performance data also provides supporting evidence that the AMD management procedures proposed were followed and successful, providing confidence to regulators and stakeholders that closure objectives proposed are achievable. The overall performance of potential AMD source management is to be assessed by monitoring (both leading and lagging) indicators to validate AMD predictions and the performance of management strategies.

Specific requirements include:

- developing a performance evaluation process to provide early warning of developing trends (triggers for change management) such as monitoring real time parameters e.g. in-situ oxygen and temperature in waste rock dumps (WRDs) and tailings storage facilities (TSFs).
- monitoring surface and groundwater quality according to water management strategies throughout mine operation and throughout the post closure period to assess the effectiveness of AMD source management.
- completing ongoing AMD assessments throughout the life of asset to confirm predictions regarding AMD potential particularly with a change to the base case mine plan. This ensures closure objectives in regard to AMD can be achieved and includes updating the AMD CSM based on new information and the transition of AMD models from operations to closure to inform operational, closure, and water management strategies.
- verifying and revising AMD management procedures to address any changes in understanding of AMD risk.
- regular reporting of key monitoring parameters (leading and lagging) and key risk indicators. This assists with routine regulatory reporting requirements and real-time identification of

developing trends.
- Reviewing and documenting the design and operating effectiveness of AMD management controls on a risk-based frequency.

4.0 IMPLEMENTATION STRATEGY

BHP is implementing the Standard via a phased and risk-based approach (noting that the requirements are minimum). Where situations exist that make compliance to the Standard problematic, an ‘if-not, why-not’ process is utilised. For example, on some of the closed legacy sites active exploration drilling programs are not taking place to facilitate the collection of data. In these situations, a tailored and fit-for-purpose approach is required.

Global AMD training modules to improve understanding of AMD risks have been developed and provided to relevant disciplines that have the ability to influence the management of AMD, e.g. exploration geologists, hydrogeologists, mine planners and technical operational personnel (production supervisors, geologists and mining engineers).

BHP’s overall aspiration is to have fully embedded management process across all assets enabling proactive management of AMD materials. The framework will also help facilitate a culture shift within BHP ensuring:

- mines are planned and operated to be environmentally smart and modern
- geochemical risk management is not an afterthought but a key driver
- environmental sustainability is actively pursued to reduce closure liabilities.

The framework should also minimise the likelihood of in perpetuity management being required.

5.0 CONCLUSIONS

AMD presents a key challenge to the successful closure of mines around the world. The BHP Global AMD Management Standard is a step change development that enables global consistency in the characterisation and management of problematic and beneficial materials across the minerals portfolio. Ultimately, the Standard will also drive the acceptance of AMD management as a business as usual, routine activity.

6.0 ACKNOWLEDGMENT

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BUILDING MINE ROCK STOCKPILES FOR SUCCESSFUL AMD MANAGEMENT AT CLOSURE

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ABSTRACT

The mining sector worldwide is experiencing significant increases in closure costs. Direct and indirect measurement of acidity loads from various minesite domains at more than 40 sites over the past 25 years has revealed that disposed mine waste rock materials are responsible for the majority of ARD / AMD pollution (60-80%) at most mine sites. This pollution is the primary cause of increasing closure expenses.

Conventional mine rock stockpile (MRS) construction typically involves disposal of well sorted, relatively dry rock materials from the back of tip-trucks down angle-of-repose slopes of previously disposed material with wide particle size distributions. This method minimises costs associated with loading, hauling and placing rock, while maintaining geotechnical stability of the MRS. However, it also optimises sulfide oxidation and minimises acid neutralisation; the approach is therefore largely responsible for long-lived water quality impacts post-closure.

Improved construction methods are available and new approaches are emerging. These are principally focused on improved control of gas transport within MRSs, both during and post construction, which can be influenced by gas disruption layers / trafficked layers, encapsulation of high-risk materials, decreasing tip head heights, and paddock dumping in thin compacted layers from the base up. Strategic placement of oxygen consuming, and pyrite passivating materials can also lower acidity production. Each of these construction methods perform differently under different physical and chemical conditions (eg. topography, climate, geochemistry) and can also be combined to achieve optimum outcomes. There are several key and immediate risk management opportunities that can be realised as a result of these improved construction methods.

Numerical modelling of acidity generation from conventional and improved MRS construction methods illustrated the ability for the improved methods to limit air-flow capacity. Controlling gas flow decreased O_2 concentrations within the MRSs and decreased acidity generation by approximately 75% over 25 years, and even further in the post-closure period (80-85%).

Some of the improved MRS construction methods are applicable to both greenfield and brownfield sites. Ideal construction methods are highly likely to be site-specific.

1.0 INTRODUCTION

The mining sector worldwide is experiencing significant increases in closure costs and is accumulating a growing number of stranded liabilities due to poor closure outcomes. Closure bonds, as well as financial assurance for operating sites, continue to increase as community and regulator expectations rise. The most contentious and persistent issue driving stakeholder expectations is poor post-closure water quality. Almost without exception, the problematic water quality issue is related to acid rock drainage or acid and metalliferous drainage[1] (ARD / AMD) associated with sulfide oxidation that invariably requires collection and treatment, not just during operations, but often in perpetuity. Collection and treatment of ARD / AMD is often unplanned, or the costs are underestimated, resulting in higher operational and closure costs.

Most mines containing reactive sulfides generate ARD / AMD from a range of site domains, including mine rock stockpiles (MRSs[2]), tailings storage facilities (TSF), open cuts and underground mine voids. Direct and indirect measurements of acidity load from various site domains at more than 40 sites over the past 25 years have revealed that sulfidic rock waste (mine rock stockpiles) typically contributes the majority of the total acidity load (60 to 80%) from most mine sites. A further 20-30% of the acidity load is often associated with TSFs. These studies incorporate a broad range of commodities, including coal, copper, cobalt, lead, zinc, silver, gold, tin, tungsten, molybdenum, uranium, iron-ore, graphite and diamonds.

With this understanding of the importance of waste rock management to successful closure, the International Network for Acid Prevention (INAP) funded a study to review, assess and summarise existing and improved mine rock stockpile construction methods (INAP,2020). This paper provides an overview of the key outcomes of this work. INAP (2020) is a public domain report.

2.0 CONVENTIONAL MINE ROCK STOCKPILE CONSTRUCTION METHODS

Conventional MRS construction typically involves releasing well sorted, relatively dry rock materials with wide particle size distributions from the back of tip trucks down angle-of-repose slopes of previously disposed material. This method is used to optimise costs associated with loading, hauling and placing rock from open pit (or underground) operations, while maintaining geotechnical stability of the MRS. This method results in coherent grainsize segregation and distinctive depositional layering, with substantial concentration of larger rock fragments in a ‘rubble’ zone at the base of the depositional zone (i.e., base of a lift). The propensity for particle size segregation typically increases as the lift height increases. These features inadvertently promote passive air (oxygen) entry through advection and can accelerate the migration and discharge of internal MRS seepage that has resulted from surface infiltration. The net effect is generally an optimised physical setting for sulfide oxidation while also minimising opportunity for acidity neutralisation.

To date, managing ARD / AMD from MRSs has largely been focussed on collection and treatment of any resultant MRS effluent (ie. MRS toe and basal seepage) as well as application of cover systems (to manage oxygen ingress and/or net percolation into the MRS). It can be argued that these approaches have proven unsustainable in many instances and have led to an industry reliance on treatment in perpetuity.

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[1] ‘ARD / AMD’, or acid rock drainage / acid and metalliferous drainage, is also referred to as metal leaching and acid rock drainage, or ‘ML-ARD’; both terms describe the same issue within the mining industry. This document will use ‘ARD / AMD’.

[2] Mine Rock Stockpiles are waste rock piles or waste rock dumps.

3.0 IMPROVED CONSTRUCTION METHODS

Improved construction methods are available and new approaches are emerging. These are principally focused on improved control of gas transport within MRSs, both during and post construction.

A total of 6 broad categories of improved MRS construction methods were assessed in this study. Four (4) of the methods are focused on geotechnical engineering approaches, and two (2) are geochemically focused methods, as defined in Table 1.

Table 1. Improved Mine Rock Stockpile (MRS) Construction Methods

MRS Construction Method	Description	Focus
Lower lift heights	Lowering lift heights to reduce the influence of segregation within an end-dumped MRS, and thereby reduce internal MRS air flow capacity.	Geotechnical
Engineered layers	Installation of horizontal engineered layers in an end-dumped MRS to facilitate vertical gas management.	Geotechnical
Base-up, layered / compacted	Building an MRS from the base-up via paddock dumping in compacted, thin lifts simultaneously retards air flow capacity and enhances carbonate and silicate neutralisation.	Geotechnical
Encapsulation	Encapsulating potentially acid forming (PAF) material with material that can achieve and maintain low air permeability to manage vertical and lateral gas transport within and to the PAF rock, thereby lowering acidity generation. Encapsulation related methods can be applied proactively (greenfield sites) and retrospectively (brownfield sites).	Geotechnical
Oxygen Consuming Materials	Strategic placement of sulfidic non-acid forming (NAF) materials around PAF mine material (eg. encapsulation style) can limit O_2 from reaching PAF material, as it is being at least partially consumed in the oxidising NAF layer, often without generating metalliferous drainage.	Geochemical
Sulfide Passivation	Sulfide passivation installations require placement of relatively thin layers of specialised alkalinity generating materials above all PAF materials, often as a component of a cover system. Alkalinity slowly flushes into the MRS via infiltrating surface water and can passivate sulfide grains with neutralisation precipitates, thereby limiting ongoing oxidation.	Geochemical

The improved MRS construction methods aim to limit the access of oxygen to sulfidic mine rock, by either:

i. Regulating air entry and movement in NAF and PAF material;
ii. Influencing pore gas oxygen concentrations by manipulating oxygen consumption; and / or
iii. Coating sulfide grains to limit reaction with oxygen.

Each of these construction methods perform differently under different physical and chemical conditions (eg. topography, climate, geochemistry) and can also be combined to produce improved outcomes.

A comprehensive and accurate physical and geochemical characterisation and classification system coupled with the formulation of an ARD / AMD risk block model and a mine rock handling strategy is fundamental to all of the improved MRS construction methods.

While the benefits and limitations of each improved MRS construction method will be site-specific, it is likely that application of any one of these methods, in isolation, will not be sufficient to achieve the necessary water quality improvements in most cases. The best water quality outcomes are predicted to be associated with the carefully considered and site-specific application of multiple improved MRS construction techniques. Base up, thin-lift compacted MRSs offer the best opportunity to work in isolation.

The six categories of improved MRS construction methods are largely introduced as proactive approaches for greenfield sites (or planned new MRSs at brownfield sites). Some of the methods are also applicable to existing MRS facilities at brownfield sites.

4.0 QUANTIFYING POTENTIAL BENEFITS OF IMPROVED METHODS

There are several key and immediate risk management opportunities that can be realised as a result of these improved construction methods.

The potential benefits of improved MRS construction methods can be quantified based on acidity loads (acidity x flow rate), where acidity is a routine chemical parameter that is measured via titration (acidity = acid + metals). As an example of how this can be achieved, acidity generation modelling was conducted for MRSs in two different mine settings, with conventional and some of the improved MRS construction methods modelled separately for each mine setting. The improved methods included shorter lift heights, vertical gas management layers, and base-up construction). The model was designed to quantify the percentage reduction in kilograms of acidity produced per tonne of waste rock placed (kg H_2SO_4/tonne) over time, taking into account:

a. Changes in airflow capacity with the MRS;

b. Changes in temperature conditions within the MRS;

c. Changes in oxygen concentration within the MRS; and

d. Changes in the stored acidity generated within the MRS.

Numerical modelling of acidity generation from conventional and improved MRS construction methods illustrated the ability for the improved methods to limit air-flow capacity. Controlling gas flow decreased O_2 concentrations within the MRSs and decreased acidity generation by approximately 75% over 25 years, and decreased acidity generation rates by 80 to 85% in the post-closure period. Decreases in acidity generation are equivalent to decreases in pollution generation from a site. The selected combination of improved MRS construction methods may require further optimisation and/or additional methods may be required to further decrease acidity generation rates.

5.0 EXISTING APPLICATIONS OF IMPROVED CONSTRUCTION METHODS

A common reason many of these improved methods are not widely implemented at current mine sites is because of the perception that their relative life-of-mine costs are greater than conventional methods, as well as a perceived lack of proof of concept at full scale implementation.

In fact, there are numerous sites around the world where various improved MRS construction methods are starting to be applied. Published references or public domain examples of various improved MRS construction methods include:

- Iron ore mine in the Pilbara region of Western Australia (Pearce et al., 2016).
- Greenhills Operations coal mine in Canada (Dockrey et al., 2015).
- Golden Cross Mine, New Zealand (Miller, 2009).
- Ban Houayxai Gold Mine in Lao PDR (Miller, 2009).
- Kelian Gold Mine on Indonesia (Miller, 2009).
- Rosebery base metal mine in Tasmania (MMG, 2016).
- Martha gold mine in New Zealand (Miller, 2009; Garvie et al., 2012 and 2014).
- Phu Kham copper-gold mine in Lao PDR (Miller, 2009; Miller et al., 2012).
- Martabe gold mine in Indonesia (Pearce et al., 2017).
- Grasberg copper-gold mine in Indonesia (Miller et al., 2003, 2006; Miller, 2009; Andrina et al., 2003, 2006).
- Brukunga pyrite mine in South Australia (Brett et al., 2011; Scott et al, 2011; Taylor et al., 2009; Stimpfl et al., 2009).

These public domain examples and other unpublished documents demonstrate the growing interest in, and application of, improved MRS construction methods (INAP, 2020). These examples provide real world evidence, by various indicators, that water quality benefits can be achieved, and that the potential exists for increased MRS construction costs to be offset by lower closure costs and closure bonding.

The benefits to mine site water quality associated with existing full-scale applications of various improved construction methods provides strong evidence to support their broader application. Some of the improved methods have only been implemented at small to medium demonstration scales but show considerable promise. Additional larger-scale demonstrations are warranted for these technologies.

6.0 CONCLUSIONS

Key conclusions from this study are:

- There is substantive and growing evidence that ARD / AMD management strategies for MRSs that are largely focussed on cover systems and the collection and treatment of MRS effluent (ie. MRS toe and basal seepage) are not sustainable.
- This paper identifies and summarises improved MRS construction methods that build on industry's recent learnings.
- A total of six (6) broad categories of improved MRS construction methods have been identified in INAP (2020) and summarised here. Four (4) of the methods are focussed on geotechnical engineering approaches and two (2) are based on geochemical manipulation.
- In summary, these methods can limit availability of oxygen to sulfidic mine rock, by either:
    i. Regulating air entry and movement in NAF and PAF material;
    ii. Influencing pore gas oxygen concentrations via manipulated oxygen consumption; and
    iii. Coating sulfide grains to limit reaction with oxygen.
- Some of these improved construction methods can be applied retrospectively at brownfield sites.

- A comprehensive and accurate physical and geochemical characterisation and classification system coupled with the formulation of an ARD / AMD risk block model and a mine rock handling strategy is integral to all of the improved MRS construction methods.
- Each improved MRS construction technique has strengths and weaknesses that are influenced by site specific conditions, such as climate, topography, rock geochemistry, and rock texture.
- It is likely that application of any one of these improved methods in isolation will not be sufficient to achieve the necessary water quality improvements in most cases. The best water quality outcomes are predicted to be associated with the carefully considered, and site-specific, application of multiple improved MRS construction techniques.
- Benefits to mine site water quality associated with existing full-scale applications of various improved construction methods provides strong evidence to support their broader application.

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DESIGN CONSIDERATIONS FOR MANAGING AMD WITH DRY STACKED FILTERED TAILINGS

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Abstract

Subaqueous disposal with water covers is considered leading practice for the prevention of acid rock generation in potentially acid forming (PAG) tailings. While full water saturation provides the highest level of chemical stability for PAG tailings, it creates the worst conditions with respect to physical stability in tailings dams. Quite simply stated, the principles for achieving chemical stability and physical stability in PAG tailings create competing design objectives.

Waste rock dumps are perhaps the best examples of dry stacked mine waste. While well drained, unsaturated dry stacked waste rock produces high strength stable structures, it is well known that 85% of the global AMD is produced by waste rock dumps.

This paper evaluates the hydraulic and structural properties of dry stack systems for filter tailings. Both internal drainage and surface water characteristic are discussed together with the associated design and performance issues that must be addressed to prevent, control and mitigate AMD in dry stack filtered tailings.

Technical Articles

IS IT POSSIBLE TO MAKE AMD DISAPPEAR? – A CASE STUDY

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ABSTRACT

There are a number of technical guidelines that can be used to determine the likelihood of Acid and Metalliferous Drainage (AMD) being generated by a mine waste material including AMIRA, 2002; CoA, 2016 and INAP 2009. Whilst high quality guidelines are very useful to the layperson, they should not be used in isolation to conclude on the likelihood of AMD being generated from a mine waste material. Additional input is generally required from an experienced and qualified geochemist to formulate a suitable sampling plan and testing regime, especially if the geochemistry of the material is complex and it is proposed to use the material for off-site activities.

This paper will present some information from a confidential case study where technical guidelines were used and arbitrary planning decisions made, without input from an experienced and qualified geochemist or from other important disciplines. The site is a former gold heap leach operation, where cyanide was used as the leaching fluid on a large stockpile of ore. The site has remained abandoned for over 25 years and comprises a heap leach pile, drainage system, open pit lake and several waste rock dump areas.

A proposal to use the heap leach residue as quarry material for road and rail infrastructure in both a sealed and unsealed condition, whilst at the same time rehabilitating the site, was approved by the local council and regulators. The approval was the subject of a legal appeal, whereby the geochemical and leaching characteristics of the material were questioned, along with the potential for impacts to human health and the environment. Potential contaminants and leachable parameters include acidity, aluminium, arsenic, copper, cyanide and zinc.

This paper highlights some of the significant knowledge gaps associated with the planned off-site use of the residue and the potential for environmental impacts to aquatic ecosystems. Fundamental AMD risks were not considered that would have been routinely assessed for the development of new mining and mineral processing operations. These knowledge gaps and AMD risks highlight the need to involve an experienced and qualified geochemist in the project team from the start as well as the potential limitations of the legal process in defining and understanding the residual AMD risks associated with the planned project.

1.0 INTRODUCTION

There are a number of excellent technical guidelines commonly used around the world to assess the likelihood of Acid and Metalliferous Drainage (AMD) being generated by mine waste materials at mining and mineral processing operations (e.g., AMIRA, 2002; CoA, 2016 and INAP 2019). However, when used in isolation, it is possible for the layperson to underestimate the likelihood of AMD from mine waste materials. Additional input is required from an experienced geochemist to formulate a suitable sampling and testing regime, especially if the geochemistry of the material is complex and the material is used off-site.

Over the past few decades, it has been clearly established that there is no ‘magic bullet’ solution for preventing AMD (Wilson, 2008.; Robertson et al, 2015, 2019) and that a range of studies need to be undertaken to fully understand and manage any potential for AMD. Depending on a variety of factors including the site location, site infrastructure, material characteristics and climate, additional studies can include block modelling, surface hydrology, hydrogeology, water balance and water quality monitoring/modelling, reactive-transport modelling (Mayer et al., 2003) and pit lake modelling (Landers et al., 2020).

2.0 CASE STUDY

2.1 Overview

This paper presents some key learnings from a confidential case study in Australia where technical guidelines were used and arbitrary planning decisions made, without input from an experienced geochemist. The site is a former gold heap leach operation, where cyanide was used as the leaching fluid on a large stockpile of ore. The site has remained abandoned for over 25 years and comprises a heap leach pile, drainage system, open pit lake and several waste rock dump areas.

A proposal to use the heap leach residue as quarry material for road and rail infrastructure in both a sealed and unsealed condition, whilst at the same time rehabilitating the site, was approved by the local council and State environmental regulators. The approval was the subject of a legal appeal, whereby the geochemical and leaching characteristics of the material were questioned, along with the potential for impacts to human health and the environment. Potential contaminants and leachable parameters include acidity, aluminium, arsenic, copper, cyanide and zinc.

2.1 Existing Data

Existing data regarding the geochemical characteristics of the site materials is sparse and there are significant knowledge gaps within recent studies undertaken at the site. The most recent study focused on sampling (15 samples) of near-surface materials at the heap leach pile which represents approximately 10 % of the total amount of approximately 4 million tonnes of material currently stored at the abandoned mine site. Therefore, the first question is how representative are the samples taken of the residue at the heap leach pile. Given that the materials have been exposed to weathering conditions for 25 years, it is likely that materials stored within the core of the heap leach pile will have different geochemical characteristics to materials on the outside of the pile.

The most recent geochemical study found that more than half of the near-surface residue was classified as Potentially Acid Forming (Low Capacity) and assumed that the bulk materials would have sufficient Acid Neutralising Capacity (ANC) to produce neutral pH seepage and low concentrations of dissolved metals and metalloids. The study also assumed that there would be no residual cyanide in the pile and that therefore the residue posed minimal risk to the environment if used for road and rail infrastructure in both a sealed and unsealed condition off-site. Notwithstanding, the most recent study ignored previous studies, which demonstrated that lower pH values and elevated concentrations of arsenic, copper and zinc in seepage as well as residual cyanide could be present in seepage. There were also no studies to determine if any aquatic ecosystems downstream of locations where the residue would be used were likely to be significantly affected by contaminants potentially released from the residue.

The most recent geochemical study demonstrated that the residue contained elevated concentrations of arsenic, and to a lesser extent copper, compared to median crustal abundance in soils. The focus of the additional studies was on arsenic as it was assumed that acid conditions would not prevail and therefore copper would be less likely to be mobile under pH neutral or alkaline conditions. In addition, the potential for aluminium and zinc dissolution and mobility in seepage was also underestimated.

2.2 Chemistry of Cyanide

The chemistry of cyanide and the potential for generation of latent acidity from the residue was largely ignored until the legal proceedings reached the latter stages of the expert witness reporting and court testimony processes. For example, the fact that cyanide forms a complex with copper, which is relatively insoluble under alkaline conditions, and could therefore remain within the core heap leach materials was overlooked. Copper cyanide is a weak acid dissociable (WAD) complex that readily dissociates under weak acid conditions and can generate copper, latent acidity and cyanide.

Figure 1 shows a photograph of the residue pile and evidence of leaching of contaminants from the pile, as confirmed by at least some of the sparse sediment and water quality monitoring data. Historical monitoring data showed that the levels of acidity, arsenic, copper and zinc in the lined parts of the seepage collection system at the site had the potential to be highly elevated compared to background concentrations in regional surface and groundwater (ANZECC & ARMCANZ, 2000; ANZG, 2018).

Fig. 1. Seepage at Heap Leach Residue Pile

The International Cyanide Management Code for the Gold Mining Industry (2019) was only referenced very late in the legal proceedings and the lack of appreciation of cyanide chemistry is a fundamental flaw in the study program. The proponents for the proposed use of the material off-site suggested that there were only "pockets of acidity" in the residue pile and that overall seepage from materials if used off-site would be alkaline. There was also an environmental management plan developed, which proposed testing of residue batches before leaving site and any material that did not meet the required specification would be returned to the open pit.

2.3 "Real World" Examples

The proponents of the project suggested that there were two "real world" examples demonstrating that the heap leach materials could be used for off-site activities with minimal risk to the environment.

Towards the end of the expert witness phase of the legal proceedings, four surface samples of pit water were collected and used to suggest that because dissolved arsenic concentrations were low, the risk to the environment from the residue was also low. The sampling program took no account of the complex nature of a final void and the plethora of studies that would be required to confidently predict that the heap leach material had not impacted the open pit. For example, there was no surface hydrology or hydrogeology work completed therefore it was not clear whether any seepage from the residue pile had reported to the open pit and by how much this had been diluted by groundwater or concentrated by evaporation at the pit lake surface. There were also no pit lake geochemical modelling or limnology studies completed to base the assumption that the pit water had not been impacted by the pile. Closer inspection of the pit lake water quality monitoring data from the four surface water samples actually showed that the pit water contained dissolved copper at a concentration 25 times the applied guideline level for 95 % protection of freshwater aquatic ecosystems. (ANZECC & ARMCANZ, 2000).

Again, late in the expert witness phase of the legal proceedings it was revealed that the proponent had sampled historical residue that had been used as road base (some 25 years ago), from road verges to check for arsenic contamination. The fact that any potentially mobile arsenic, cyanide and metals such as aluminium, copper, and zinc would have long since been leached from the material into the environment was not considered.

During discussion of these “real world” examples before and during court proceedings, it became very clear that simplistic explanations of some fundamental geochemistry terms and definitions were required. In particular, it had to be explained in some detail that the term “acid leachability” is much broader than commonly understood by the layperson and that the correct definition for AMD is Acid and Metalliferous Drainage.

3.0 CONCLUSIONS

This paper has highlighted that the lack of involvement of an experienced and qualified geochemist in the project team at the early stages of a planned mining or mineral waste reuse project can undermine the development of a sound understanding of the residual AMD risks. In this case, a number of parameters including dismissal of historical sampling and monitoring data, a poorly designed AMD characterisation program and lack of knowledge of cyanide chemistry has increased the potential for environmental impacts due to release of latent acidity and dissolved metals/metalloids into surface and groundwater resources. As the site is no longer a mining lease a contaminated land approach appears to have been favoured by the proponents. Consequently, fundamental AMD risks were not considered that would have been routinely assessed for the development of new mining and mineral processing operations.

There also appears to be limitations in the legal process with respect to defining and understanding the residual AMD risks to aquatic ecosystems associated with the planned project. The wheels of justice turn slowly as the outcome of the disputed development and subsequent legal proceedings is still pending some four years after commencement. Should the development be allowed to go ahead, it is logical to conclude that there may well now be a method of making AMD disappear.

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PYRRHOTITE IS NOT PYRITE: CONSEQUENCES FOR REDUCED AMD ASSESSMENT AND RELEASE

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ABSTRACT

The standard assessment of acid and metalliferous drainage (AMD), assumes that all measured sulfur is pyrite with an associated oxidation reaction to form sulfuric acid. This is not the case where pyrrhotite is the majority sulfide with the predominant reaction (often >80%) forming elemental sulfur, not sulfate and acid, according to:

$$\mathrm{Fe}_{(1-x)}\mathrm{S} + \frac{3(1-x)}{4}\mathrm{O}_2 + \frac{(1-x)}{2}\mathrm{H}_2\mathrm{O} \rightarrow (1-x)\mathrm{FeOOH} + \mathrm{S}^0$$

This is not recognised in current assessments, but occurs in practice in tailings storage facilities (TSFs). A basis for correction of maximum potential acidity (MPA) for pyrrhotite content is presented. Three case studies illustrate the reality of this important correction in AMD assessment and control.

At Savannah Nickel, the TSF tailings are potentially acid forming (PAF) from standard AMD assessment (8–9 wt% S) but remain near neutral pH and S^0 is assayed at depth and in hardpan. Pyrrhotite, rather than pyrite, is the main sulfide gangue mineral usually associated with nickel sulfide deposits, but this geochemical difference has not been recognised in standard testing of wastes from these deposits. At Renison Tin, tailings in TSFs with pyrrhotite and minor pyrite have been reassessed using mineralogy. The pyrrhotite correction reduced the MPA calculation for the high sulfur tailings from 860 ± 70 to 330 ± 30 kg H_2SO_4 t^{-1}. The corrected net acid production potential (NAPP) for the low sulfur tails is −70 ± 40 kg H_2SO_4 t^{-1} (i.e. non-acid forming, NAF) with some low capacity neutralisation potential when used as capping material. This is consistent with the LST covers successfully controlling the acid in surface waters on the dams. At Hillgrove's copper-gold mine, low-S waste rock gave nett acid production potential values ranging from PAF to NAF (7.9 to −3.9 kg H_2SO_4 t^{-1}). Full mineralogical and sulfur speciation analysis enabled correction of NAPP to −3.1 to −13.6 kg H_2SO_4 t^{-1} with the neutralisation rate found to always exceed the rate of acid generation. These findings enabled this low-S, low carbonate waste to be correctly redefined as NAF with major benefits for site remediation. There are implications of similar findings for low-S mine waste rock internationally. The methods represent a significant advance in more strategic, cost-effective environmental planning.

1.0 INTRODUCTION

Although oxidation of iron sulfides is recognised as the primary cause of AMD, generally no distinction is made between different iron sulfides in standard acid-base accounting (ABA) assessment of acid potential which is based on the assumption that total S or, more correctly, sulfide S assays represent pyrite (INAP, 2009; AMIRA, 2002). This remains current despite the fact that it has long been recognised that oxidation of pyrrhotite produces elemental sulfur (S^0) as well as sulfate with the former reaction generating no net acidity (Thomas et al., 1998, 2000, 2001; Belzile et al., 2004). The observation of S^0 production in high-pyrrhotite tailings wastes (e.g. Schippers et al., 2007; Heikkinen and Räisänen, 2008) as well as leach and flotation products (e.g.

Wang, 2008) from nickel, tin, copper and other mines has been documented. A number of previous laboratory studies of single mineral and simulated mine wastes have confirmed that the oxidative dissolution of pyrite invariably produces sulfate as the major final product but, in the oxidation of pyrrhotite, significant quantities of S^0 have been identified (Cruz et al., 2005, Mikhlin et al., 2002, Kalinkin et al., 2000, Nicholson and Scharer, 1994). Specifically, Janzen et al. (2007) measured the mean rate of pyrrhotite dissolution, using 12 sources of pyrrhotite and found that the relative ratio of release of ferrous to sulfate ions was 10% implying that 90% of the sulfur was oxidised to form S^0.

The work by Schumann et al. (2015) specifically quantified the contribution of reaction to S^0, and reduction in acid production, in the overall oxidation of pyrrhotite. In this study, synthetic mine wastes containing 5 wt% pyrite or pyrrhotite, together with 5 wt% chlorite, 10 wt% feldspar (amazonite) and 80 wt% quartz produced 71 % and 6 % respectively of the expected acidity based on acid base accounting during 120 weeks of kinetic leach column (KLC) oxidation test conditions. These tests demonstrated that oxidation of pyrite was dominated by the reaction to produce sulfuric acid (98 %), while pyrrhotite oxidation primarily produced S^0 (85 %) (Eq. [1]) and consequently significantly less acidity (≈5 %) than would be expected based on acid production calculations or NAG testing.

$$\mathrm{Fe}_{(1-\mathrm{x})}\mathrm{S} + \frac{3(1-\mathrm{x})}{4}\mathrm{O}_2 + \frac{(1-\mathrm{x})}{2}\mathrm{H}_2\mathrm{O} \rightarrow (1-\mathrm{x})\mathrm{FeOOH} + \mathrm{S}^0 \qquad [1]$$

Nickel mine tailings containing nearly 30 wt% pyrrhotite also produced much smaller than expected acidity (<1 %) after 107 weeks of leaching. The case studies discussed below illustrate the necessity to recognise this fundamental difference in AMD assessment.

2.0 CORRECTION TO AMD ASSESSMENT

Firstly, the NAG (net acid generation) test has been shown to be unrealistic for pyrrhotite containing samples in waste storage. This highly oxidising test forces all pyrrhotite to react to acid and sulfate products (Stewart et al., 2003) whereas it is known that, not only under KLC (AMIRA, 2002) conditions, but also in real tailings storage conditions, the alternative reaction to S^0 occurs predominantly.

Secondly, the next requirement is estimation of the pyrite and pyrrhotite contents of the waste. This can only realistically be done by quantitative XRD or MLA of the waste mineralogy; chemical tests are difficult and unreliable. The advantage of this determination is that corrections to both maximum potential acidity (MPA) and full estimation of acid neutralisation capacity (ANC) and rates including non-carbonate sources can then be made. The correction sequence developed by Blue Minerals Consultancy (BMC) is based on the conservative assumption that 20% (actually <10 %) of the pyrrhotite produces acid. Sulfides that do not produce acid, particularly sphalerite and galena, can be removed from the Sulfide S based on quantitative mineralogy. The steps are then, if the sulfides are only pyrite and pyrrhotite:

1. Non-sulfate S = CRS assay (wt%)
2. Sulfide ***S*** = CRS − S^0 (wt%), (assay by acetone extraction)
   MPA* = 30.6 × ***S*** (wt%)
   NAPP* = MPA* − ANC (corrected for S^0 content)
3. Sulfide mineralogy = *x* wt% pyrite + *y* wt% pyrrhotite
4. ***X*** pyrite S wt% = *x*(64.14/119.98) (S in pyrite)
5. ***Y*** pyrrhotite S wt% = *y*(32.07/87.92) (S in pyrrhotite)
6. $MPA_{corr} = 30.6 \times [SX/(X+Y) + 0.2SY/(X+Y)]$ kg H_2SO_4 t^{-1} (20 % acid from pyrrhotite)
7. $NAPP_{corr} = MPA_{corr} - ANC$

The effect of this correction can result in cost savings for AMD control and, in some cases, reclassification of potentially acid forming (PAF) to non-acid forming (NAF) wastes with major implications for storage. The site case studies will now illustrate this.

3.0 CASE STUDIES

3.1 Savannah Nickel Mine (SNM)

Geochemical information using standard ABA classification tests, presented in the original approvals documentation for the Savannah Nickel Mine (SNM) in the Kimberley region of Western Australia in 2002, predicted that the SNM tailings (19 wt% pyrrhotite) would be PAF and would be likely to pose a significant long-term risk to the environment from potential seepage. Based on this geochemical assessment, regulators took a conservative approach requiring return of tailings materials to the open pit void at end of mine life as a condition of consent. An independent peer review of the long-term tailings storage strategy at the site in 2008 found that tailings were much less reactive than originally indicated.

To explain this, on-going investigations into the geochemistry of the tailings in the tailings storage facility (TSF; Robertson et al. 2015) studied the oxidative behaviour of pyrrhotite-containing tailings both in laboratory leach columns and *in situ* in the SNM TSF. Core samples were taken through the full depth of the tailings deposited over a five year period in the TSF. The presence (by assay) of S^0 in the bulk tailings hardpan and at depth plus lack of dissolved O_2 measured in the tailings pore water below the tailings hardpan surface suggested that reaction [1] was likely to be favoured. An estimate of the relative amounts of oxidation to S^0 and SO_4^{2-} in the hardpan was made based on the results of sulfur speciation suggesting that sulfide sulfur had decreased from 9.2 wt% in the tailings to 1.0 wt%. S^0 content increased from 0.1 wt% to 7.1 wt%. This equates to an 86 % conversion of sulfide sulfur to S^0. These results also suggest that under the conditions prevailing in the TSF, further oxidation of S^0 is very slow in comparison to pyrrhotite oxidation, and that therefore the acidity generated by pyrrhotite oxidation will be substantially less than that predicted from ABA and NAG tests. A pyrrhotite correction was not done for these tailings.

Similar results were obtained in standard AMIRA kinetic leach columns of SNM mine tailings (Schumann et al., 2015). About 90 % of the oxidised sulfur in the tailings leached at 50 % saturation, and around 80 % of the oxidised sulfur in the tailings leached at 75 % saturation, reacted to produce S^0 and no acidity. Consequently, measured acidities were around 6 % of the predicted acidity in the tailings leached at 50 % saturation and less than 0.2 % of the predicted acidity in the tailings leached at 75 % saturation. This was due not only to oxidation to S^0, but also to the majority of acidity produced by the oxidation pathway to sulfuric acid being neutralised by non-carbonate magnesium silicates present in the tailings.

More recently, three tall KLC tests were established with average levels of saturation of 50, 75 and 100 % to investigate geochemical processes likely to occur in the tailings stored in the TSF in the post-operational period (Robertson et al., 2015). After 18 months "weathering" of the tailings:

- Leachates from the fully saturated column are pH neutral with no acidity; there is little evidence of pyrrhotite oxidation (≈6 % estimated);
- At 75% saturation, leachate pH dropped to 4.5 with low levels of acidity, ≈15 % of the pyrrhotite had oxidised and dissolution of magnesium silicates (enstatite and anthopyllite) was also occurring;
- At 50 % saturation, the pH dropped to 4 with acidity 10 times greater than leachate from the 75 % saturation, around 57 % of the pyrrhotite oxidised with the main geochemical processes occurring essentially the same as at 75 % saturation at increased rates.

These results confirm that even under unsaturated conditions, the dominant reaction pathway for pyrrhotite oxidative dissolution in tailings produces S^0 which, in the absence of further oxidation, is a non-acid producing reaction. At 50 % saturation, where nearly 60 % of the pyrrhotite in the tailings had oxidised, the acidity measured in the leachate is only 0.2 % of the expected acidity based on ABA analysis. Therefore it is likely that even if fully saturated conditions cannot be maintained post-operation, oxidation of pyrrhotite will result in a very significantly reduced acidity load than is predicted by standard static geochemical tests.

3.2 Bluestone Mines Joint Venture (BMJV): Renison Tin Mine

BMJV plans to reprocess the tailings from the Renison AB and C TSFs to produce new tin and copper products. The first stage of obtaining DPEMP approval with regard to AMD control is, in part, geochemical assessment requiring review of contemporary and historic Renison tailings geochemical data and development of acid-base accounting from pre-existing and new data. A central outcome of the BMC review undertaken was that the sulfide in the high sulfide tailings (HST) is primarily pyrrhotite, with minor pyrite. The implications of this are that, while oxidation of the minor pyrite is dominated by the reaction to produce sulfuric acid, pyrrhotite oxidation primarily produces S^0 in TSF storage and consequently much less acidity than would be expected based on acidity calculated from total sulfur (sulfate and S^0) oxidised. Previous CSIRO reports and contemporary measurements showed that predominant conditions in the pore waters from all three dams (at the time) were reducing. These observations explain both the maintenance of ferrous iron even in high pH conditions, where it would normally have precipitated as $Fe(OH)_3$ releasing acid, and the reaction of pyrrhotite to S^0 rather than sulfate.

Renison utilises a system of calculation of MPA based on Total S, and MPB_{Ren} (maximum potential basicity, as a substitute for ANC) based on total C (assuming all C is present as carbonate). MPB_{Ren} is calculated as 30.6 × C (wt%) × (32.07/12.01) kg H_2SO_4 t^{-1}. $NAPP_{Ren}$ is then equal to MPA minus MPB_{Ren}. This enables an estimate of possible nett acid production potential based on assay data alone.

To assess the efficacy of the current use of the low sulfur tailings (LST) stream as capping on HST in the TSF, corrections based on mineralogy were applied. The mineralogy of each stream derived from XRD analysis is shown in Table 1. As sulfide S quantification derived from assays was not available a modified form of the correction to MPA described in Section 2.0 was applied. For correction of MPA, to give $MPA_{corr\text{-}Ren}$, the mineralogy of the sulfides from the HST (including arsenopyrite) was used (Table 1) together with Total S for HST and LST. It was assumed that the proportionality of the sulfides is the same in the LST as the HST(note: no sulfides were identified by XRD in the LST). The correction factor applied to the MPA, for both LST and HST, to give $MPA_{corr\text{-}Ren}$ was (Py(S) + AsPy(S) + 0.2(Pyrr(S))/Total(S) = 0.39, i.e. $MPA_{corr\text{-}Ren}$ = 0.39 × MPA. A correction was also applied, in a similar manner, to MPB to remove the component of C due to the presence of siderite to give $MPB_{corr\text{-}Ren}$. $NAPP_{corr\text{-}Ren}$ is then calculated as $MPA_{corr\text{-}Ren}$ minus $MPB_{corr\text{-}Ren}$.

Table 2 provides a comparison of the MPA, MPB, $NAPP_{Ren}$ and BMC-corrected values applied to a 5 year Renison spreadsheet. The HST assays given in the spreadsheet return a $MPA_{corr\text{-}Ren}$ of 330 ± 30 kg H_2SO_4 t^{-1} as opposed to the standard calculation which would yield 860 ± 70 kg H_2SO_4 t^{-1}. The HST $NAPP_{Ren}$ is reduced on correction from 830 ± 70 to 300 ± 30 kg H_2SO_4 t^{-1} remaining PAF high capacity as expected. For the LST, the $NAPP_{corr\text{-}Ren}$ on correction is slightly less negative but clearly NAF. The corrections at Renison do not alter the classifications but now correctly reflect the mineralogy of both HST and LST for TSF planning and maintenance including some low capacity neutralisation potential when used as capping material. This is consistent with the LST covers successfully controlling the acid in surface waters on the dams.

Table 1. **Mineralogical composition (wt%) of C Dam LST and HST tailings.**

	LST Q2FY18	HST Q2FY18
Quartz	26.0	4.2
Magnetite		0.7
Pyrrhotite		40.7
Pyrite		6.4
Arsenopyrite		5.6
Ankerite/Dolomite	4.6	
Calcite	1.3	2.8
Siderite	3.6	0.7
Amphibole	3.5	
Schorl	9.3	
Plagioclase	4.5	
K-Feldspar	4.4	
Chlorite	3.0	2.0
Mica (muscovite, phlogopite)	25.5	1.1
Talc	7.8	5.4
Non-diffracting/unidentified	6.5	30.5

Table 2. **MPA, MPB$_{\mathrm{Ren}}$ and NAPP$_{\mathrm{Ren}}$ compared with MPA$_{\mathrm{corr\text{-}Ren}}$, MPB$_{\mathrm{corr\text{-}Ren}}$ and NAPP$_{\mathrm{corr\text{-}Ren}}$ calculated from this same data. All values have units kg H_2SO_4 t^{-1}.**

	LST (*n* = 1443)			HST (*n* = 29)		
	Ave ± stdev	Min	Max	Ave ± stdev	Min	Max
MPA	30 ± 10	8	132	860 ± 70	719	1025
MPB$_{\mathrm{Ren}}$	110 ± 60	0	513	30 ± 10	17	50
NAPP$_{\mathrm{Ren}}$	−90 ± 50	−493	81	830 ± 70	686	1002
MPA$_{\mathrm{corr\text{-}Ren}}$	10 ± 3	3	50	330 ± 30	275	392
MPB$_{\mathrm{corr\text{-}Ren}}$	80 ± 40	0	344	26 ± 8	14	41
NAPP$_{\mathrm{corr\text{-}Ren}}$	−70 ± 40	–336	18	300 ± 30	248	373

3.3 Hillgrove Kanmantoo Copper Mine

Hillgrove Resources Limited was until 2019 extracting unoxidised material from an open pit near Kanmantoo in South Australia. The usual host rock in the open pit is a garnet-andalusite-biotite schist (GABS) within which are zones of copper sulfides characterised by chlorite, magnetite, quartz, chalcopyrite, pyrrhotite with minor pyrite. The principal garnet is Fe-rich almandine. In 2014, the waste rock was assessed using standard AMD tests (e.g. AMIRA 2002) as containing 45.5 Mt NAF material and 48.9 Mt PAF material.

In the period 1970 to 1976, under previous owners, the copper bearing material was mined and processed, and the non-ore material from the open pit was dumped nearby as waste rock. The waste rock dump was not capped upon mine closure in 1976 and has been open to the environment for over 40 years. There was no sulfur assaying of the rock at the time of dumping, but recent studies from the current mining operation suggest that the sulfur content of the 1970's waste dump is between 0.1 to 5 wt%. Hillgrove Resources re-opened the open pit for mining in 2011 and has been dumping waste rock with varying sulfur content since then over the top of the 1970's waste rock dump. From 2011, fresh waste rock was defined as PAF if the total sulfur content was >0.3 wt% requiring, by statutory regulation, encapsulation at end of mine life to remove the risk of AMD.

Waste rock with less than 0.3 wt% sulfur was dumped separately and was to be used as the encapsulation material around and over the PAF material at the closure of the open pit.

Site water well monitoring results, however, indicate that the 1970's waste dump exposed to atmospheric oxidation for over 40 years, has not contributed to AMD. This assessment is not consistent with predictions from standard ABA tests of PAF characteristics. A new study of the AMD potential of these rocks was initiated in 2017 to understand this apparent discrepancy (Gerson et al., 2019). The aim was to ascertain, by detailed examination of the acid and neutralisation generation capacities and rates, whether waste rock with greater than 0.3 wt% sulfur has the potential to generate acid. If a significantly greater volume of rock is non-acid forming, there would be a significant impact on environmental planning, costs and an opportunity to create a substantially thicker encapsulation cover over the PAF material.

Using standard procedures on 12 new samples, the NAPP was found to range from PAF to NAF (7.9 to −3.9 kg H_2SO_4 t^{-1}). Full mineralogical consideration of sulfide minerals, using MLA for low S samples, and confirmed by synchrotron X-ray diffraction data, gave varying ratios of pyrite/pyrrhotite. This together with sulfide S assay were used to calculate $NAPP_{corr}$ (Section 2.0). This re-evaluation gave $NAPP_{corr}$ from −3.1 to −13.6 kg H_2SO_4 t^{-1}. The full mineralogy of samples also showed the following average composition of almandine of 13 ± 4 wt% and andalusite of 11 ± 2 wt% both of which can contribute neutralisation at rates effective in AMD control (Miller et al., 2010). A complete analysis of acid and neutralisation generation rates described in Gerson et al, (2019) found that the neutralisation rate will always exceed the rate of acid generation.

After external peer review, this analytical approach resulted in the SA Government reclassifying the AMD potential of the Hillgrove waste rock with less than 0.6 wt% total sulfur with considerable benefit for long-term dump remediation. On-going monitoring of water well pH is continuing and further verification of these results will be undertaken as more data are available.

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FIELD KINETIC TESTING RESULTS AT THE ANTAMINA MINE, PERU

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ABSTRACT

Antamina oversees an extensive program of kinetic testing on the waste produced at their Cu-Zn mine in the northern Andes. This program involves both field barrels (mass~350kg) and much larger field piles (mass~20,000t), which presents an opportunity to understand the geochemical processes of the mine waste and to investigate the scale-dependence of processes involved in the oxidation of a large range of sulfidic mine waste. The program has been ongoing since 2005, with approximately a decade of data available for many barrels and piles.

Waste is classified on the basis of lithology and potential reactivity, and development of acidic, neutral and saline drainage water quality from the field kinetic testing allows the mine to understand the site-specific factors of importance for the waste, to inform water quality modelling and to implement appropriate mine waste management plans.

Field piles have dimensions 36 x 36 x 11m and incorporate up to five lysimeters for collection of leachate water from different parts of their interiors. Five such piles have been constructed, each from different types of waste rock. All five piles are instrumented with more than 20 receiving stations for collecting leachate water, with additional instrumentation included in each pile.

160 field cells have been set up to study the weathering processes affecting the waste rock. Specifically, the focus is on the chemical changes observed in contact water seeping through the barrels. Leachates are collected with a monthly frequency during the wet season, and with a higher frequency at the beginning of the wet season.

Spatial variations in sulfide oxidation rate are identified within one of the field piles, which do not simply correspond to spatial variations in waste chemistry. Alternative reasons for these variations are discussed. Leachate water quality data are compared from piles and barrels containing the same waste material, and differences in their water quality are discussed. In particular, the contrast in water/rock ratio is identified as the dominating factor responsible for differences in leachate water quality from metre scale barrels and 10 metre scale waste rock piles. Caution should be exercised when using metre-scale tests to infer leachate water quality from full scale waste rock dumps.

1.0 INTRODUCTION

The Antamina mine is one of the largest Cu-Zn mines in the world and is situated in the Peruvian Andes. Ore is mined from a large skarn deposit, formed by the intrusion of quartz monzonite into limestone. In addition to Cu and Zn, Ag, Mo and Bi are abundant in the orebody.

Antamina experiences a tropical rainforest climate (‘Af’) according to the Koppen classification system, however the average temperature is lowered by the site’s high altitude (4000-4500 m). The ambient air temperature typically ranges between 0.1°C to 15.3°C. Annual rainfall is 1870 mm on average, and follows a strongly seasonal cycle with most of the rain falling during the summer between October and April. Mining activities take place continuously throughout the year.

Waste rocks at Antamina include limestone, hornfels, marbles, intrusives, endoskarn and exoskarn. These are classified according to their metalliferous leaching potential as Class A (high), Class B (marginal) or Class C (low). To study the potential for Acid and Metalliferous Drainage (AMD) at Antamina, kinetic tests are being undertaken of waste rock material contained in field barrels (250-350 kg) and field piles (~25,000 t). This study reviews results from both types of structure, undertaken on the same type of waste material.

2.0 FIELD PILES

The field piles were constructed between 2007 and 2010 by Antamina in collaboration with the University of British Columbia. They have dimensions 36m x 36m x 11m, and all their drainage is captured and metered by basal lysimeters. These are formed from impermeable geomembranes underlying each pile in the overlapping configuration shown in Figure 1 (top right panel). Drainage collection is facilitated by a 3° slope (towards lysimeter C). Sub-lysimeters A, B and C are 4m x 4m in area, while lysimeter D collects leachate from the remainder of the footprint of each pile (96% of the footprint by area). Water from all four lysimeters is collected in a ‘composite tank’, which provides an integrated measure of the water quality for each pile.

The piles were constructed according to the methods in Corazao Gallegos (2007) and Bay (2009). A 1.5m thick basal layer of sieved waste rock (particle size <10cm) protects Lysimeter D. This is overlain by three sloped panels of waste work, constructed by end-dumping from haul trucks in three distinct ‘tipping phases’ (indicated in Figure 1, bottom panel). The grain size distribution was not manipulated during the tipping phases, except for removal of the largest boulders (>1m in diameter). The intention was to reproduce the fining upwards particle gradation that is believed to occur in full-scale waste-rock piles (Stockwell et al. 2006, Vriens et al. 2018).

The upper surface of each pile was compacted by traffic, and sub-lysimeters arranged A and B are positioned vertically beneath this surface. In contrast, lysimeters C and D predominantly collect water draining through the uncompacted slopes of each pile. These dip at a 37° angle of repose.

Five piles have been constructed using different mixtures of waste rock (see Table 1). Records of leachate chemistry to date (Figure 2) indicate that only one of the piles is producing acidic water: pile UBC-2, which is formed from materials known to be potentially acid forming, namely intrusive (Class A in the mine’s waste rock classification scheme) material.

Table 1 Lithological composition of the five UBC field piles (Beckie et al. 2011), and geochemical data from representative samples taken to construct field barrels.

Pile Name	Waste rock mixture	Total S (wt.%)	ANC (kg $CaCO_3$/t)	NAPP (kg $CaCO_3$/t)
UBC-1	Marble and hornfels	0.21	755	752
UBC-2	Intrusive	0.62	8	-11
UBC-3	Exoskarn	1.78	79	20
UBC-4	Marble and hornfels (17%, 83%)	0.62	678	194
UBC-5	Intrusive and marble (34%, 66%)	0.59	635	642

The majority of Antamina’s waste rock material is not potentially acid forming, but due to the presence of intrusives, the mine has put considerable effort into understanding the properties of the mine waste and in developing waste management strategies for operations and closure that account for the presence of these potentially-acid forming materials. This paper focuses exclusively on UBC-2 intrusive material. This pile has an approximate mass of 21,780 t.

UBC-2 contains intrusive waste rock with a high leaching potential. Its concentrations of zinc, arsenic and sulfur define it as class A (‘reactive’; Zn>1500ppm, As>400, S>3%). The intrusive waste rock comprises quartz and K-feldspar, with accessory plagioclase, muscovite, calcite and trace molybdenite and pyrite (Peterson, 2002). Particle size distributions for UBC-2 are shown in Figure 2.

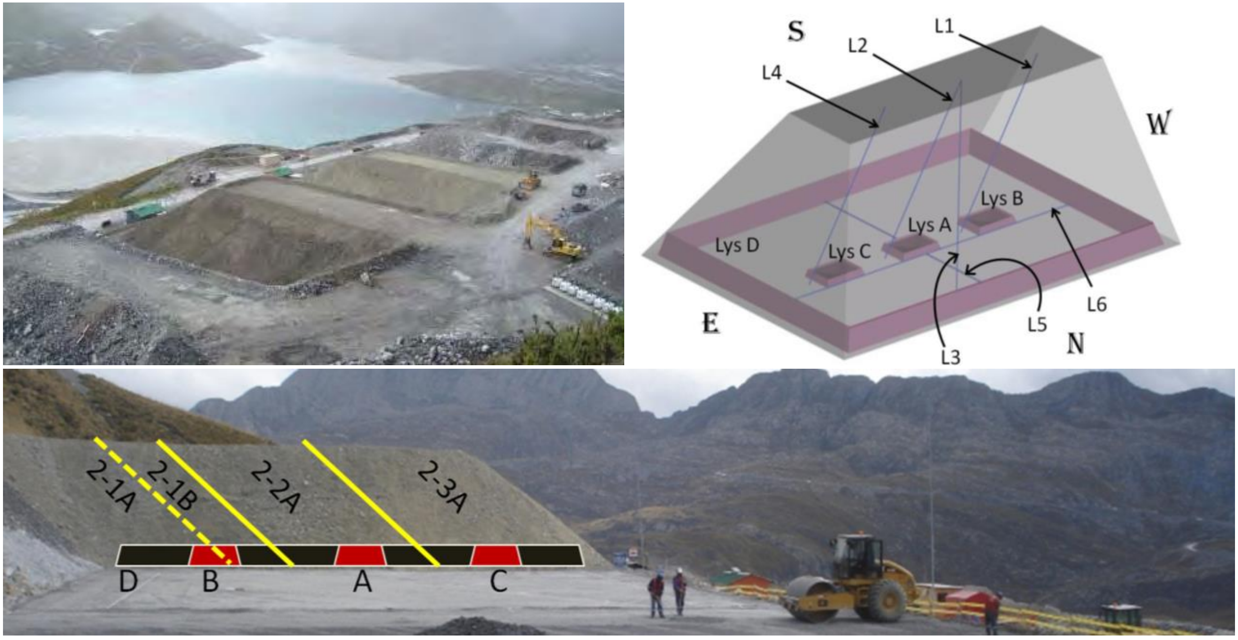

Figure 1 Geometry and internal structure of the field piles. Top left: view of the completed piles, looking obliquely downstream (Beckie et al. 2011). Top right: schematic of the internal structure of a single pile (Peterson, 2002). Bottom: cross-section of UBC-2, indicating the positions of the lysimeters (Peterson, 2002). The boundaries between tipping phases are indicated by the yellow lines, and the source volumes for the field barrels are labelled.

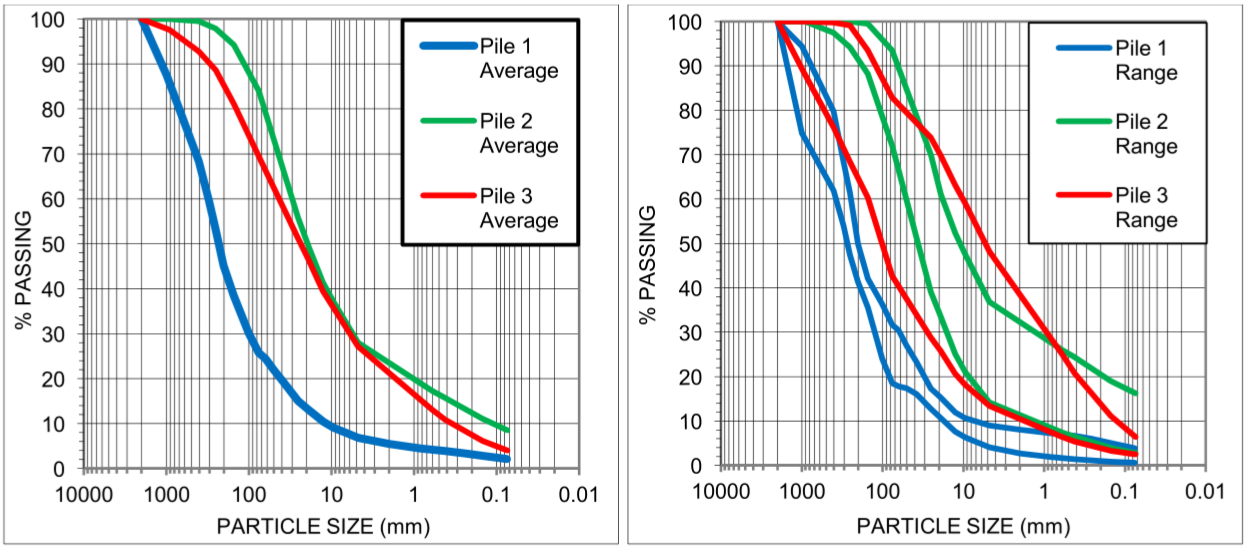

Fig. 2. Particle size distribution for field piles 1-3 (Peterson, 2002). The left figure shows averages of the materials in each pile (i.e. from each tipping phase), while the right figure shows the maximum and minimum proportions measured for each size fraction.

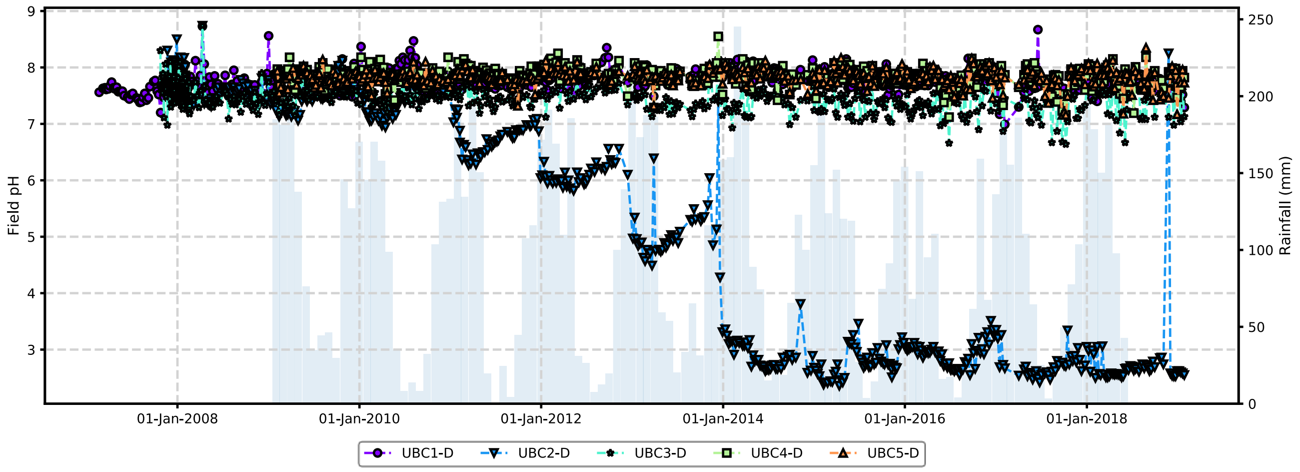

Figure 3 pH of leachates from the basal lysimeters (D) in each of the 5 field piles. For consistency, the leachate samples shown are from the same lysimeter ('lysimeter D') in each pile.

3.0 FIELD BARRELS

Representative samples from each field pile's tipping phase have been taken and placed in ~1m tall instrumented 60L barrels (Figure 4), constructed according to the methods of Aranda (2009). The barrels are unsealed, with their top surfaces uncovered to allow infiltration by rainwater and microbial colonization. Six barrels were constructed from UBC-2 waste rock, containing material from the protective basal layer and each of the three tipping phases. These are summarized in Table 2.

The material in each barrel was selected through a coning and quartering process applied to ~16t samples of waste rock, from which particles >10cm diameter were removed.

Figure 4 Field barrels. Photograph from Beckie et al. (2011).

Table 2 Sampling locations and geochemical data for the field barrel contents from the UBC-2 field pile.

Field barrel	Location	Total sulfur concentration (wt.%)	NNP ($kgCaCO_3/t$)	NPR ($kg/CaCO_3/t$)
UBC-2-0A	Protective layer	0.61	10.09	1.49
UBC-2-1A	First tipping phase (TP1)	0.20	5.91	1.90
UBC-2-1B	First tipping phase (TP1)	4.24	-124.34	0.06
UBC-2-2A	Second tipping phase (TP2)	0.62	-11.22	0.42
UBC-2-2B (duplicate)	Second tipping phase (TP2)	-	-	-
UBC-2-3A	Third tipping phase (TP3)	1.54	-40.97	0.15

4.0 RESULTS AND DISCUSSION:

Field Piles

Timeseries of leachate pH for the lysimeters A-D are shown in Figure 7. Data from the composite tank is denoted by E in the figure. The greatest contrast in pH profiles is between lysimeters A and B, which have both continued to produce circum-neutral leachates, and C and D, which have produced acidic leachates. These results suggest that acidification due to sulfide oxidation is progressing within the core of the pile more slowly than in the flanks (beneath the sloping surfaces). Sulfate concentrations of leachates lend further support to this view (Figure 5). Leachate from lysimeters A and B have maintained remarkably constant sulfate concentrations ~1,500 mg/L for a decade, while leachates from lysimeters C and D and the composite tank (E) have seen concentrations rise ten-fold or more. Yet further support comes from records of alkalinity; the constituent whose exhaustion is typically indicative of protracted sulfide oxidation. Bicarbonate alkalinity (Figure 6) at lysimeters A and B have approximately retained their original values (between 50 and 150 $mgCaCO_3/L$) while lysimeters C and D and the composite tank (E) have seen their alkalinity depleted. Taken together, these data strongly imply that the circum-neutral pH of water leaching from the core of UBC-2 reflect the relatively lower rates of sulfide oxidation (compared with the exterior zones of the pile), rather than secondary processes raising the pH post-oxidation.

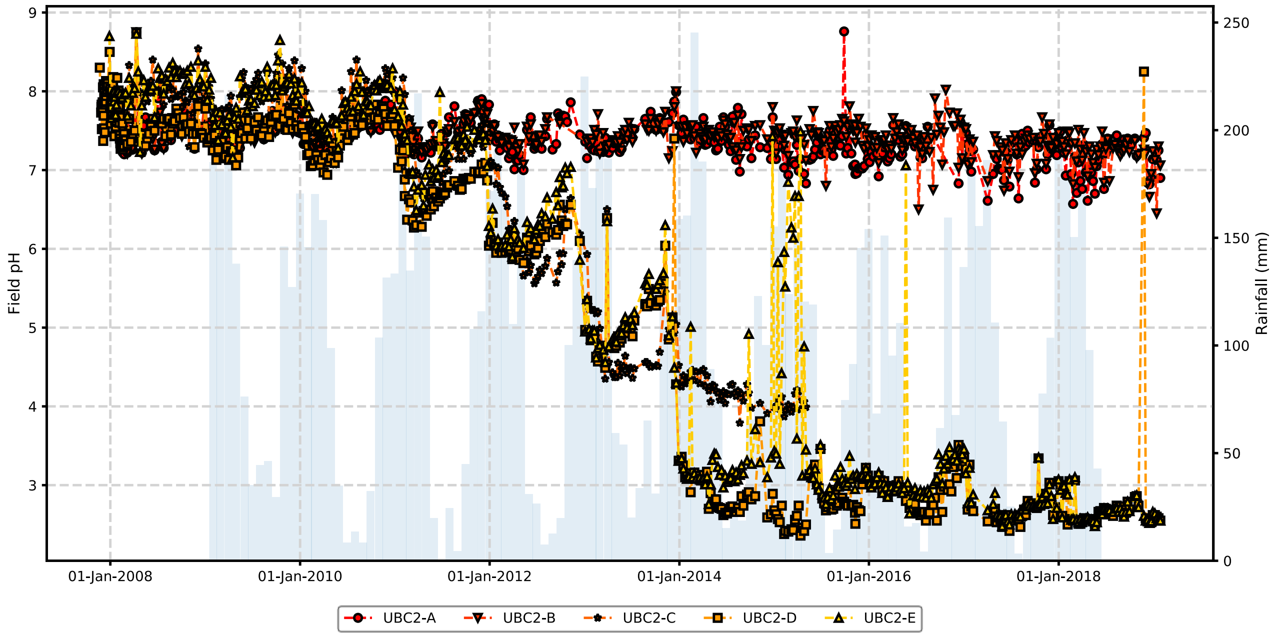

Figure 5 Timeseries of leachate pH from the lysimeters in the UBC-2 field pile.

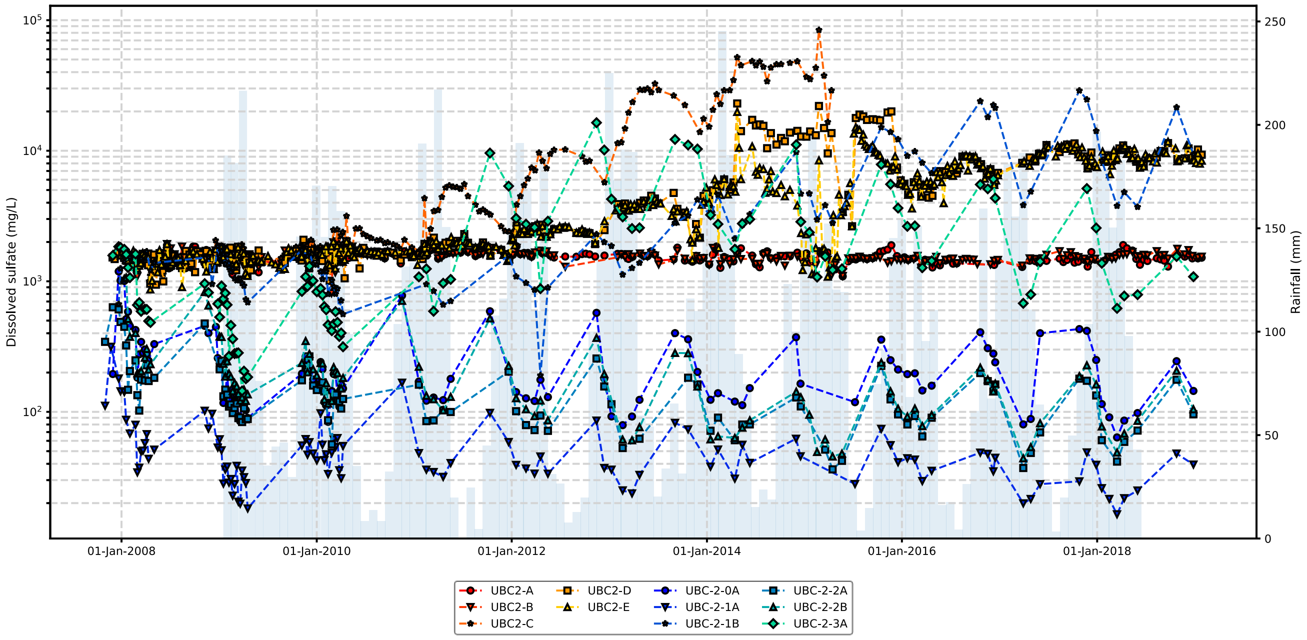

Figure 6 Sulfate concentrations in leachates. Field pile leachates are shown in hot colours, barrel leachates in cool colours.

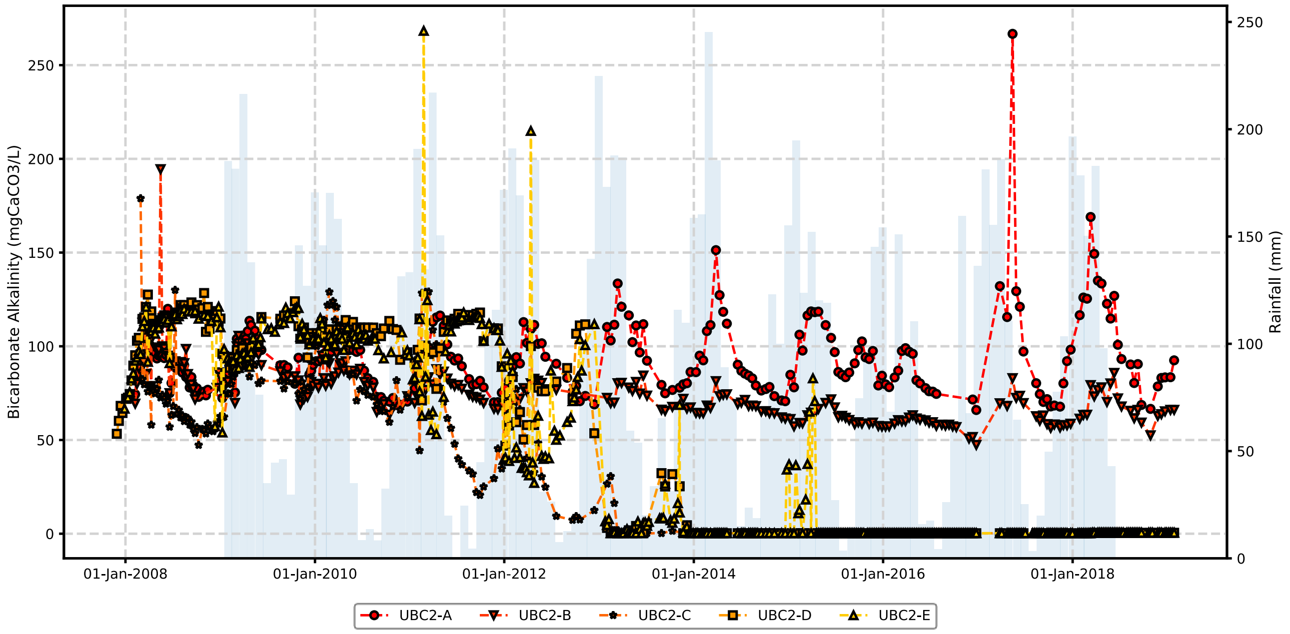

Figure 7 **Timeseries of bicarbonate alkalinity in leachates from UBC-2.**

What is the reason for this contrast in oxidation rate? Ordinarily, spatial variation in waste rock chemistry could be invoked, however this cannot be the case for UBC-2 because both the sulfur concentration and the deficit between neutralizing and acid-producing materials within this pile are largest for the material overlying lysimeter A (designated ‘UBC-2-1B’; see Table 2), which reports circum-neutral leachate water. Lysimeter C reports significantly more acidic water than lysimeter A, despite the fact that its overlying material (‘UBC-2-3A’) is less-acid generating by the metrics employed in Table 2.

Alternative (non-chemical) explanations are provided by geometric properties of the test piles, in particular: the position of a particular waste batch within the pile, and the waste batches’ grain size and pore volume. Waste rock in the core of UBC-2 differs from waste rock in the flanks in both respects: a) it is located further from the surfaces of the pile (further from the external supplies of both oxygen and water), and b) it comprises smaller particles on average due to the pile’s fining-upward sequence (the fine-grained uppers section are absent at the flanks). In addition, the top surface of the pile – which overlies lysimeters A and B only – has been compacted by traffic, to form a layer that might restrict the ingress of oxygen and water. The relative importance of these three variables (position within the pile, grain-size, the existence of a compacted layer) is of great interest to waste managers who seek to identify the design characteristics for waste dumps that minimise acidic drainage. All three are considered briefly below, assuming oxygen to be the limiting-reactant in each case[3].

Position within the pile: Besides simply the distance from the nearest surface, the position of waste within a pile (i.e. whether the nearest surface is a ceiling or a side) can profoundly affect oxidation rate. Data on full-size waste rock dumps indicates that oxygen ingress can be mostly limited to the flanks, where advection cells can be sustained by the heat generated by sulfide oxidation (e.g. Fourie et al. (2020), this session). Whether such effects control oxygen access at UBC-2 is uncertain due to the dumps smaller size and much lower internal temperature (~10°C compared with >200°C within full-scale dumps). Identification of advection cells at UBC-2, which could be achieved by identifying hotspots within its flanks, would place lower bounds on the scale- or temperature-dependence of such processes.

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[3] This assumption is supported by the year-round production of leachate water by the pile, maintained by the 1.2 m/year of rain delivered by Antamina’s monsoonal climate.

Particle size and pore volume: The efficient transport of oxygen through the pile depends on the maintenance of a network of interconnected pore spaces (diffusion of oxygen through water being extremely slow). Reduction of unsaturated pore volume will be more readily achieved by finer material. The removal of boulders during construction, along with the pile's fining-upward sequence might inhibit oxygen transport in the pile's upper levels if the material there is sufficiently fine. The particle size distributions for UBC-2 (Figure 2) indicate an abundance of sub-millimetre sized particles. This line of reasoning is counter to the 'standard' assumption that finer materials promote faster reaction rates due to their larger surface-area. Such an assumption is probably valid under well oxygenated (unsaturated) conditions but becomes irrelevant if gaseous transport through the pile is prevented by pore water. The climatic conditions present a further dimension to the question of pore space saturation; in particular the frequency and intensity of rainfall. Short intervals between rainfall events might leave insufficient time for evaporation, leading to permanent saturation of pore spaces in the upper levels of the pile. This is likely the case during the wet season (October to April) when the water balance is net-positive, however the upper levels may dry out significantly during the dry months.

The compacted layer: Where a compacted layer has sufficiently low permeability, capping the pile can inhibit infiltration and oxygen transport. If sufficiently impermeable, such a cap might also divert rainwater onto the flanks of the pile, modifying the dominant flow regime (e.g. preferential rather than matrix flow) and promoting the liberation of reaction products.

Field Barrels

Timeseries of leachate pH for the field barrels are presented in Figure 8. Only two of these barrels (UBC-2-3A and UBC-2-1B) have produced acidic leachate water. Sulfate concentrations in the barrel leachates (Figure 5) are an order of magnitude lower on average than those from the field pile, even the leachates from lysimeters A and B. This may be partly explained by the contrast between the piles' and barrels' water:rock ratio per unit area. Water draining through a field pile must pass through a significantly taller column of rock than water draining through a field barrel. Consequently, lower concentrations of sulfate are to be expected in the barrels even given equal sulfide oxidation rates, due to the additional water available for dilution. This effect is probably compounded further by evaporation from the piles. Comparisons with local rain gauges indicates that only 36% of precipitation infiltrates fully through UBC-2 (2008-2009 wet season; Beckie et al. 2010), effectively concentrating the sulfate by at least two times. By comparison, evaporation from the field barrels is likely to be negligible due to the shorter infiltration distance and barrel's impermeable plastic sides.

Sulfate concentrations in both the field piles and field barrels follow annual cycles which are ~6 months out-of-phase with each other, reflecting the different infiltration regimes in the two types of structure. Sulfate concentrations from the piles rise during the wet season and fall during the dry season, suggesting that promotion of sulfide oxidation is at least as important as flushing of the reaction products. In contrast, sulfate concentrations from the barrels fall during the wet season, because the primary effect of the rain is to dilute concentrations and remove reaction products from the barrel.

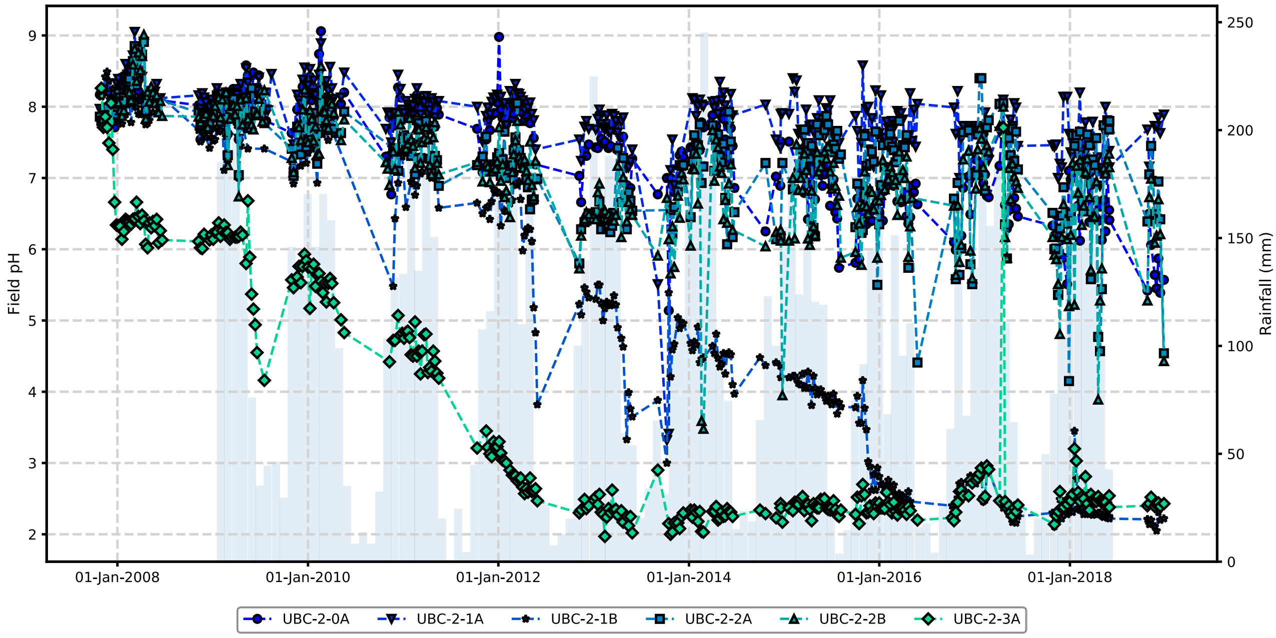

Figure 8 Timeseries of leachate pH from the UBC-2 field barrels.

5.0 SUMMARY

Antamina maintains a well-resourced geochemical characterization laboratory and undertakes research into the chemistry of drainage from the various waste rock materials on site. In collaboration with the University of British Columbia, Antamina uses these resources to manage mine waste and devise appropriate placement strategies for closure. Identification of the dependence of sulfide oxidation rate on mine waste geochemistry, grain size, pore volume, infiltration regime and oxygen accessibility allow sites such as Antamina to put measures in place to manage the mine waste during operations and closure.

The data presented here demonstrate that large spatial variations in sulfide oxidation rate can occur even within small waste dumps such as the 25,000 t field piles considered here. Indeed, the geometric aspects of waste rock (its position with a dump and its local grainsize/porosity) can actually overwhelm the effects of chemistry, as demonstrated by the production of near-neutral leachates from the most sulfur-rich portions of UBC-2; otherwise an acid-generating pile.

The full-size waste dumps at Antamina mine have masses between 300 Mt and 1500 Mt and can be up to 250 m tall. While only a small fraction of this size, the field piles discussed here provide insights into the rate-limiting reactant and drainage characteristics of waste rock piles that are more representative in scale than the humidity cells typical of standard kinetic tests. The importance of scale is further underlined by the differences in leachate chemistry between the field barrels and field piles. These differences demonstrate that caution should be exercised when using metre-scale test to infer weathering rates in full-sized storage facilities.

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DISSOLUTION OF SECONDARY SULFATE MINERALS: IMPLICATIONS FOR EFFECTIVE ACID AND METALLIFEROUS DRAINAGE MITIGATION

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ABSTRACT

Secondary hydroxysulfate minerals such as jarosite and alunite often precipitate in ferric- and aluminium-rich, acidic and oxic acid and metalliferous drainage (AMD) environments formed predominantly by pyrite oxidation. However, when the rate of pyrite oxidation passes its peak and the pH starts to increase, these secondary minerals start to re-dissolve, releasing acidity and metals. The presence of latent acidity in the forms of jarosite-alunite mineral group complicates assessment of the rates of AMD generation from potentially acid-forming waste rocks and tailings. To better enable prediction of the contributions from these secondary sulfate minerals, the relationships between pH and the rate of dissolution for natrojarosite and alunite, for comparison with pyrite, have been determined. In single mineral unstirred systems, the dissolution rates of natrojarosite and alunite in the pH range 2–7 were in the order of 10^{-14} *to* 10^{-13} *mol* m^{-2} s^{-1}*, slowest at pH 3.4 and 5.5, respectively. At pH above these respective minima, natrojarosite and alunite dissolution results in acid release. The surface area-normalised dissolution rates of both minerals were 2–3 orders of magnitude smaller than that of pyrite under the same conditions, and were 2–4 orders of magnitude slower than the rates of stirred dissolution of synthetic jarosite and alunite reported in the literature. In mixed mineral mini-column dissolution tests, pyrite oxidation proceeded at almost the same rate in the longer term (>50 days), regardless of the presence or absence of natrojarosite or alunite. As the presence of these secondary minerals does not impact significantly on pyrite oxidation rates, their contributions to AMD can be taken into account separately enabling accurate calculation of the neutralisation rates needed to effectively manage AMD.*

1.0 INTRODUCTION

Acid and metalliferous drainage (AMD) is recognised as a critical global environmental issue, resulting predominantly from the oxidation of pyrite (FeS_2) – the most abundant sulfide mineral on the earth – through chemical and microbially-mediated reactions with surface water and oxygen. AMD is often associated with low pH, typically <4, and elevated concentrations of toxic metal(loid)s such as As, Cd, Fe, Pb and Zn (Qian et al., 2018), most of which are damaging to environment and human health. The acid and toxic runoff can adversely impact environments along hydrologic gradients hundreds of kilometres from the source within relatively short times (Hochella et al., 1999). Treatment of runoff can be required for hundreds to thousands of years or "in perpetuity"

(Septoff, 2005). The United Nations has recently reported AMD to be the second biggest environmental global issue after global warming (Tuffnell, 2017).

While extensive studies have been carried out on AMD management (Johnson and Hallberg, 2005; Zhou et al., 2019), little attention has been paid to latent or ‘stored’ acidity due to secondary mineralisation during AMD formation. Latent acidity is a legacy issue, the understanding of which is critical for long-term AMD management. The primary contributors to latent acidity are secondary (hydroxy)sulfate minerals such as jarosite ($KFe_3(SO_4)_2(OH)_6$) and alunite ($KAl_3(SO_4)_2(OH)_6$). When the pH of AMD wastewaters starts to increase (e.g. during AMD recovery), these secondary minerals will re-dissolve and release the ‘stored’ acidity (e.g. Eqs. 1 and 2). Such latent acidity complicates the long-term AMD management plan and needs to be considered.

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3 + K^+ + 2SO_4^{2-} + 3H^+ \quad (1)$$

$$KAl_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Al(OH)_3 + K^+ + 2SO_4^{2-} + 3H^+ \quad (2)$$

Although the dissolution of jarosite and alunite has been widely investigated (Elwood Madden et al., 2012; Miller et al., 2016; Zahrai et al., 2013), stirring or shaking was always applied during previous studies, in contrast to quiescent (static) conditions commonly encountered in natural AMD environments. Therefore, understanding of the dissolution behaviours of these secondary minerals under AMD-relevant conditions is limited. It also remains unknow whether these secondary minerals will impact pyrite dissolution, which depends upon the pH and availability of oxidants (e.g. Fe^{3+}). The aim of this work was, therefore, to understand the dissolution behaviours of secondary sulfate minerals and their impact on pyrite dissolution kinetics under AMD-relevant conditions, and eventually help to develop greater AMD predictive capability.

2.0 EXPERIMENTAL METHODOLOGY

2.1 Materials

Natural natrojarosite, pyrite, alunite and quartz (<38 µm for natrojarosite and alunite and 38–75 for pyrite and quartz) were used for leaching experiments. Note: quartz was only used in mini-column leaching (Section 2.2). No impurity phases were detectable by powder X-ray diffraction (XRD) in the pyrite, quartz and alunite. The natrojarosite was found by XRD to contain 89 ± 5 wt.% natrojarosite, 6 ± 2 wt.% quartz, 2 ± 1 wt.% gypsum, 2 ± 1 wt.% kaolinite, and 1 ± 1 wt.% illite (Qian et al., 2019). Bulk assay analysis showed that the natrojarosite contained 3.6 wt% Na and 1 wt% K, both of which commonly exist as solid solutions in the structure of jarosite group of minerals (Qian et al., 2019); as this sample has significantly more Na than K, it is referred to as natrojarosite in this study. Note: the dissolution rate of natrojarosite was found to be generally comparable with those of jarosite (Zahrai et al., 2013). Although jarosite is more commonly found in AMD environments, kinetic dissolution results for the natrojarosite used in this work can be applied to estimate the dissolution rate of jarosite.

The BET surface areas of the sized natrojarosite, alunite and pyrite mineral samples were measured, using a Micromeritics Gemini 2375 instrument, to be 7.38 ± 0.05, 2.15 ± 0.03, and 0.35 ± 0.01 $m^2\ g^{-1}$, respectively.

2.2 Leaching Experiments

Mini-column leaching experiments (Table 1) were performed to investigate the influence of natrojarosite or alunite on pyrite dissolution. The column leaching set-up was similar to standard kinetic leach column tests (Qian et al., 2017), but at much smaller scales and funnel sizes (diameter 57 mm; depth 31 mm) and without heating. 15 mL of Milli-Q water was used for weekly watering, to keep columns wet, and 40 mL Milli-Q water was used for four-weekly flushing out of leachates for solution collection and elemental concentration analysis using ICP-OES.

Batch dissolution experiments (Table 1) were carried out, using the same sized single minerals of pyrite, natrojarosite and alunite samples as for mini-column leaching in 1 L wide-mouth Nalgene® HDPE bottles, under quiescent air-saturated and controlled pH (2–7) conditions at room temperature (22 ± 2 °C). Either LiOH or HCl was used for preparing leach solutions, depending on the desired pH. LiOH and HCl were chosen rather than KOH, NaOH or H_2SO_4 to avoid the introduction of the constituent elements (K, Na and S) of alunite, natrojarosite and pyrite. It is recognised that solution conditions (LiOH and HCl) used in this work are not typical of AMD environments and their potential impact on the dissolution of natrojarosite is yet to be explored. However, previous studies suggested that solution compositions (e.g. H2SO4 vs. HCl) have relatively minor impact on the dissolution kinetics of jarosite (see Table 1 in Zahrai et al. (2013)), with generally less than an order of magnitude difference at a specific pH. pH was monitored regularly and maintained manually, using HCl, for all batch dissolution experiments at pH 2–5. Control of pyrite dissolution at pH 6 and 7 with LiOH failed, due to extremely rapid decreases in pH (from pH 6 to 4.9), and therefore these experiments were terminated. pH for the dissolution of natrojarosite and alunite at pH 6 and 7 was controlled using LiOH.

Table 1. Conditions of the batch dissolution and mini-column experiments

Type of experiment	pH	Pyrite (g)[a]	Natrojarosite (g)[a]	Alunite (g)[a]	Quartz (g)
Batch dissolution	2–7	2.0	N.A.	N.A.	N.A.
	2–7	N.A.	8.4	N.A.	N.A.
	2–7	N.A.	N.A.	6.9	N.A.
	Uncontrolled	2.0	N.A.	N.A.	N.A.
	Uncontrolled	N.A.	8.4	N.A.	N.A.
	Uncontrolled	N.A.	N.A.	6.9	N.A.
Mini-column leaching	Uncontrolled	2.0	N.A.	N.A.	48.0
	Uncontrolled	2.0	8.4	N.A.	39.6
	Uncontrolled	2.0	N.A.	6.9	41.1

[a] The masses of natrojarosite and alunite were chosen to give similar amounts of S as that from 2 g of pyrite; N.A. – Not applicable

3.0 RESULTS AND DISCUSSION

3.1 Mini-Column Leaching

The S released from natrojarosite or alunite (Fig. 1a) in the pyrite-natrojarosite or pyrite-alunite column leaching experiments was calculated based on Na (for natrojarosite; see Supplementary Material in Qian et al. (2019)) and Al (for alunite; see Supplementary Material in Qian et al. (2019)) and the Na/S and Al/S ratios in the bulk samples (0.4 and 1.5 respectively, determined using bulk assay). The S released from pyrite was then calculated by subtracting dissolved S from natrojarosite or alunite from the total amount of dissolved S measured (Fig. 1b). The mineral dissolution rates (half the S release rate) were then calculated based on linear regressions. The dissolution of natrojarosite was found to occur more rapidly in the first 50 days than in the subsequent 70 days. This may result from the relatively high initial pH (effluent pH 5.5–4.0) as compared to the pH range of 3.5–3.2 in the later stages of reaction. For alunite, there was a delay of about 21 days prior to dissolution, likely due to the formation of Al-containing precipitates as a result of relatively high pH during this period (> pH 5). The possible Al precipitation may result in underestimation of the alunite dissolved in the mixed pyrite-alunite leach column. The dissolution rate of alunite remained almost unchanged after 21 days.

The presence of natrojarosite was found to have likely reduced the rate of pyrite dissolution up to about 50 days. The reduced initial pyrite dissolution rate may be due to adsorption of aqueous sulfate species by Fe (oxy)hydroxides formed on natrojarosite surfaces (Geelhoed et al., 1997; Parfitt and Smart, 1978). Subsequent to 50 days, the rate of pyrite dissolution for all leach columns remained the same, suggesting that the presence of natrojarosite or alunite does not impact pyrite dissolution in the longer term.

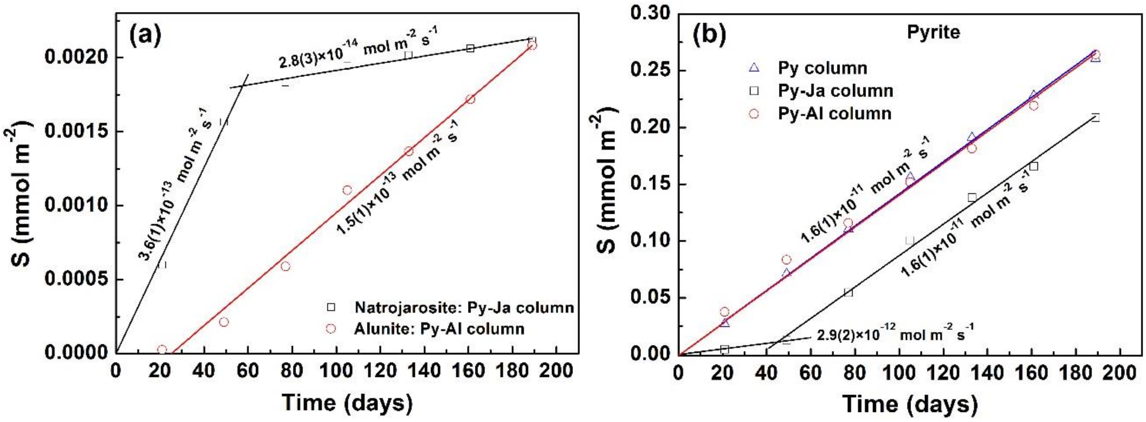

Fig. 1. **The surface area-normalised cumulative S released as a function of time for jarosite in the mixed pyrite-natrojarosite mini-column (a), alunite in the mixed pyrite-alunite mini-column (a), and pyrite in the pyrite-only and mixed column leaching experiments (b). Solid lines represent linear fittings. The S release rates (twice the jarosite, alunite and pyrite dissolution rates) are given in (a) and (b). Standard errors from linear regressions are given in parentheses. Al – Alunite; Ja – Natrojarosite; Py – Pyrite.**

3.2 Batch Dissolution

For natrojarosite dissolution at pH 2, no variation in pH was observed as the H^+ was sufficiently concentrated for the pH to not be makedly affected by natrojarosite dissolution. However, HCl was required to maintain the natrojarosite dissolution at pH 3, suggesting that the dissolution reaction consumes acid. At pH 4 for the natrojarosite dissolution, the pH remained at ±0.1 without the use of HCl or LiOH; this indicates that natrojarosite can buffer to around this pH. LiOH was required to stabilise the pH at pH 5–7, suggesting that natrojarosite dissolution at these pH results in release of H^+. Similar to natrojarosite dissolution, no pH adjustment was needed for alunite dissolution at pH 2. The alunite batch dissolution experiments at pH 3–5 required HCl, indicating that dissolution consumes acid. In comparison, at pH 6 and 7 LiOH addition was required to maintain constant pH, indicating acid production.

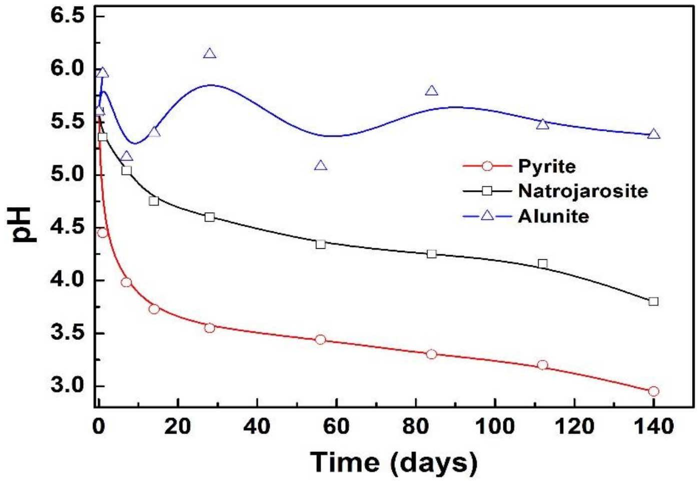

Fig. 2. **Variation of pH for uncontrolled batch dissolution of pyrite, natrojarosite, and alunite**

The pH of the alunite leachate (Milli-Q water) for the uncontrolled dissolution experiment was initially 5.6 at day 0 and fluctuated, on average, around 5.5 from day 1, suggesting that no significant acidity is released (Fig. 2). The solution pH during both the pyrite and natrojarosite dissolution under uncontrolled pH conditions decreased remarkably in the first 10 days (Fig. 2). Thereafter the decrease slowed to give a final pH of 3.8 for natrojarosite and 2.9 for pyrite over the next 130 days. These pH variations suggest that natrojarosite may pose a more significant AMD risk than alunite.

The dissolution of natrojarosite significantly decreased from pH 2 to pH 3 and then increased until pH 7 (Fig. 3a). In comparison, the dissolution of alunite decreased remarkably from pH 2 to 4 and then slightly increased with increasing pH (Fig. 3b). For both natrojarosite and alunite, long-term dissolution rates (after 14 days) were calculated with the initial BET surface areas used for normalisation. It was found that the dissolution of natrojarosite and alunite followed “V-shape” trend with minima at pH 3.4 for natrojarosite dissolution and pH 5.5 for alunite dissolution (Fig. 3c). At pH below the inflection point the dissolution reactions are acid consuming (Eqs. 3 and 4), whereas above the inflection point the reactions are acid generating (similar to jarosite dissolution shown in Eqs. 1 and 2). For AMD remediation, the contribution of these secondary sulfate minerals to acid generation should only be considered when the pH of AMD wastewaters is above the inflection point. The pH values for minimum dissolution rates of natrojarosite and alunite are similar to those reported for the dissolution of synthetic jarosite and alunite (Elwood Madden et al., 2012; Miller et al., 2016). The proposed acid-generating and -consuming mechanisms are also consistent with observations of the acid (HCl) or base (LiOH) solutions required to adjust pH during dissolution experiments (see above). The pH shift of the inflection point from pH 3.4 for natrojarosite to pH 5.5 for alunite is likely due to the pH value of the first hydrolysis constant of Fe3+ and Al3+ dissolved from natrojarosite and alunite (see Fig. 7 in Miller et al. (2016)). Compared with the dissolution of synthetic jarosite and alunite reported in previous studies (Elwood Madden et al., 2012; Miller et al., 2016), the dissolution of natrojarosite and alunite under quiescent conditions, similar to those largely encountered in AMD environments, is 2–4 orders of magnitude slower.

$$KFe_3(SO_4)_2(OH)_6 + 6H^+ \rightarrow K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \quad (3)$$

$$KAl_3(SO_4)_2(OH)_6 + 6H^+ \rightarrow K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O \quad (4)$$

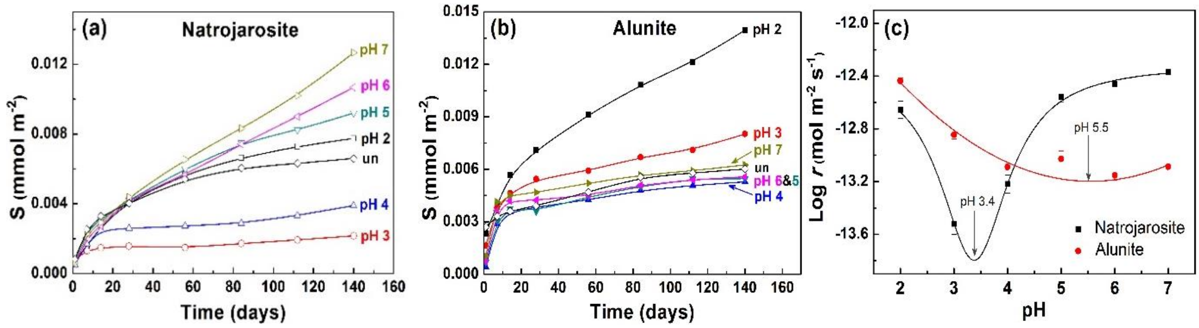

Fig. 3. **Surface area-normalised S release (a and b) as a function of time for the dissolution of natrojarosite and alunite at various pH, and the corresponding surface area-normalised dissolution rates presented on a log scale as a function of pH (c). Solid lines are given in (a)–(c) as guides to the eye. For clarity experimental errors (± 10%) are not included in the figure. Note: K and Fe data were not used for calculation of the natrojarosite dissolution rate due to K contamination from the pH/Eh probe and Fe precipitation above pH 3; Al data were not used for calculation of the alunite dissolution rate due to Al precipitation above pH 4 (see Supplementary Material in Qian et al. (2019)).**

For pyrite dissolution, a linear correlation between the dissolution rate (calculated based on S release; Fig. 4a) and pH was found in the pH range 2 to 5 (Fig. 4b), suggesting that pyrite oxidation under quiescent conditions is controlled by dissolved O_2 (Williamson and Rimstidt, 1994). Using the rate law (Eq. 5) developed by Williamson and Rimstidt (1994), the rates of pyrite dissolution were also calculated to be (2 ± 1, 3 ± 2, 4 ± 2, 5 ± 3)$\times10^{-10}$ mol m^{-2} s^{-1} at pH 2, 3, 4 and 5, which are approximately 5 times greater than the dissolution rates determined from our batch dissolution experiments. These differences may result from the different conditions, i.e. quiescent dissolution conditions in this work *vs*. stirred conditions applied in previous studies, and suggest that pyrite dissolution may be partly controlled by diffusion.

$$r = 10^{-8.19(\pm 0.1)} \frac{m_{O_2}^{0.5(\pm 0.04)}}{m_{H^+}^{0.11(\pm 0.01)}} \qquad (5)$$

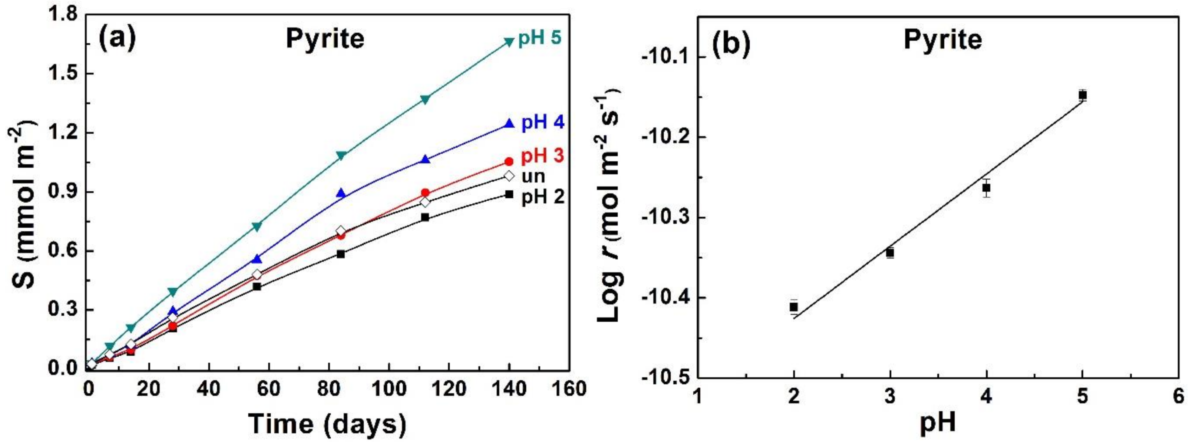

Fig. 4. **Surface area-normalised S release as a function of time for the dissolution of pyrite at various pH (a), and the calculated dissolution rates presented on a log scale (b). Solid lines are given in (a) and (b) as guides to the eye. For clarity experimental errors (± 10%) are not included in the figure. ‘un’ – uncontrolled pH.**

4.0 Conclusions

The dissolution rates of natrojarosite or alunite were found to decrease and then increase with increasing pH under quiescent conditions, following a ‘V-shape’ trend with minima at pH 3.4 for natrojarosite and pH 5.5 for alunite. Compared with the dissolution of synthetic jarosite and alunite under stirred conditions, the dissolution of natrojarosite and alunite under quiescent conditions, similar to those expected in AMD environments, is 2–4 orders of magnitude slower. Mini-column leaching showed that the presence of alunite or natrojarosite did not appear to have any influence on the dissolution of pyrite in the long term.

Although surface area normalised pyrite dissolution rates are orders of magnitude greater than jarosite or alunite, these secondary sulfate minerals nearly always have appreciably greater surface area per unit mass than pyrite. Therefore their contribution to acid generation requires to be be considered in AMD control. The amounts of alunite and jarosite present should be quantified for accurate assessment of stored acidity and amounts of neutralising materials needed. Importantly rates of acid production and neutralisation also need to be matched for effective and sustainable remediation in the longer term. As the presence of these secondary sulfate minerals does not impact significantly on pyrite oxidation rates, the rate relationships with pH derived can be applied for calculation of the necessary rate of neutralisation required. As both jarosite and alunite release acidity on increasing pH (>3.4 for natrojarosite and >5.5 for alunite in this study), this assessment will be valuable in aged and remediated mine wastes as the pH increases.

5.0 ACKNOWLEDGEMENTS

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ASSESSING THE LEACHING POTENTIAL OF SOLUTES FROM WASTE ROCKS EPISODICALLY AND CONTINUOUSLY EXPOSED TO SALINE AND HYPERSALINE CONDITIONS

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ABSTRACT

Current standard analytical tools used to estimate the long-term leaching potential of solutes from waste rocks episodically or continuously submerged by water are not designed to study the effect of saline and hypersaline water. Subsequent impact on ground and surface water quality, as in mine pit lakes, is poorly understood. The objective of this study was to apply kinetic tests better suited to determining long-term leaching potential of waste rocks that are episodically or continuously exposed to saline and hypersaline conditions. The kinetic leach study was conducted over 24 months on fresh and weathered rock and tailings material. Wet conditions in equilibrium with atmosphere were studied using large columns (submerged) for studying saturated and potentially reducing conditions. Salinity levels studied included 0 (deionised water), 1,000, 10,000, 25,000, and 100,000 mg L-1 of NaCl. Leachates were analysed for water-soluble Al, Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cl, Cr, Cs, Cu, Fe, Li, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Th, Ti, Tl, U, V and Zn, by ICP-AES/MS and F by Ion specific electrode.

Total S for all the samples were low (0.04-0.11%) and all the samples were classified as non-acid forming (NAF). This study provided useful information on the dissolution of solutes under circum-neutral and slightly alkaline conditions, but not acidic conditions. Leachate pH values derived from use of unbuffered pH 4 leaching solutions were typically circum-neutral because of pH buffering characteristics of minerals in the samples. Concentrations of most elements, notably Ag, increased with increasing salinity. Leachates were typically oxic (based on Eh measurements), and moderately to highly aerobic (based on dissolved oxygen measurements) and consequently concentrations of elements such as Fe and Mn were low. Due to low S content of samples, there is relatively little opportunity to consume DO from the water cover layer of saturated column for sulfide oxidation such as decaying organic matter. Elements of interest for water quality in potential pit lakes included F, B, Ag (at high salinity) and hexavalent Cr (under highly oxic conditions).

1.0 INTRODUCTION

In the evaluation of a mine development project, an important aspect is the potential for environmental impact, especially the leaching of metals and other elements (Bowell et al., 2000). Mining waste not only occupies large areas of land, but may also cause environmental pollution, particularly by harmful elements released after heavy rainfall (Dan et al., 2011). Projected mine wastes must be characterized and their drainage quality predicted before the mining activity in order to apply efficient management solutions capable of minimising adverse impacts on natural waters. An accurate prediction of potential drainage chemistry is a key factor in choosing successful cost-effective, proactive measures (Price, 2009). Acid generation potential and related mobilisation of metals/metalloids in mine waste depends on the balance between acid production capacity and acid neutralizing capacity (ANC) in the rock matrix, the specific minerals present, and the availability of water and oxygen (Dan et al., 2011). However, there are instances where the acid generation potential of mine waste is low and yet metals/metalloids (e.g. Se and As oxyanions) may be mobilised under alkaline or neutral conditions (Kwong et al., 2000).

Current tests used to inform the extent of release of metals/metalloids and acid production include static tests, submerged column methods, kinetic leaching and sequential leaching protocols (Usher et al., 2017). For rocks likely to be continuously exposed to saline and hyper-saline solutions, it is more appropriate to conduct long-term leaching trials using submerged columns where the rock is continuously exposed to conditions that mimic their natural environment. Current analytical tools, especially standard kinetic tests (AMIRA 2002), used to estimate the long-term metal/metalloid (including metal containing oxy anions) leaching potential of rocks exposed to saline, hypersaline and sodic water are not fit for purpose as the standard tests use deionised water. These test use deionised water as the test leaching solution and hence these methods do not mimic materials that are exposed to saline and hyper-saline solutions. Thus, the impact on ground and surface water quality is poorly understood. This is of particular concern since these data are needed to inform the hydrodynamic models that are used to support mine site closure planning and approval. The main aim of the research was assessing the leaching potential of solutes from waste rocks episodically and continuously exposed to saline and hypersaline conditions.

2.0 MATERIAL METHODS

Five rock samples from fresh/weathered rock and tailings material from iron ore mining in the Pilbara region of WA were identified as Lithology 1, Lithology 2, Lithology 3, Tailings 1 and Tailings 2. The experimental design for different treatments application to all the rock samples are shown in Table 1.

Table 1. Experimental design for application of different kinetic leaching treatment to the test samples.

Test sample	Mineral Composition	Kinetic column	Submerged column
Lithology 1 (Lith 1)	50% Goethite, 40% Hematite, 10% Kaolinite	Deionised water	
		pH 7; 1000 mg L^{-1}	
		pH 7; 10,000 mg L^{-1}	pH 7; 10,000 mg L^{-1}
		pH 7; 25,000 mg L^{-1}	
		pH 7; 10,000 mg L^{-1}	pH 7; 25,000 mg L^{-1}
		pH 4; <10 mg L^{-1}	pH 7; 100,000 mg L^{-1}
		pH 9; <10 mg L^{-1}	
Lithology 2 (Lith 2)	30% Goethite, 25% Kaolinite, 20% Quartz, 15% Hematite, 10% Smectite	Deionised water	
		pH 7, 1000 mg L^{-1}	
		pH 7; 25000 mg L^{-1}	
		pH 4; <10 mg L^{-1}	pH 7; 25000 mg L^{-1}
		pH 4; 1000 mg L^{-1}	
		pH 9; <10 mg L^{-1}	
Lithology 3 (Lith 3)	35% Goethite, 25% Hematite, 30% Quartz, 10% Kaolinite	Deionised water	
		pH 7, 1000 mg L^{-1}	
		pH 7; 10000 mg L^{-1}	
		pH 7; 25000 mg L^{-1}	
		pH 4; 1000 mg L^{-1}	pH 7; 25000 mg L^{-1}
		pH 9; 1000 mg L^{-1}	pH 4; 10,000 mg L^{-1}
Tailings 1 (T1)	55% Goethite, 20% Hematite, 25% Kaolinite	Deionised water	
		pH 7; 10,000 mg L^{-1}	pH 7; 10,000 mg L^{-1}
		pH 4; <10 mg L^{-1}	
Tailings 2 (T2)	55% Goethite, 25% Hematite, 20% Kaolinite	pH 7; 25000 mg L^{-1}	
		pH 4; 1000 mg L^{-1}	pH 7, 25000 mg L^{-1}

Firstly, standard AMIRA columns were used for kinetic leach tests (AMIRA 2002) for 2 years. Secondly, submerged tall columns (50 cm height.) were saturated with a 10 cm liquid layer above the test material to study the saturated and potentially reducing conditions, movement of oxygen towards the bottom was restricted and some reduction would occur. Note: a 10 cm layer does not prevent oxygen ingress to the underlying waste –at least several metres cover would be required, but this is not practical in a laboratory context. The 10 cm layer is appropriate for the solute flushing requirements and will provide evidence of the effects of reduced (but no zero) oxygen ingress rates on solute dissolution. Approximately 250-300 mL of leachates were collected from the base of the columns weekly for the first four weeks and monthly thereafter for 23 months under 25 ± 2 °C. The amount of solution removed from the column was topped with the same pH adjusted solution to keep a constant head. Different treatments of salinity level applied to different lithology and tailings samples in both AMIRA and submerged column are shown in Table 1.

3.0 ANALYSIS

All the samples were fully characterised for mineralogy by XRD/SEM, total elemental composition by four-acid digestion plus ICP/AES and by XRF, acid-base accounting (ABA) and related analyses [ANC, net acid generation (NAG), pH (NAG), S, SO_4-S, chromium reducible S (CRS), and total actual acidity (TAA)]. Leachate samples filtered through a 0.2 µm filter were analysed for water-soluble Al, Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cl, Cr, Cs, Cu, Fe, La, Li, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Sn, Sr, Th, Ti, Tl, U, V and Zn by ICP-AES/MS; F by Ion Specific Electrode; alkalinity (bicarbonate, carbonate and total); acidity; free acidity if pH is <4.5 and total acidity if pH <8.3.

4.0 RESULT AND DISCUSSION

4.1 Sample characterisation

Total S (TS) concentrations were low, ranging from 0.04% to 0.11% (Table 2). The SO_4-S concentrations, reported in Table 1, were very low for all the test samples, but represented approximately 50% of TS in the tailings. Consequently, oxidisable S (measured directly as CRS, or indirectly as the difference between TS and SO_4-S) concentrations were low. All test samples were classified as NAF. The NAF classifications were confirmed by circum-neutral NAG pH values and TAA values of <1 mol $H^+ t^{-1}$.

Table 2. Acid base accounting characterisation for three lithology and two tailings.

	Lithology 1	Lithology 2	Lithology 3	Tailings 1	Tailings 2
ANC (kg H2SO4 t^{-1})	1.6	5.7	1.4	5.1	3.8
NAG (kg H2SO4 t^{-1})	<0.5	<0.5	<0.5	<0.5	<0.5
pH (NAG)	7.3	7.1	7.5	7.6	7.4
S-S04 (%)	0.01	<0.01	<0.01	0.05	0.04
S (%)	0.04	0.1	0.03	0.11	0.09
CRS (%)	<0.005	<0.005	<0.005	<0.005	<0.005
TAA (moles H+ t^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0

Note: ANC- acid neutralisation capacity; NAG- net acid generation; TAA- total actual acidity.

As expected for highly ferruginous materials, all test samples contained iron oxides as the dominant mineral phase; mainly goethite and hematite, with minor amounts of maghemite (maximum 4-8%) in several samples. Quartz was a major gangue mineral, notably in Lithology 2 and 3. Traces of calcite (<1%) were detected in Lithology 2, and Tailings 2. Clay minerals, mainly kaolinite and possibly minor smectite, were present in all samples, but notably Lithology 3 (up to 48%).

4.2 AMIRA (kinetic) and submerged column leach study

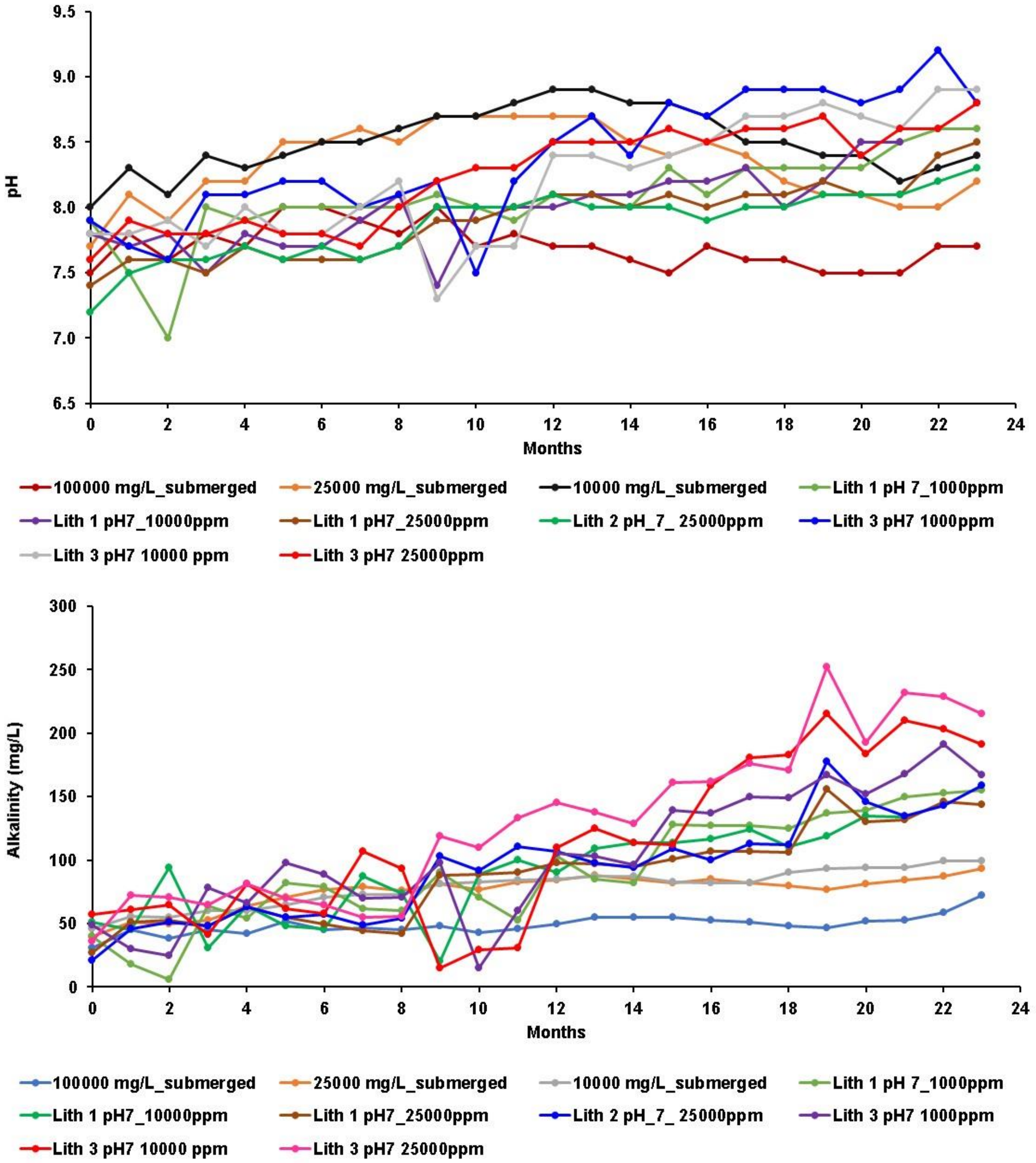

Fig. 1. Leaching curves for pH and alkalinity for AMIRA and submerged columns for different lithologies and tailings samples. (Note: Lith- lithology).

Leachate pH values were typically circum-neutral to slightly alkaline (Fig. 1). Results suggested that the leachate pH values are controlled mainly by the inherent pH of the sample and the buffering capacity of key minerals, rather than acidity/alkalinity of the leaching solutions. Lower pH solutions from month 12 from columns leached with the pH 4 leaching solution suggest that the most (but not all) of the buffering capacity of this sample may have been consumed by this time.

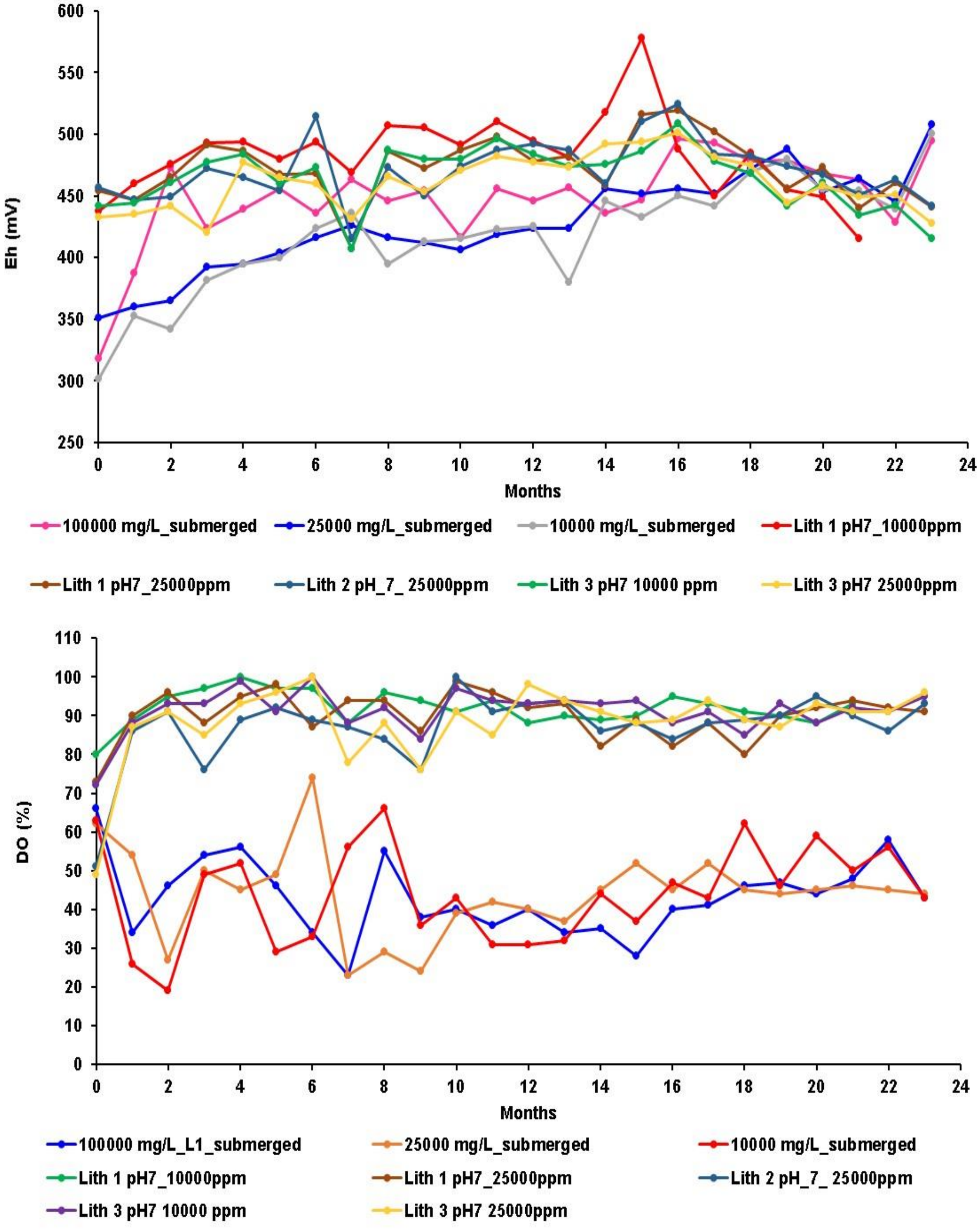

Fig. 2. Leaching curves for redox potential (Eh) and dissolved oxygen (DO) for AMIRA and submerged columns for different lithologies and tailings samples. (Note: Lith-lithology).

Salinity of the leaching solution also had a minor effect on leachate pH values. Mostly, leachate pH values decreased with increasing salinity (Fig. 1). The decrease in pH in response to increased salinity (TDS) of the leaching solution was interpreted as a consequence of displacement of exchangeable acidity from the exchange sites of clay minerals in the sample by Na ions in the leaching solution.

Alkalinity increased over time for columns in equilibrium with the atmosphere (AMIRA column) however, the submerged column (25,000 mg/L TDS) behaved differently (Fig. 1); alkalinity concentrations increased from 106 to 276 mg $CaCO_3$ L^{-1} for the third to fifth leachates, and then decreased steadily to last three leachate (172 mg $CaCO_3$ L^{-1}). The reasons for this anomalous behaviour are not clear but may relate to different rates of exchange in CO_2 and evapoconcentration.

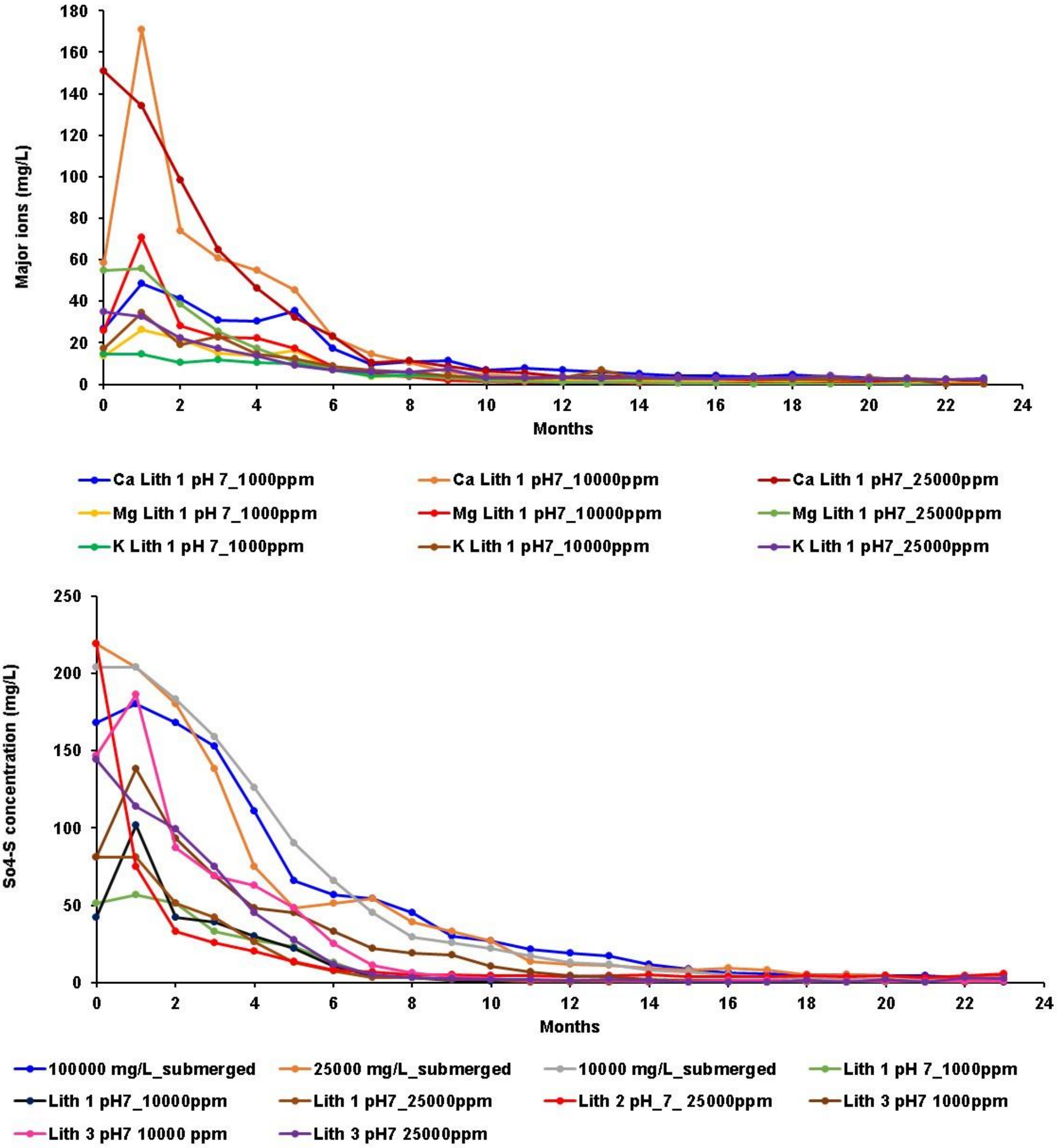

Fig. 3. Leaching curves for major ions (Ca, Mg, Na and K) and SO4-S for AMIRA and submerged columns for different lithologies and tailings samples (Note: Lith-lithology).

Minor variations for redox potential (reported as Eh value, mV) and dissolved oxygen (DO, reported as % saturation) noted between sample type and column technique, with the lowest values for both parameters typically recorded for the first two leachates and relatively stable thereafter (Fig. 2). Generally, moderately oxic (Eh 300 to 500 mV) and aerobic (DO >60%) conditions prevailed throughout the leaching experiment. Lower DO values (typically 20 to 60%) were recorded for the sealed, submerged tall columns. Note: a 10 cm layer does not prevent oxygen ingress to the underlying waste – at least several metres cover would be required, but this is not practical in a laboratory context. The 10 cm layer is appropriate for the solute flushing requirements and will provide evidence of the effects of reduced (but no zero) oxygen ingress rates on solute dissolution. Under a saturated leaching environment, sulfide oxidation will preferentially occur in the absence of a more proficient DO scavenger such as decaying organic matter (Kwong et al.,2003). However, all the test samples in the present study were low in S content (Table 2), so therefore relatively little opportunity to consume DO from the water cover layer.

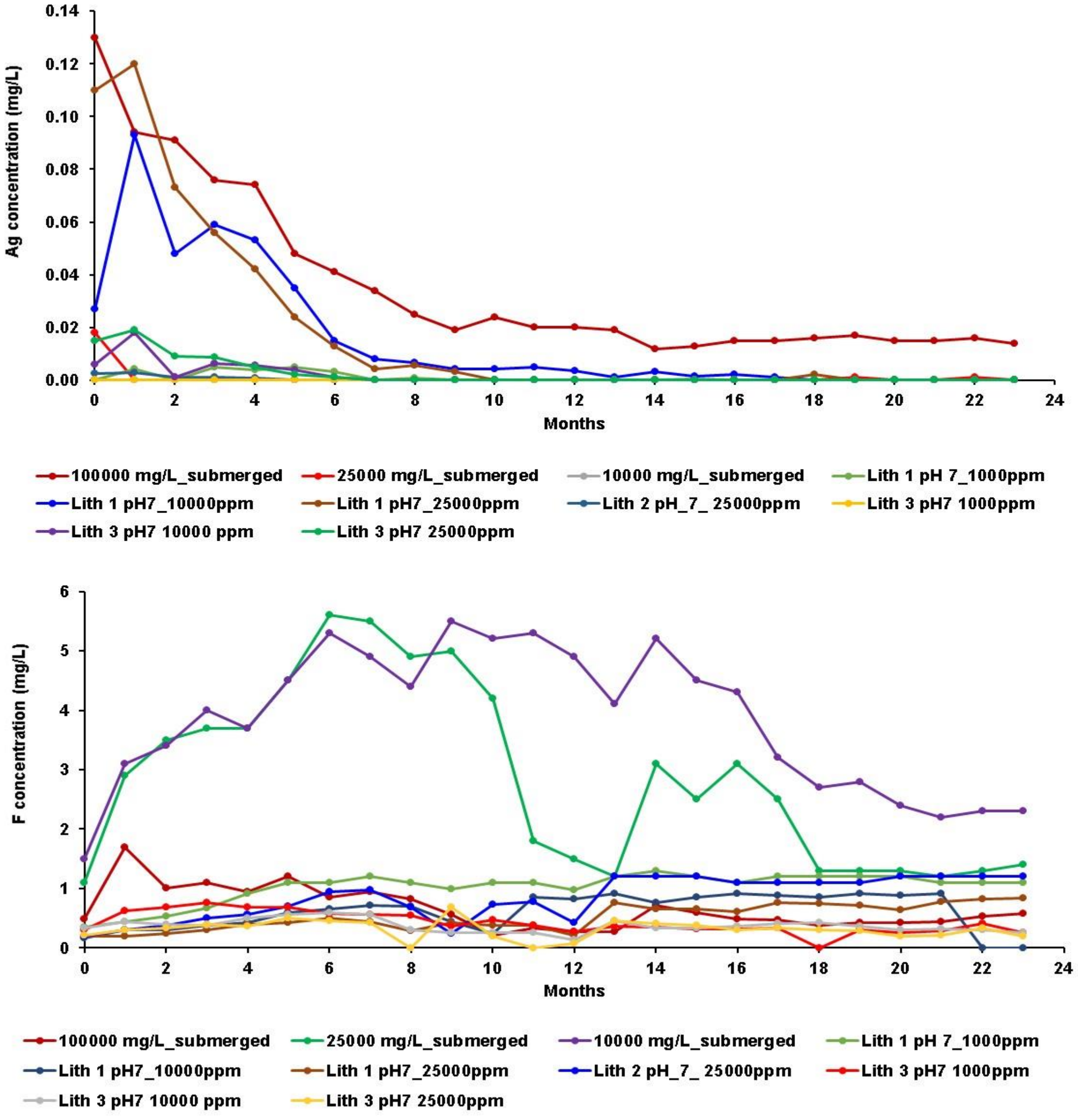

Fig. 4. Leaching curves for Silver (Ag) and Fluoride (F) for AMIRA and submerged columns for different lithologies and tailings samples (Note: Lith- lithology).

The rate of "wash-out" for the major ions (Fig. 3) decreased over time, which is consistent with the displacement of exchangeable cations in clay soils, with elevated concentrations of Na in the leaching solution being the displacing cation. Concentration of SO_4 decreased with time (Fig. 3). Concentrations of Ba were expected to increase due to the resulting dissolution of $BaSO_4$, in accordance with Le Chatelier's Principle. PHREEQC modelling confirmed that leachates were saturated with respect to barite (Saturation Index (SI) = 0.96), and also gypsum ($CaSO_4.2H_2O$, SI 0.25), but under-saturated with respect to the corresponding strontium sulfate (celestite, $SrSO_4$, SI = -0.25). Comparison of the leaching curves demonstrate that concentrations of major cations were initially greater in the high TDS leaching solutions, but then decreased significantly over time irrespective of salinity.

The highest Ag concentration was 0.11 mg L^{-1}, measured in leachates of Lithology 1 leached with high salinity solutions. Elevated Ag concentrations were recovered for the first five or more solutions with leaching fluids at higher TDS, with the first two leachates from each treatment increasing with increasing salinity (Fig. 4). The behaviour in each case was typical of “wash out” behaviour. PHREEQC modelling (first leachate at 100,000 mg L^{-1}. TDS: 100,000 mg L^{-1} of NaCl is < 2 molL^{-1}). indicated that Ag concentrations were unlikely to be controlled by solution equilibria with common Ag minerals, as indicated by SI values; cerargyrite (AgCl) -10.64, Ag_2CO_3 -37.48, Ag_2O -39.85, Ag_2SO_4 -41.48, $AgF.4H_2O$ -28.18, metallic Ag -14.9. The dominant form (>99%) of dissolved Ag was the chloro complex ion, $AgCl_2^-$. Although the accuracy of the modelling may be lacking, it clearly supports the hypothesis/explanation that common Ag minerals are expected to be soluble at elevated chloride concentrations. These predictions are consistent with the dissolution of sparingly soluble Ag minerals by very higher chloride concentrations, favouring the formation of the stable and moderately soluble chloro complex ion. PHREEQC also predicted that several other ions, if present at detectable concentrations in highly saline solutions, would also be present as chloro complex ions, rather than free hydrated or hydroxy complex ions. These metals were Zn as $ZnCl_4^{2-}$, Ni as $NiCl^+$, Cu as $CuCl_3^-$, Co as $CoCl^+$, Cd as $CdCl_3^-$. Therefore, it is sufficiently accurate to support the hypothesis that several metal ions are expected to be present as stable chloro complex ions – i.e. the model is fit for purpose.

Results indicate higher potential for F dissolution at under circum-neutral conditions compared to slightly alkaline conditions (Fig. 4). It suggests that F dissolution is unlikely to be controlled by mineral solubility equilibria, although fluorite may approach saturation at higher Ca concentrations to that used in the model (5.6 mg L^{-1}). The elution behaviour of F is more likely to be controlled by surface adsorption reaction with hydrous iron oxide surfaces, such as goethite (FeOOH). Surface sorption of F on goethite has been widely studied (Bolan and Barrow 1984) and is dependent on factors including temperature, ionic strength (salinity), pH and competitive ions, such as phosphate and molybdate.

Slightly elevated Cr concentrations noted (up to 0.015 mg L^{-1} in Lithology 3 and Tailings 2 leachates) in the kinetic leach. However, lowest concentrations were recorded for the submerged (25,000 mg L^{-1} TDS) which suggest that availability of DO by exchange with atmospheric oxygen may be a contributing factor affecting Cr dissolution. Solution speciation modelling was informative in that it predicted that almost all of the dissolved Cr was predicted to be present in the hexavalent (chromate) form, with the dominant ion being CrO_4^{2-} with minor $NaCrO_4^-$ and $HCrO_4^-$.

5.0 CONCLUSIONS

This study provided useful information on the dissolution of solutes under circum-neutral and slightly alkaline conditions. Leachate pH values derived from use of unbuffered pH 4 leaching solutions were typically circum-neutral as a consequence of the pH buffering characteristics of minerals in the samples. Concentrations of most elements, notably Ag, increased with increasing salinity. Leachates were typically oxic (based on Eh measurements), and moderately to highly aerobic (based on DO measurements) and consequently concentrations of elements such as Fe and Mn were very low. Elements of interest for water quality in potential pit lakes include F, B, Ag (at high salinity) and hexavalent Cr (if oxic conditions are maintained). Concentrations of solutes from the lithologies under study are predicted to be low, as a consequence of the highly ferruginous and low sulfide contents. The presence of hydrous iron oxides is expected to restrict concentrations of metalloids (notably arsenic and selenium, but also antimony and bismuth) to very low levels. PHREEQC geochemical modelling indicated that concentrations of many elements (notably Ag, B, Cd, Co, Cu, Cr, Pb, Ni, Pb and Zn) were not controlled by the solubility of specific mineral phases and the solubility of metals including Ag, Co, Cd, Ni could be enhanced with increasing salinity by formation of chloro- complex (notably $AgCl_2^-$ in highly saline conditions).

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THE APPLICATION AND TESTING OF A TIME EXTENDED PASTE pH TEST FOR PYRRHOTITE IN WASTE ROCK SORTER TRIAL

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ABSTRACT

Renison Tin mine has recently commissioned an ore and NAF-PAF waste rock sorter. After crushing, the primary ore sorter is based on density to collect cassiterite in rock for processing. This is followed by separation of NAF from PAF waste rock, with pyrrhotite and minor pyrite, by the COM Tertiary EM sorter. The objective of this study was to develop a direct and simple approach applicable to the rejected NAF wastes, for application during operations, and for continued testing of the efficacy of the EM sorter. Consequently, a Time Extended Paste pH test (GARD 5:1) was proposed and tested.

Sub-samples of six 'NAF' reject waste rock aggregates from 12-hour shift samples over one week, were examined as ground composites. These six samples were all confirmed to be NAF using standard and pyrrhotite-corrected acid-base-accounting methodologies and Extended Time Paste pH tests. Importantly, both the test and modelling demonstrated rapid initial alkalinity generation suggesting that greater acid neutralising capacity (ANC) may be required for long-term neutral drainage than indicated by a maximum potential acidity MPA (calculated using sulfide S) to ANC ratio of 1. Hence an ANC/MPA* cut off of 1.5, above which the waste rock is defined as NAF, is recommended.*

It is proposed that NAG pH measurements are not used for assessment of these wastes. It has been demonstrated that this test overestimates the amount of acidity generated by pyrrhotite-containing materials due to the highly oxidising nature of the NAG test which does not occur in waste rock and tailings. The NAG test results in the oxidation of pyrrhotite sulfide entirely through to sulfate, an acid forming pathway, instead of a large portion reacting to form elemental sulfur and can result in erroneous identification of PAF or Uncertain sample classification.

1.0 INTRODUCTION

Renison Tin mine has recently commissioned an ore and NAF-PAF waste rock sorter. After crushing, the selection of waste rock uses X-Ray Transmission (XRT) based on density, to separate gangue particles from value cassiterite (6.7−7.1 g cm^{-3}). The waste rock contains pyrrhotite and minor pyrite. The XRT ore sorter is followed by separation of NAF from PAF waste rock by the COM Tertiary EM sorter that recognises magnetic susceptibility and conductivity of materials. It is principally magnetic susceptibility that is the criterion for separation in this system. Pyrite has low magnetic susceptibility (diamagnetic) and is effectively invisible to the EM sorter. Sorting of NAF from PAF is therefore essentially based on pyrrhotite content. As the pyrite content is not a factor in the EM sorting, the NAF to PAF cut off in the EM sorter 'assumes' that the pyrite and pyrrhotite contents are sufficiently correlated to enable identification of PAF material based on pyrrhotite only.

The objectives of this study were to assess the efficacy of the NAF-PAF separation and to develop a direct analytical approach for continued assessment that could be carried out at the Renison site by SGS, applicable to pyrrhotite-containing wastes, for application during operations. In this regard a Time Extended Paste pH test was proposed. Sub-samples of six NAF waste rock aggregates, each composited from 12-hour shift samples over one week, were examined.

2. CHARACTERISATION

Powder X-ray diffraction (XRD) was carried out on ground samples from six waste rock aggregates with 15 wt% added corundum (for amorphous or identified phase quantification). The pyrite content was found to range from 0.7 to 1.4 wt% and the pyrrhotite content from 1.3 to 2.9 wt% (Table 1). No other sulfide minerals were identified by XRD. The carbonates identified were calcite (0.5–1.2 wt%), dolomite (2.5–9.9 wt%) and siderite (0.7–1.8 wt%). There are also reactive silicate minerals (i.e. tourmaline, chlorite) that may provide additional neutralisation in long-term storage.

Table 1. Mineralogy (wt%) derived from quantitative XRD analysis

	OSW1	OSW2	OSW3	OSW4	OSW5	OSW6
Pyrite	1.5	2.0	2.5	1.5	0.7	1.4
Pyrrhotite	2.9	1.3	1.5	2.1	1.6	1.5
Dolomite	6.1	3.3	5.9	2.5	9.9	5.2
Calcite	1.2	0.7	1.2	0.5	1.3	0.6
Siderite	1.8	1.8	1.8	1.2	0.7	1.0
Tourmaline (dravite)	11.1	7.2	9.8	8.9	5.8	9.4
Clinopyroxene	3.4	4.9	3.8	3.9	4.0	2.6
Chlorite (chamosite)	10.3	8.8	8.4	10.1	9.1	8.9
Amphibole (actinolite)	6.8	13.0	8.9	9.1	9.5	11.7
Plagioclase (albite)	5.4	12.1	6.0	7.2	8.6	7.7
Quartz	39.4	30.3	36.3	38.2	26.4	31.6
Rutile	0.9	1.2	1.0	1.2	0.8	1.1
Biotite (phlogopite)	2.8	4.9	5.0	4.9	4.0	4.9
Sodalite (?)	0.9	0.7	0.8	0.9	0.8	0.6
Talc	3.3	0.7	0.9	0.0	2.8	1.0
Amorphous or unidentified	2.3	7.0	6.4	7.7	13.9	10.7

Measurements of organic and inorganic carbon and sulfide sulfur have been used, in conjunction with the mineralogy, to assess the acid forming potential of these samples. Table 2 shows that the sulfide sulfur (CRS – chromium reducible sulfur) accounts for almost all the sulfur present (average 93 ± 4 %) with, on average, 1.4 ± 0.5 wt% sulfide sulfur present across the six samples. Similarly, inorganic carbon accounts for almost all the carbon present (average 94 ± 4 %) with, on average, 1.2 ± 0.3 wt% inorganic carbon present across all six samples. The wt% of sulfide S and inorganic carbon have been calculated from the quantitative mineralogy (Table 3) and are closely similar to the assayed values providing confidence in both methodologies.

NAPP^1 (Table 3) has been calculated with ANC based on the inorganic carbon concentration and maximum potential acidity (MPA*) calculated using the CRS sulfide assay. Siderite dissolution does not provide neutralisation as the acid consumed upon CO_3^{2-} dissolution is regenerated upon oxidation of Fe^{2+} to Fe^{3+} and subsequent hydrolysis (Eqn. [1]). In a refinement of the NAPP^1 calculation the contribution of inorganic carbon due to siderite, based on QXRD, has been removed from ANC^1 and NAPP^2 has been calculated.

$$\mathrm{FeCO_3 + 1.5H_2O + 0.75O_2 \rightarrow Fe(OH)_3 + H_2CO_3} \qquad [1]$$

Table 2. **Sulfur and carbon assays for all six waste rock samples (all in wt%)**

	Total S	Sulfide (CRS)	Sulfide (QXRD)	Total C	Organic C	Inorganic C	Inorganic C (QXRD)
OSW1	2.04	1.95	1.80	1.31	0.07	1.24	1.12
OSW2	1.13	1.08	1.54	1.11	0.05	1.06	0.70
OSW3	2.09	1.84	1.87	1.50	0.06	1.44	1.09
OSW4	1.55	1.37	1.56	0.85	0.05	0.80	0.51
OSW5	0.85	0.84	0.93	1.62	0.07	1.55	1.52
OSW6	1.16	1.06	1.27	1.27	0.18	1.09	0.86
Ave±stdev	1.5±0.5	1.4±0.5	1.4±0.3	1.3±0.3	0.08±0.05	1.2±0.3	0.9±0.4

Table 3. **Calculation of nett acid production potential using a number of different approaches. All units of MPA* and NAPP are kg H_2SO_4 t^{-1}**

	MPA*	NAPP[1]	NAPP[2]	$S^0/(S_{aq}+S^0)$	NAPP[3]
OSW1	60	–42	–27	0.28	–43
OSW2	33	–54	–38	0.08	–41
OSW3	56	–61	–46	0.23	–59
OSW4	42	–23	–13	0.10	–17
OSW5	26	–101	–95	0.09	–97
OSW6	32	–57	–48	0.40	–61
Ave±stdev	42±14	–60±30	–45±10	0.2±0.1	–60±30
OSW1+pyrite	150	55	69	0.19	40

Pyrrhotite oxidation produces, in part, elemental sulfur, which is a non-acid forming reaction (Eq. [2]) rather than sulfate, which is acid forming (Eqn. [3]) (Janzen et al., 2000; Schumann et al., 2015; Gerson et al., 2019). Here a correction factor is used based on the measured elemental sulfur formed divided by the total reacted sulfur (aqueous sulfate plus elemental sulfur) both measured at the end of each of the Time Extended Paste pH tests (Table 3). This factor is then applied to MPA* (30.6 × CRS S wt%). The resulting NAPP[3], after elemental S correction, on average across OSW1 to OSW6 is –60±30 kg H_2SO_4 t^{-1}. The average value of $(1 - S^0/(S_{aq}+S^0))$ where S_{aq} represents sulfate is 0.8±0.1 which can be applied as a generic correction to MPA* for these waste rocks.

$$\mathrm{Fe}_{(1-x)}\mathrm{S} + (0.5 - 0.5x)\mathrm{H_2O} + (0.75 - 0.75x)\mathrm{O_2} \rightarrow (1-x)\mathrm{FeOOH} + \mathrm{S^0} \qquad [2]$$

$$\mathrm{Fe}_{(1-x)}\mathrm{S} + (1.5 - 0.5x)\mathrm{H_2O} + (2.25 - 0.75x)\mathrm{O_2} \rightarrow (1-x)\mathrm{FeOOH} + \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \qquad [3]$$

This correction factor for MPA* of 0.8 is greater than the relative acid production expressed as a fraction of that expected based on total oxidised sulfide observed for pyrrhotite tailings in storage facilities (Robertson et al., 2015) and in kinetic leach columns (Schumann et al., 2015). In these environments, the solution redox potential (Eh) is likely to be considerably less (e.g. Renison C-Dam lysimeter sampling returned an Eh of 25–31 mV) than the fully oxygenated and stirred Time Extended Paste pH tests (average Eh 390–460 mV across the duration of the tests) due to their quiescent nature and low rates of oxygen transport. Moreover the Extended Time Paste pH tests gave rise to an average final pH of 8 (Table 4) and under alkaline conditions elemental sulfur is less stable (Pourbaix, 1974).

The concentrations of Pb (average 100±100 mg kg^{-1}), Zn (average 400±400 mg kg^{-1}) and Cu (average 400±200 mg kg^{-1}) may indicate the presence of sulfide minerals present below the detection level by XRD. The average concentrations of these elements would equate to a total sulfide concentration, assuming the presence of galena, sphalerite and chalcopyrite respectively, of 640 mg kg^{-1}. As these minerals are non-acid forming on dissolution this sulfide contribution *may* be removed from CRS sulfide assay for calculation of MPA* but as this contribution is less than 5% of the total sulfides this correction is considered to be negligible.

To examine the potential for inclusion of waste rock with greater sulfide content, the sample of OSW1 with 6.1 wt% pyrite addition was also examined. This concentration of pyrite addition was chosen to ensure a PAF sample using conventional criteria, i.e. NAPP >0 and NAG pH <4.5. NAPP[2] for OSW1+pyrite was 40 kg H_2SO_4 t^{-1} and the NAG pH was 2.4 classifying the sample as PAF.

3. TIME EXTENDED PASTE PH TESTS

The Time Extended Paste pH test protocol is based on the standard paste pH methodology using a 5:1 water:solid ratio (http://www.gardguide.com/index.php?title=Table_5-1) modified with extended time and gentle agitation. 500 g of crushed sample (–2 mm) were placed in each of three 4.5 L screw-capped plastic jars. The caps contained a small hole to allow ready exchange of air within the bottle while minimising evaporation. Milli-Q water (2.5 L) was placed in each jar and the jars were placed on a laboratory shaker table. The water level was checked twice weekly and water was added to keep the amount of water constant. After shaking for a specified time, each jar was removed and the solids allowed to settle. Samples were collected after 166, 336 and 670 hours shaking. For brevity, data for 670 h only are given in Table 4. pH and Eh were measured in the supernatant. A portion of supernatant was removed and filtered through a 0.45 μm membrane filter. EC, alkalinity and acidity were then measured in the filtrate. Solution assays were carried out on the final leachate after 28 days with a portion of the filtrate acidified with nitric acid prior to analysis.

To obtain a sub-sample of the solids following extraction, the bottle was shaken and a portion of the suspension removed. The suspension was filtered through a 0.45 μm membrane and the solid residue was air-dried for 48 h. The air-dried solids were placed in a sealed argon-purged plastic bag and stored at –20°C. A portion of the solid residue was removed and, after thawing, pulverised before extraction for elemental sulfur analysis.

The pH at the end of the Time Extended Paste pH tests for OSW1 to OSW6 ranged from 7.9 to 8.1 (Table 4). No acidity was measured with measured alkalinity ranging across 0.25–0.32 kg H_2SO_4 t^{-1}. The values for alkalinity measured at 670 h (28 days) were in excellent agreement with the values for calculated alkalinity (Table 4). For each test, the sulfate concentration progressively increased suggesting no precipitation of secondary sulfate phases.

The amounts (as % of that available in the wastes) of Na, Mg, Ca and K leached; in all cases was less than 1 %. The total sulfur reacted (S_{aq} + S^0) was less than 2 % in all cases for OSW1 to OSW6 with a minimum of 0.8 %. These relative amounts, although small, suggest sufficient neutralisation capacity to match acid generation during, at least, initial leaching. It is noted that this analysis does not take into consideration which neutralising phases are being consumed. It is possible that, after consumption of rapidly dissolving neutralising phases, the remaining slowly dissolving phases will not be able to keep up with the rate of acid generation.

Table 4. pH, Eh (mV SHE), conductivity (μS cm^{-1}), alkalinity (kg H_2SO_4 t^{-1}) and sulfate (mg kg^{-1}) measurements for OSW1 to OSW6 including OSW1+pyrite at 670 h. Acidity was calculated using solution sulfate concentration, alkalinity was calculated using solution Ca, Mg Na and K concentrations. Calc. alkalinity (kg H_2SO_4 t^{-1}) = alkalinity – acidity

	pH	Eh	Conductivity	Alkalinity	Calc. alkalinity	SO_4^{2-}
OSW1	8.1	404	325	0.33	0.37	380
OSW1+py	8.1	404	356	0.30	0.35	480
OSW2	8.0	382	263	0.33	0.34	250
OSW3	7.9	396	335	0.27	0.29	485
OSW4	8.0	391	285.2	0.27	0.29	340
OSW5	8.0	365	245	0.31	0.31	230
OSW6	8.1	400	301	0.27	0.28	385

The rate of sulfate release into solution was greater for OSW1+pyrite compared to OSW1, i.e. 480 mg kg^{-1} compared to 380 mg kg^{-1} after 670 h. The pH was not affected by this with the final pH in both cases being 8.1. Eh was also not affected but conductivity was slightly increased (Table 4). Measured alkalinity was also very similar for OSW1+pyrite compared to OSW1 as was calculated net alkalinity (Table 4). These results indicate that there is sufficient alkalinity present, at least initially, to neutralise the acidity generated from the increased pyrite content.

4. NAG TESTING OF PYRRHOTITE CONTAINING WASTES

The NAG test requires the addition of 250 ml of 15% H_2O_2 solution to 2.5 g of material (<75 μm). The sample is left to react overnight. It is then heated for one to two hours and left to cool after which the pH is measured. Hydrogen peroxide is highly oxidising as compared to common oxidants found in AMD systems. The standard oxidation potential of peroxide is 1.78 V as compared to Fe^{3+} with an oxidation potential of 0.77 V (http://hyperphysics.phy-astr.gsu.edu/hbase/Tables/electpot.html).

This high oxidation potential induced by the use of hydrogen peroxide is useful for rapid assessment of pyrite content but is not realistic in terms of an AMD environment and results in the reaction of pyrrhotite through to sulfate (Eqn. [3]) which is an acid producing reaction. Stewart et al. (2003) have demonstrated that a single stage NAG test will result in oxidation to sulfate of approximately 95 to 100% of the sulfur contained in pyrrhotite (Table 5). Reliance on the NAG test for characterisation of wastes containing significant pyrrhotite will result in waste classifications of PAF which may not be appropriate.

The more realistic scenario in a pyrrhotite mine waste environment is reaction through to elemental sulfur (Eqn. [2]). Schumann et al. (2015) demonstrated in kinetic leach columns containing 5 wt% pyrrhotite in simulated mine waste that 85% of the oxidised sulfide reacted to form elemental sulfur with approximately 5% of the acid production expected based on reacted sulfide. In a further study (Robertson et al., 2015) examining the behaviour in situ of pyrrhotite-containing mine tailings, it was concluded that “Despite containing almost 30% pyrrhotite, the tailings generate only a fraction of the acidity predicted by classical static geochemical test techniques…”.

Table 5. Behaviour of pyrrhotite during NAG testing (from Stewart et al. (2003))

%S in original mineral	Stage	S released by stage (% of total)	Equivalent NAG acidity released by stage (kg H_2SO_4 t^{-1})*	NAG pH
4.2	1	95	121	2.2
	2	13	17	2.6
	3	3	4	3.0

	4	1	1	3.7
0.3	1	135	12	3.1

* Calculated based on S released into NAG solution.

5. ANC/MPA* CUTOFF

The average value of ANC/MPA* for all samples analysed by SGS (using Sobek ANC) is 3 with a standard deviation of ±2. For the samples considered to be NAF by all ABA measures (i.e. excluding PAF, and UC based on inapplicable NAG pH) the equivalent values are 3.4 ± 2.0. A considerable proportion of samples that are currently classified NAF will be excluded should a cut-off of ANC/MPA* of 3 be used for demarcation (Fig. 1).

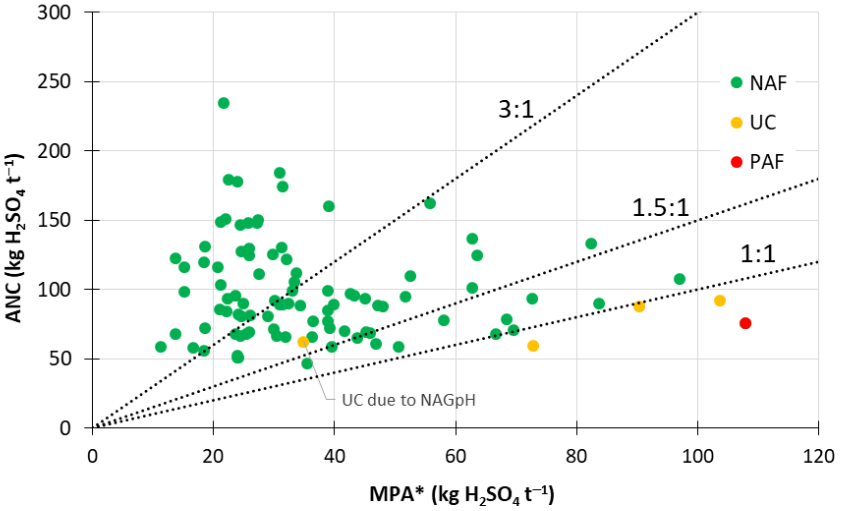

Fig. 1. **Scatter plots of ANC versus of MPA*. Data from SGS evaluation of NAF discard waste rock**

Both the Time Extended Paste pH tests and modelling of acid and neutralisation generation rates (using the method of Gerson et al. (2019)) show that greater alkalinity than acidity will be generated initially. This suggests that on longer term storage, marginal wastes may become acid generating should an ANC/MPA* ratio of 1 be adopted. It has therefore been proposed that an ANC/MPA* ratio of 1.5 should be used as shown in Fig. 1. The only current UC (uncertain) waste that exceeds this ratio was characterised on the basis of a NAG pH <4.5 with NAPP* (measured ANC, MPA* from CRS S) <0. All other UC wastes had NAG pH >4.5 and NAPP* >0. The PAF waste was characterised as having NAG pH <4.5 and NAPP* >0.

6. CONCLUSIONS

Samples OSW1–OSW6 all gave rise to pH >7 over the duration of the Time Extended Paste pH test in accord with their predicted NAF behaviour. The OSW1+pyrite sample was predicted to be PAF but also returned a pH >7 due to the high initial rates of release of alkalinity from calcite and dolomite. It is concluded that the Time Extended Paste pH test is applicable to track initial acidity versus alkalinity generation and also the release of metals, metalloids and sulfate.

Improved ANC, MPA*, ANC/MPA* with a cutoff of 1.5, and Extended Time Paste pH measurements have been recommended. Further refinement of the ANC/MPA* cut off will be evaluated during operations. NAG pH is known to be inappropriate for systems containing significant concentrations of pyrrhotite. MPA is improved by using the sulfide S concentration (CRS, to give MPA*) rather than total S. Corrections for non-acid generating sulfides in this system are negligible. ANC should be measured by Sobek ANC measurement with H_2O_2 addition for precipitation of aqueous iron. It may be calculated using inorganic C minus any contribution from siderite but this evaluation excludes rapid non-carbonate ANC.

This suite of analyses is cost-effective and readily run on-site enabling rapid examination of the efficacy of the waste rock sorter and, using the Extended Time Paste pH tests, examination of kinetic leach behavior. A greater number of these tests than kinetic leach column or oxygen consumption testing can be run enabling better sampling and representation of the waste rock and enabling any change in behaviour of the waste rock to be readily identified.

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WALLROCK ACIDITY CONTRIBUTIONS TO PIT LAKE WATER QUALITY IN THE PILBARA

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ABSTRACT

Common sources of acid and metalliferous drainage (AMD) at mine sites include waste rock, tailings, pit wallrock and/or underground mine voids. Open cut iron-ore mines in the Pilbara region of Western Australia initially focus management efforts on waste rock as the primary risk to water quality, but turn their attention to pit lake water quality management during closure planning.

Quantifying acidity generation from wallrock has always been challenging. A new procedure, based on oxygen consumption testwork, has been developed to determine the acidity generation rates (AGRs) of specific lithologies as a function of surface area, moisture content and sulfur content. Two samples of black, carbonaceous Mt McRae Shale containing low (1.5 wt.%) and high (20.4 wt.%) pyrite concentrations were tested to quantify the relationship between acidity generation and the surface area of reactive wallrock exposures.

Oxygen consumption rates (OCRs) were measured for multiple sub-samples of the low and high pyrite material, with sub-sample surface areas ranging from 50-450 cm^2*. The OCR data show that the low pyrite sample consumed 0.7-0.9 mol* O_2/m^2*/year, which is equivalent to an AGR of 20-25 g* H_2SO_4/m^2*/year, and the high pyrite sample consumed 11-15 mol* O_2/m^2*/year, which represents an acidity generation rate (AGR) of 300-400 g* H_2SO_4/m^2*/year. When normalised to 1.0 wt.% pyrite, these AGRs are effectively comparable at 27-40 g* H_2SO_4*/wt.%* FeS_2/m^2*/year.*

These preliminary results indicate that pit wallrock containing a 1,000 m^2 *exposure of Mt McRae Shale, with an average pyrite content of 1 wt.%, would generate 30-40 kg* H_2SO_4*/year. This is a very low estimate that does not appear to account for water quality in pit lakes with black shale wallrock exposures in the Pilbara or elsewhere. These laboratory data suggest that sulfidic pit wallrock in the Pilbara may not be the principle source of acidity (acid and metals) contributing to pit lake water quality.*

Although more work is required to confirm these preliminary results, similar conclusions may be inferred for pit wallrock at many other mine sites worldwide. Pit sub-drill waste rock, pit wall talus / scree and reactive fill associated with haul road construction may well be the major acidity sources for most pit lakes.

1.0 INTRODUCTION

The Pilbara region is situated in the northern part of Western Australia, covering an area of approximately five hundred thousand square kilometres. At some iron ore mines in the Pilbara, waste rock and wallrock comprise highly reactive sulfidic materials. Sulfidic materials from the Mt McRae Shale (MCS) have the potential to generate AMD when exposed to atmospheric oxygen.

The Mt McRae Shale (approximately 30 m thick) consists of alternating bands of black, pyritic, carbonaceous shale and chert and is commonly capped with pyritic chert bands. It forms the footwall to the ore horizons in the Brockman Iron Formation and hence is commonly exposed during mining. Several zones within the unit contain abundant pyrite (up to 20 wt.%) with nodules up to 5 cm across (Tyler, 1994). The black shale more typically contains between 0.5-2 wt.% pyrite. The MCS has been regionally metamorphosed to greenschist facies and multiply deformed. It is regarded as a significant AMD hazard throughout several iron ore mines in the Pilbara.

Detailed AMD management strategies for these sites generally aim to address all mine materials with the potential to generate AMD, with a focus on the sulfidic MCS waste rock, if present. Residual surface exposures of MCS in pit walls, however, can often be more difficult to manage. It is understood that pyrite oxidation within wallrock exposures is responsible for poorer water quality reporting to temporary pit water storages or pit lakes. While the empirical association is evident, the relationship between the surface area of MCS (or other sulfidic wallrock) exposed in pit walls and acidity generation rates (i.e. pollution generation rates) from the wallrock remain unclear.

Modelling has been conducted to help predict pit water treatment requirements as well as long term pit lake water quality issues following sulfide oxidation, but the models are based on input assumptions that have yet to be properly validated. For example, it is not clear how far oxygen can penetrate into wallrock exposures of MCS materials.

Laboratory testwork using oxygen consumption techniques has been conducted to attempt to quantify acidity generation rates (AGR) from sulfidic MCS wallrock as a function of surface area. The purpose of the testwork was to assist with quantifying acid and metalliferous drainage (AMD) treatment requirements in pit ponds and lakes at iron ore mines in the Pilbara, although it could have wider implications for pit lakes and the focus of site-wide AMD management strategies throughout the mining industry.

2.0 METHOD

To assess the relationship between the pit wallrock surface area of MCS and its acidity generation rate, the following scope of works was undertaken (Earth Systems, 2018 and 2019):

- Sample selection, preparation and physical testing of multiple coherent samples of MCS. Preparation included the production of multiple geometric rock sub-samples with a diamond saw.
- Static geochemical characterisation of the sample, including mineralogy, acid-base accounting, net acid generation (NAG) suite, acid buffering characteristic curve (ABCC) and NAG leachate chemistry.
- Multiple oxygen consumption tests, each containing a different number of rock sub-samples in order to quantify acidity generation rates as a function of geometric rock surface area.

2.1 Sample Collection and Preparation

Two MCS rock samples, each weighing approximately 15 kg, were collected from an iron ore mine in the Pilbara. The samples, identified as MCS-WR1 and MCS-WR2, were representative of MCS rock containing relatively high and low pyrite contents, respectively, based on visual assessment of pyrite abundance in the field. The samples had dimensions not less than 380 mm (L) x 230 mm (W) x 200 mm (H), were essentially unoxidised, physically competent, more massive than thinly bedded and fracture-free. Abundant pyrite nodules distributed along bedding planes were clearly visible across the uncut surface of the MCS-WR1 sample.

Each sample was cut into a series of regular geometric prisms with surface areas ranging from 50-450 cm^2. The cross-section was smooth and regular so that the surface area of each sub-sample could be easily measured. A total of 23 and 37 sub-samples, respectively, were produced from MCS-WR1 and MCS-WR2.

2.2 Physical Characterisation

The gravimetric moisture content of each sample was measured by weighing a representative sub-sample, before and after drying at 105°C for 24 hours, in accordance with standard laboratory methods. The dimensions, volume, mass and density of the geometric sub-samples were also measured. Variable pyrite contents resulted in some variation in the density of sub-samples.

2.3 Static Geochemical Characterisation

Multiple off-cuts from each sample (MCS-WR1 and MCS-WR2) were produced during sample preparation using a diamond saw. For each sample, a ~2 kg representative sub-sample from the off-cuts was dispatched to a NATA accredited laboratory, for static geochemical characterisation testwork, including:

- Acid-base accounting including maximum potential acidity (MPA), acid neutralising capacity (ANC), and net acid producing potential (NAPP);
- NAG suite;
- Sulfur and carbon speciation;
- Major and trace element chemical analysis; and
- NAG leachate chemistry.

A 20 g pulp from each sample (MCS-WR1 and MCS-WR2) was subjected to Quantitative X-Ray Diffraction (QXRD) analysis including determination of amorphous (non-crystalline) content.

2.4 Oxygen Consumption Kinetic Testwork

Oxygen consumption tests (Davis *et al*., 2014) were conducted on each sample to quantify acidity generation rates as a function of geometric rock surface area. For each sample, a series of five oxygen consumption vessels were loaded with up to 13 geometric prisms, with total rock surface areas ranging from 370-3,700 cm^2. Vessels were then sealed, and internal oxygen and carbon dioxide concentrations were measured every 10 minutes for at least 6 weeks to quantify oxygen consumption rates (OCRs).

3.0 SAMPLE CHARACTERISATION RESULTS AND DISCUSSION

3.1 Physical Characterisation

Physical characteristics of the samples included:

- Average densities of 2.54 g/cm^3 (MCS-WR1) and 2.30 g/cm^3 (MCS-WR2).
- Moisture contents of 1.22 wt.% (MCS-WR1, Tests 1-5), 1.30 wt.% (MCS-WR1, Tests 6-10), 1.26 wt.% (MCS-WR2, Tests 1-5), 1.83 wt.% (MCS-WR2, Test 6) and 1.23 wt.% (MCS-WR2, Tests 7-10).

3.2 Mineralogy

The dominant minerals in MCS-WR1 are muscovite (44.3 wt.%), quartz (24.6 wt.%) and pyrite (19.6 wt.%). Muscovite (45.3 wt.%) and quartz (37 wt.%) were also dominant in MCS-WR2. The key reactive (acid-forming) sulfide mineral is pyrite (FeS_2) in both samples (19.6 wt.% and 1.2 wt.% in MCS-WR1 and MCS-WR2, respectively). No carbonate minerals were identified in either sample.

3.3 Geochemistry

The key results from the sulfur speciation, carbon speciation, acid-base accounting, NAG suite, and major and trace element composition analytical data for MCS-WR1 are:

- The total sulfur content is 10.90 wt.%. The sample is highly sulfidic, containing 8.79 wt.% sulfide sulfur.
- According to QXRD results, the dominant reactive sulfide mineral is pyrite. Based on the total sulfur content, the calculated pyrite content is 20.4 wt.%, quite similar to that indicated in the QXRD results (19.6 wt.%).
- The MPA based on pyrite content is 334 kg H_2SO_4/t and the ANC is below the detection limit of 0.5 kg H_2SO_4/t, resulting in a NAPP of 334 kg H_2SO_4/t.
- The $NAG_{7.0}$ data is 218 kg H_2SO_4/t, still strongly acid generating, but substantially less than the NAPP data.
- The total carbon content is 3.09 wt.%. Considering the ANC is less than 0.5 kg H_2SO_4/t, the carbon content in MCS-WR1 is probably in the form of organic carbon, which supports the assumption of bituminous material based on the QXRD data.

The key results for MCS-WR2 are:

- The total sulfur content is 0.79 wt.%. The sample is sulfidic, containing 0.48 wt.% sulfide sulfur.
- According to QXRD results, the dominant sulfide mineral is pyrite. Based on the total sulfur content, the calculated pyrite content is 1.5 wt.%, quite similar to that indicated in the QXRD results (1.2 wt.%).
- The MPA based on total sulfur content is 24.2 kg H_2SO_4/tonne and the ANC is below the detection limit of 0.5 kg H_2SO_4/tonne, resulting in a NAPP of 24.2 kg H_2SO_4/tonne.
- The $NAG_{7.0}$ data is 20 kg H_2SO_4/tonne, still acid generating, and very similar to the NAPP data.
- The total carbon content is 4.62 wt.%. Considering the ANC is less than 0.5 kg H_2SO_4/t, the carbon content is probably in the form of organic carbon, which supports the assumption of bituminous material based on the QXRD data.

3.4 NAG Leachate Chemistry

The NAG leachate chemistry results identify the likely key mobile elements from the highly sulfidic MCS-WR1 sample to be aluminium, iron, manganese, copper, nickel, arsenic, cobalt, lead, zinc, selenium and chromium. With the exception of arsenic, lead and selenium, the same elements were also elevated in the NAG leachate from the less sulfidic MCS-WR2.

3.5 Key Findings

Key findings from the sample characterisation data (Section 3.1 to 3.4) include:

- The MCS-WR1 sample tested contains 20.39 wt.% pyrite and no detectable ANC. It has a NAPP value of 334 kg H_2SO_4/tonne. It is classified as having a high potential for acid generation. In comparison, the MCS-WR2 has a much lower pyrite content (~1.48 wt.%) and also no detectable ANC. It has a NAPP value of 24.2 kg H_2SO_4/tonne and is therefore a moderate potential for acid generation.
- Approximately 10 wt.% of the samples (MCS-WR1 and MCS-WR2) are inferred to be amorphous bituminous carbon.
- The high reactive carbon content of the sample is predicted to be responsible for discrepancies between NAPP and NAG values and is also predicted to be responsible for

retarding sulfide oxidation rates and providing a limiting influence on the progression of oxidation processes in wallrock. This impedance is believed to be evident in the widespread formation of white (melanterite / rozenite) crystals (rather than ferrihydrite) along sulfidic MCS horizons in pit walls.

- NAG leachate data indicates that key mobile components in solution are likely to include aluminium, iron, manganese, copper, and nickel with lesser zinc, cobalt and chromium.
- It is possible that the slightly elevated CO_2 concentrations recorded in all testwork vessels (during the subsequent oxygen consumption testwork) are related to the oxidation of the bituminous carbon, as the ANC values were below detection limits and the QXRD did not detect carbonate minerals. This is consistent with the reactive carbon content retarding sulfide oxidation.
-

4.0 OXYGEN CONSUMPTION TEST RESULTS AND DISCUSSION

Oxygen consumption rate (OCR) data for both samples (MCS-WR1 and MCS-WR2) are plotted against surface area in Figures 1 and 2. In both figures, results for sample MCS-WR1 are shown in red (squares for Test 1 to 5 and circles for Test 6 to 10) and results for sample MCS-WR2 are shown in blue (diamonds for Test 1 to 5 an triangles for Test 6 to 10).

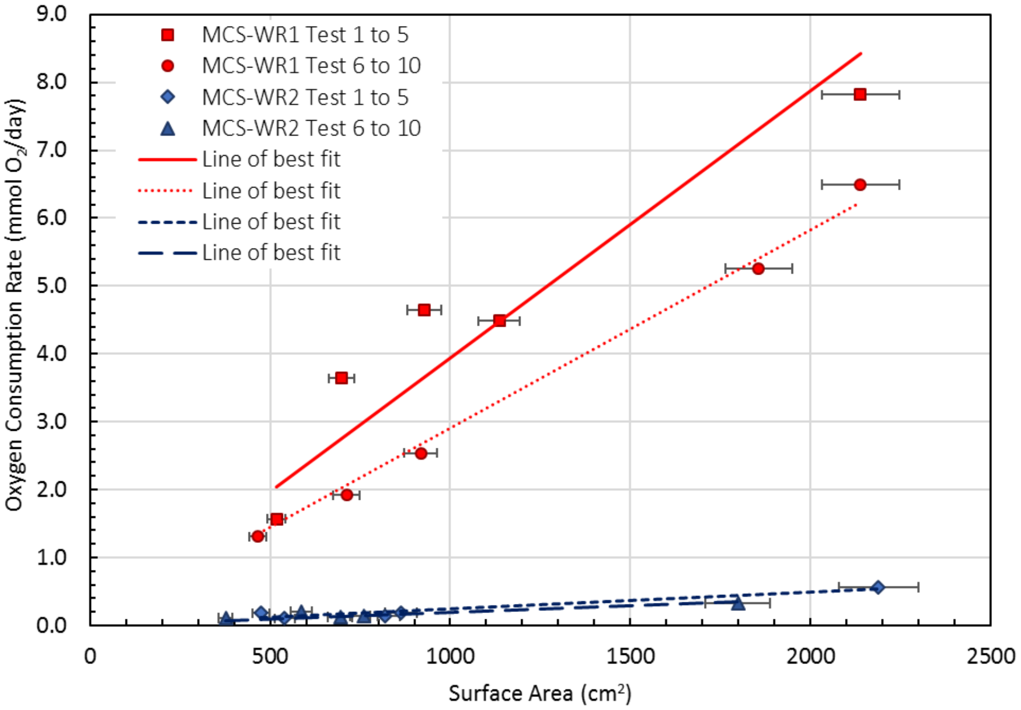

Figure 1: Oxygen consumption rate of MCS wallrock samples as a function of surface area.

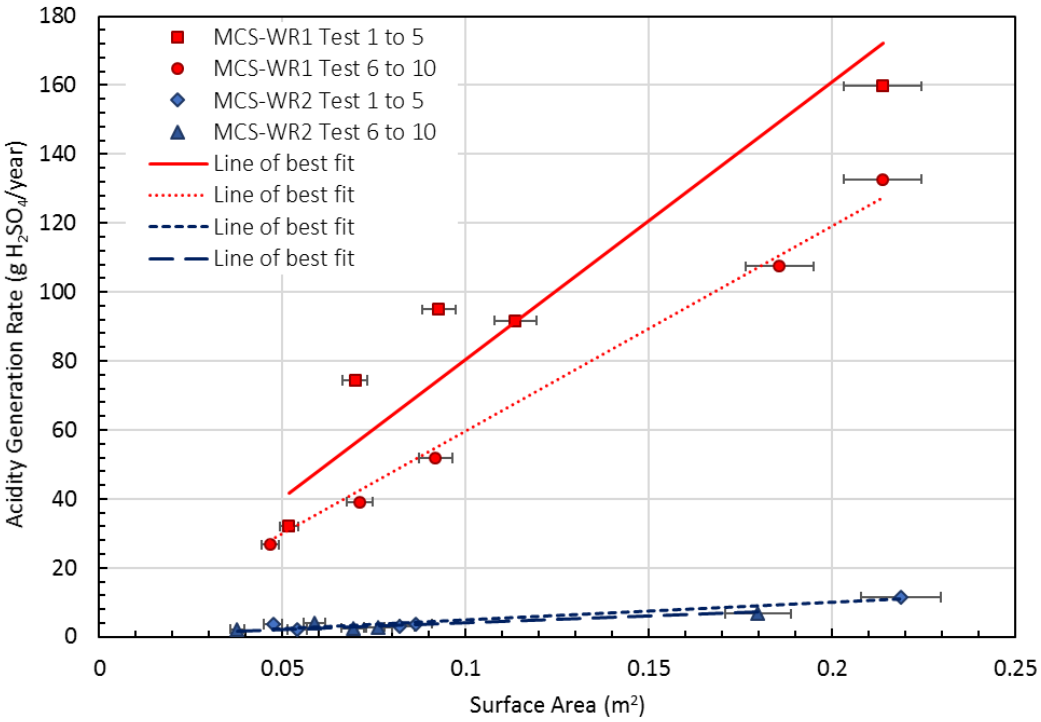

Figure 2: Acidity generation rate of MCS wallrock samples as a function of surface area.

Key results from the testwork are summarised below:

- Figures 1 and 2 confirm that there is a strong positive linear relationship between increasing oxygen consumption (and therefore acidity generation) and increasing rock surface area;
- Small variations from the line of best fit for Tests 1-5 may be attributed to the varying content of pyrite within sub-samples, or small variations in the starting sample moisture content;
- The minor decrease in oxygen consumption rates (OCR) between Tests 1-5 and Tests 6-10 are probably associated with a marginal sample moisture increase following the first test series (1-5);
- Highly sulfidic MCS (19.6 wt.% pyrite) with a surface area of 1,000 cm^2 can consume between 3-4 mmol of oxygen per day. This is equivalent to 1.10-1.46 mol of oxygen per 1,000 cm^2 per year, or approximately 11-15 mol O_2/m^2/year.
- The same surface area (1,000 cm^2) of less sulfidic MCS (1.2 wt.% pyrite) can consume between 0.20-0.25 mmol of oxygen per day. This is equivalent to 0.075-0.090 mol of oxygen per 1,000 cm^2 per year, or 0.75-0.90 mol O_2/m^2/year.

The OCR data are discussed below and converted into acidity generation rates (AGR) based on the interpreted relationships between oxygen consumption and acidity generation for the samples.

When oxygen consumption testwork had been completed, abundant white, needle-like, crystalline salts were observed in close spatial association with the bedding-parallel layers of pyrite nodules. The crystals were analysed by QXRD techniques and found to be dominated by rozenite ($FeSO_4.5H_2O$) and melanterite ($FeSO_4.7H_2O$). The implication of these assemblages is that pyrite oxidation in the testwork vessels only partially progressed, consuming only 3.5 mol of O_2 for every mol of H_2SO_4 produced, rather than 3.75 mol of O_2 for 2 mol of H_2SO_4 produced when the pyrite oxidation reaction goes to completion.

It is considered likely that the bituminous carbon content of the pyritic MCS is responsible for retarding sulfide oxidation. The implication of this conclusion is that the oxygen consumption data is only responsible for approximately 50% of the acidity generation that will routinely occur in association will full pyrite oxidation. This likely means that the additional 50% of the acidity will probably form once the melanterite is flushed from the relatively reducing environment established by bituminous MCS materials. Hence, for the purposes of this study, acidity generation calculations (provided below) based on the laboratory oxygen consumption data assume that 2 mol of H_2SO_4 are eventually released from every 3.5 mol of O_2 due to dissolution of secondary acid salts that formed as a result of the pyrite oxidation reaction (not 3.75 mol as based on the conventional pyrite oxidation reaction).

Based on measured OCR data, the acidity generation rate (AGR) for MCS-WR1 with 20.39 wt.% FeS_2 is 600-800 grams H_2SO_4/m^2/year. The corresponding estimate for MCS-WR2 with 1.48 wt.% FeS_2 is 40-50 grams H_2SO_4/m^2/year (refer to Figure 2).

If we normalise the AGR for MCS-WR1 containing 20.39 wt.% FeS_2 to a sample with only 1 wt.% FeS_2 by dividing the AGR by 20.39, then we have an AGR that is representative of an MCS sample with 1 wt.% FeS_2. The FeS_2 normalised AGR is 30-40 grams H_2SO_4/wt.% FeS_2/m^2/year (refer to Figure 3; results for sample MCS-WR1 and MCS-WR2 are shown in red and blue, respectively). Similarly, if we normalise the AGR for MCS-WR2 containing 1.48 wt.% FeS_2 to a sample with 1 wt.% FeS_2 by dividing the AGR by 1.48, then we have an AGR that is representative of an MCS sample with 1 wt.% FeS_2. The FeS_2 normalised AGR is 27-34 grams H_2SO_4/wt.% FeS_2/m^2/year (refer to Figure 3). As the normalised AGR is roughly equal for both samples, regardless of their different pyrite contents, we can now apply these AGR to MCS containing any pyrite concentration.

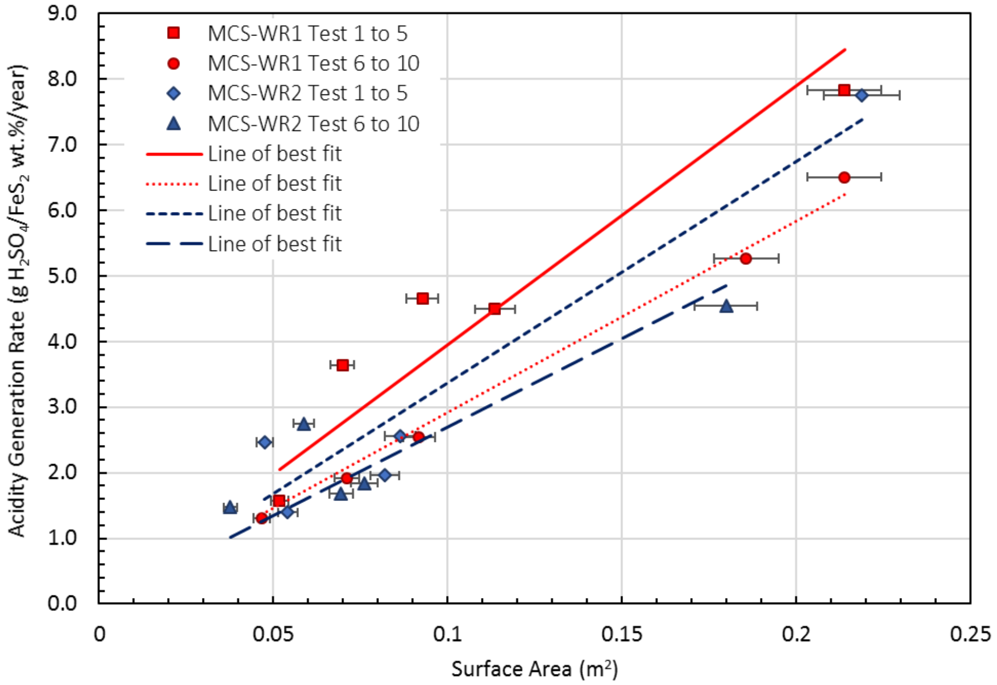

Figure 3: Acidity generation rate of MCS wallrock samples as a function of surface area after normalising the pyrite content to 1 wt.%.

Figure 4 extrapolates the laboratory acidity generation rate data to estimate acidity generation from large wallrock exposures. For example, a 1,000 m^2 exposure of MCS wallrock is estimated to produce 30-40 kg H_2SO_4/wt.% FeS_2/year based on sample MCS-WR1 (or approximately 27-34 kg H_2SO_4/wt.% FeS_2/year in the case of sample MCS-WR2). This is based on sample moisture contents of 1.2-1.3%, and the laboratory results (eg. Figure 3) indicate that higher moisture contents may produce even lower acidity generation rates.

These acidity generation rate numbers are remarkably small relative to common pit pond or pit lake acidity loads associated with a small one-off rainfall event. For example, based on typical acidity concentrations of 2,000-3,000 mg $CaCO_3$/L, a pit water pond volume of 1 ML would correspond to an acidity load in the order of 2,000-3,000 kg H_2SO_4. Only 1 wt.% of this load could be attributed to a one-year exposure of 1,000 m^2 of sulfidic wallrock containing an average pyrite content of 1 wt.%.

Acidity generation data can be extrapolated to full scale pit walls (i.e. using Figure 4), although it should be noted that extrapolated data could be subject to inaccuracies associated with surface roughness estimates, variable sulfide and carbonate concentrations and wallrock moisture content.

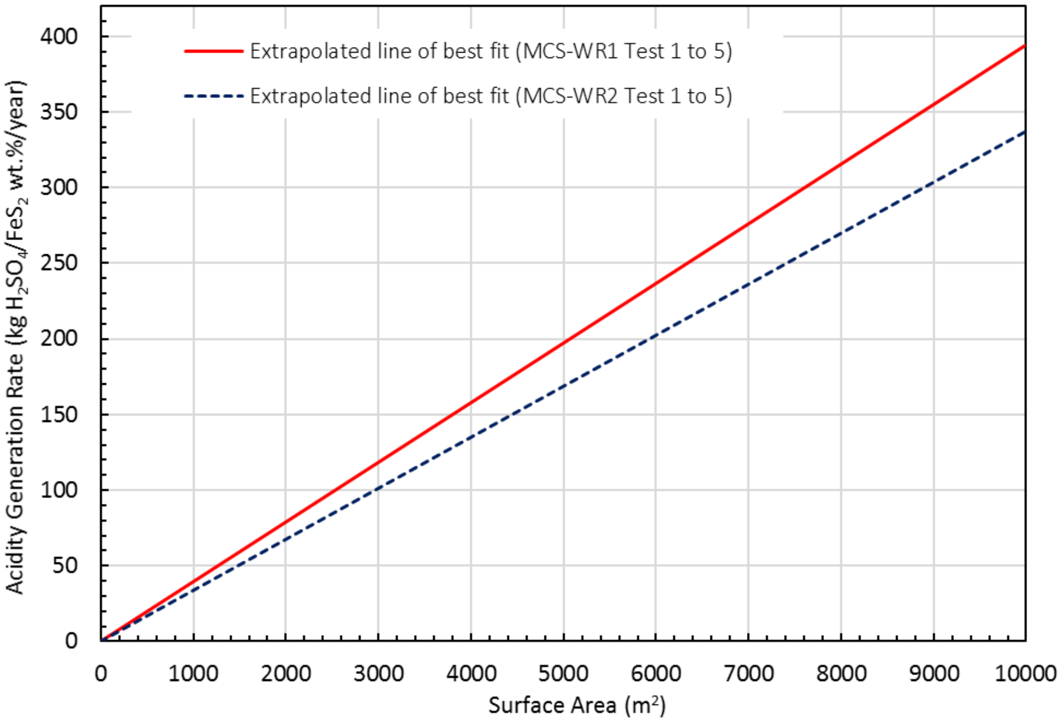

Figure 4: Predicted acidity generation rate in an open cut as a function of reactive wallrock surface area after normalising the pyrite content of two MCS wallrock samples to 1 wt%.

If the normalised AGR values for wallrock are representative (refer to Figure 4), then as yet unidentified sources of acidity need to be identified to adequately explain the acidity loads typically flushed into pit lakes. Investigations identified the following three potential acidity sources in addition to the exposed (visually obvious) wallrock:

- Sub-drill zones in pit floors (1-2 m thick over drilled and blasted sub pit floor waste rock material);
- Wallrock talus and scree (increasing over time as wallrock decomposes / weathers); and
- Chemically reactive fill used to construct haul roads.

The largest of the above sources could initially be the sub-drill zone in many pits. This potential source of acidity has been largely overlooked, however simple management strategies could be developed to mitigate the potential impacts of this material during operations. Proactive management costs are expected to be low relative to full pit lake treatment.

5.0 CONCLUSIONS

Acidity generation from sulfidic pit wallrock represents only a small component of in-pit acidity generation. Other sources of far more chemically reactive sulfidic rock appear to be required to explain the typical magnitude of acidity generation measured in pit ponds and pit lakes. This is inferred from the following key study results:

- Oxygen consumption testwork showed a strong, positive linear correlation between surface area and oxygen consumption for both sulfidic wallrock materials tested.
- Oxygen consumption rates ranged from 11-15 mol O_2/m^2/year for exposure of MCS-WR1, and from 0.75-0.90 mol O_2/m^2/year for exposure of MCS-WR2.
- Based on the production of 2 mol of H_2SO_4 for every 3.5 mol of O_2, acidity generation rates (AGRs) for MCS-WR1 were 600-800 grams H_2SO_4/m^2/year, and for MCS-WR2were 40-50 grams H_2SO_4/m^2/year.
- AGRs normalised to 1 wt.% FeS_2 for both samples showed very similar values (27-40 grams H_2SO_4/m^2/wt.% FeS_2/year) despite major differences in sulfide content.
- AGRs and pyrite normalised values indicate that acidity generation from wallrock materials is remarkably low. This study indicates that wallrock exposure of 1,000 m^2 of MCS containing 1 wt.% FeS_2 would only generate 27-40 kg of H_2SO_4/year. An equivalent acidity load could be derived from the oxidation of only 40-50 tonnes of MCS containing only 1 wt.% FeS_2 and oxidising at typical MCS waste rock oxidation rates (i.e. 5 wt.% of available FeS_2 decomposes/year).
- The surface roughness and fracture density of pit-based exposures of MCS suggest that diamond saw surfaces will significantly underestimate exposed surface areas in pit walls, perhaps by a factor of 5-100. Nevertheless, even if in-pit surface areas are under-estimated by up to two orders of magnitude, wallrock acidity generation estimates based on the modified surface area estimates still remain far too low to account for typical acidity loads in pit ponds and pit lakes.

The typical acidity loads encountered in pit ponds and pit lakes following rainfall events are more likely to have been produced by (a) reactive rubble on pit floors (sub-drill zone) following blasting that was retained to provide a flat operating surface, (b) sulfidic (waste) rocks spalled off reactive wallrock batters and lying on old bench tops due to blasting or weathering (i.e. in pit talus and scree), and (c) ramps cut through, or constructed from, sulfidic waste as part of pit access works.

If these conclusions regarding wallrock acidity are valid, new targeted management measures could be developed to retard pit lake water quality impacts.

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EFFECT OF TEMPERATURE ON LEACHING FROM PILBARA MATERIALS

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ABSTRACT

In the dry climatic conditions of the Pilbara, waste rock dumps are expected to have a low porewater content. Low water-rock contact ratios, slow transport rates and long residence times within waste rock dumps may result in percolation with a high solute content and solubility controls are expected to influence seepage chemistry. Elevated temperatures may arise within dumps, due to the oxidation of contained reactive sulfidic material, with consequent changes in leaching rates and mineral solubility. Understanding these effects is key to understanding future seepage quality.

Four Mt McRae Shale samples, a lignite and a sulfidic BIF sample were subjected to de-ionised water leach extract testing at four temperatures (20°C, 40°C, 60°C and 80°C). The samples were residues from prior kinetic testing and contained high levels of accumulated sulfidic oxidation products (e.g. sulfates, hydroxysulfates and oxyhydroxides). Geochemical modelling tools were employed to evaluate how well available thermodynamic datasets could reproduce measured trends.

Leachate chemistries were dominated by acidity, Al, Fe and SO_4. Temperature effects on solute concentrations were relatively minor, showing slight increases in dissolved Fe and SO_4 concentrations, and a minor reduction in pH values with increasing temperature. Concentrations of Si (all samples), Na and K (some samples) showed positive correlations with temperature, whereas Ca and Mg leached from lignite and the sulfidic BIF showed no consistent trend with temperature.

Available thermodynamic datasets were found to be incomplete with respect to temperature dependent enthalpy data so that calculations at temperatures other than for standard conditions (25°C) are subject to uncertainty. Notwithstanding these limitations, a comparison of the outcomes from calculations using three different databases (HATCHES NEA v20, minteq.v4 and wateq4f) showed similar lists of potentially solubility controlling mineral phases. Soluble mineral phases were inferred to be combinations of Fe and Al sulfates and hydroxysulfates (jarosites were identified in mineralogical studies), silicates, and, for the lignite and sulfidic BIF leachates, gypsum. The results for the lignite samples showed strong correlations amongst Mg, Al and SO_4 concentration trends, indicative of a possible common mineral phase.

Keywords: Leaching, geochemical modelling, thermodynamic data

1. INTRODUCTION

Solute production in dumps of sulfidic material is governed by sulfide mineral oxidation – as sulfides oxidise, acidity and other soluble or sparingly soluble products may enter into solution. In the dry climatic conditions of the Pilbara, water infiltration to dumps may be slow and residence times within the dump long. Significant proportions of reaction products from the oxidation of sulfides may be stored as secondary mineral precipitates rather than being transported to the dump base. Mineral solubility controls will therefore be key to understanding future seepage quality.

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Sulfide oxidation is exothermic and, within reacting materials, temperatures may become elevated compared to ambient values. This paper documents the findings of preliminary testing to assess the effects of temperature on solute concentrations in contact with secondary minerals formed in weathered samples of typical sulfidic mine wastes from the Pilbara, in particular the lithologies comprising: black Mt McRae Shales (MCS), a lignite and a sample of sulfidic banded iron formation (BIF). Sample residues from prior kinetic testing were selected for the assessment. Such residues contain high levels of sulfidic reaction products and the leachates generated could therefore be expected to reflect the solubility of typical sulfide reaction products (e.g. sulfates, hydroxysulfates and oxyhydroxides). The program combined laboratory testing with interpretative geochemical speciation modelling.

2. METHODS AND MATERIALS

2.1 Sample descriptions and properties

Six samples representing residues from a prior kinetic leach testing (using a free draining column approach, based on AMIRA, 2002) were selected for testing. The samples contained high levels of sulfide and generated significant acidity during column testing. The residues were placed in storage upon termination of the columns (between 1 and 3.5 years). Storage was under aerated conditions and sulfide oxidation was expected to have continued during the storage period.

Prior to testing, the residues were submitted for geochemical characterization (acid-base accounting and mineralogical assessment) and the results are shown in Table 1.

Table 1. Sample descriptions and properties

Sample ID		HEC004504	HEC004507	HEA0320-19-PAF	GEY080	ZNE812	Sulfide#4
Rock type (and abbreviation)		Mt McRae Shale (MCS)	Mt McRae Shale (MCS)	Mt McRae Shale (MCS)	Mt McRae Shale (MCS)	Lignite (LIG)	Sulfidic BIF (BIF)
Mineral	**Mineral Class**	**Mineral abundance (wt%) for sample ID**					
Pyrite	Sulfide	4	1	5	6	<1	1
Jarosite	Sulfate	2	1	1	2	1	1
Gypsum						1	
Siderite	Carbonate						2
Quartz	Silicates and alumino-silicates	34	44	33	55	29	53
K feldspar				1		1	
Kaolin		2	1	6	13	23	
Illite/ Muscovite		15	18	33	2		
Sepiolite							2
Zussmanite						1	5
Hematite	Oxides and oxy-hydroxides	5	3	<1	1		3
Magnetite			3				<1
Rutile						<1	
Anatase		<1	<1		<1	<1	
Gibbsite			<1				
Goethite		10	5		1	<1	9
Expanding clay	-					4	
Amorphous[1]	-	28	23	20	20	40	23
Parameter	**Units**	**Acid-base accounting**					
Total S	%	4.88	1.81	3.84	4.09	1.12	1.46
Sulfate-S[2]	%	0.74	0.49	0.44	0.68	0.77	0.49
ANC/Stored acidity[3]	kgH_2SO_4/t	-17	-12	-9	0	-17	-21
Class	-	PAF	PAF	PAF	PAF	PAF	PAF

Notes:

S – sulfur; BIF – Banded iron formation; ANC – acid neutralising capacity; PAF – potentially acid forming.

[1] Calculated by difference (i.e. 100 – (sum of absolute estimates); carbonaceous content is expected to contribute to these relatively high values

[2] Sulfate sulfur by HCl-digestion. Some hydroxysulfate minerals may not be fully dissolved, leading to under-estimation of sulfate sulfur content of the samples (Lapakko, 2002).

[3] Negative values indicate that the samples contained stored acidity

2.2 Leach Method

Representative sub-samples were collected and submitted for leach extraction testing at a 2:1 liquid to solids (L:S) contact ratio, using de-ionised water, for a contact time of 12 hours. The tests were completed at ambient temperature (approximately 20°C), and at 40°C, 60°C, and 80°C. For the tests completed at 40°C and above, the DI water was pre-heated and the leach vessel was maintained at the target temperature in a water bath. The leach vessel was manually agitated every half hour over the 12 hour leach period.

On completion, the liquid was separated from the solids and preserved at the test temperature to ensure that secondary effects (i.e. re-mineralisation, were the solutions to cool) did not influence solute concentrations. All leachates were filtered using a 0.2 μm filter and preserved as required prior to analysis. The pH and EC, however, was measured for an unpreserved portion of the leachate once cooled to ambient temperature.

Test work was carried out at the Intertek/ Genalysis laboratory in Perth.

3. RESULTS

Figure 1 shows the effect of temperature on pH. All samples generated acidic leachates, consistent with the earlier column tests and geochemical characterization of the residue samples. The leachate pH values generally decreased with increasing temperature for the MCS samples but increased between 40°C and 80°C for the BIF. The results for the lignite sample were variable.

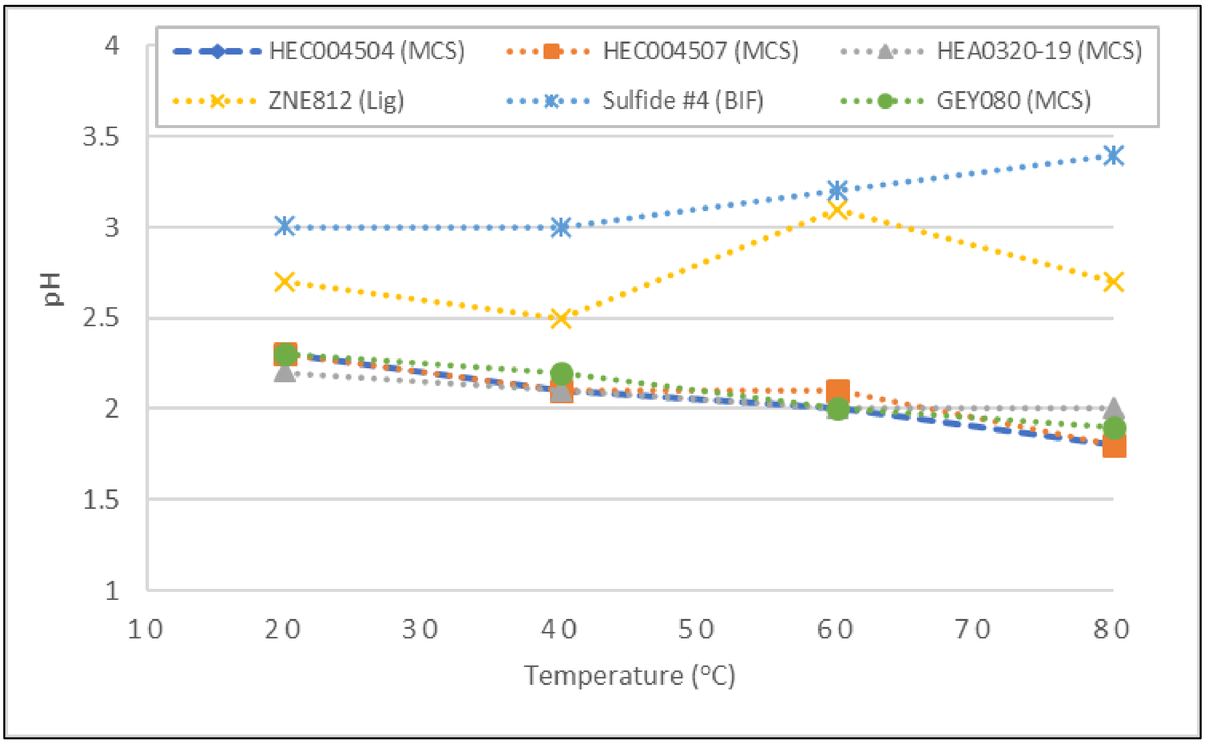

Fig. 1. **Variation in leachate pH with temperature**

In most cases, the major element chemistry of the leachates was dominated by dissolved Al, Fe and SO_4. The highest temperature leach tests resulted in significant Si concentrations when compared to the corresponding ambient temperature leach results. In the case of the lignite and the sulfidic BIF samples, significant dissolved concentrations of Ca and Mg were present. Concentrations of SO_4, Si, Fe and Al plotted as a function of temperature are shown in Figure 2.

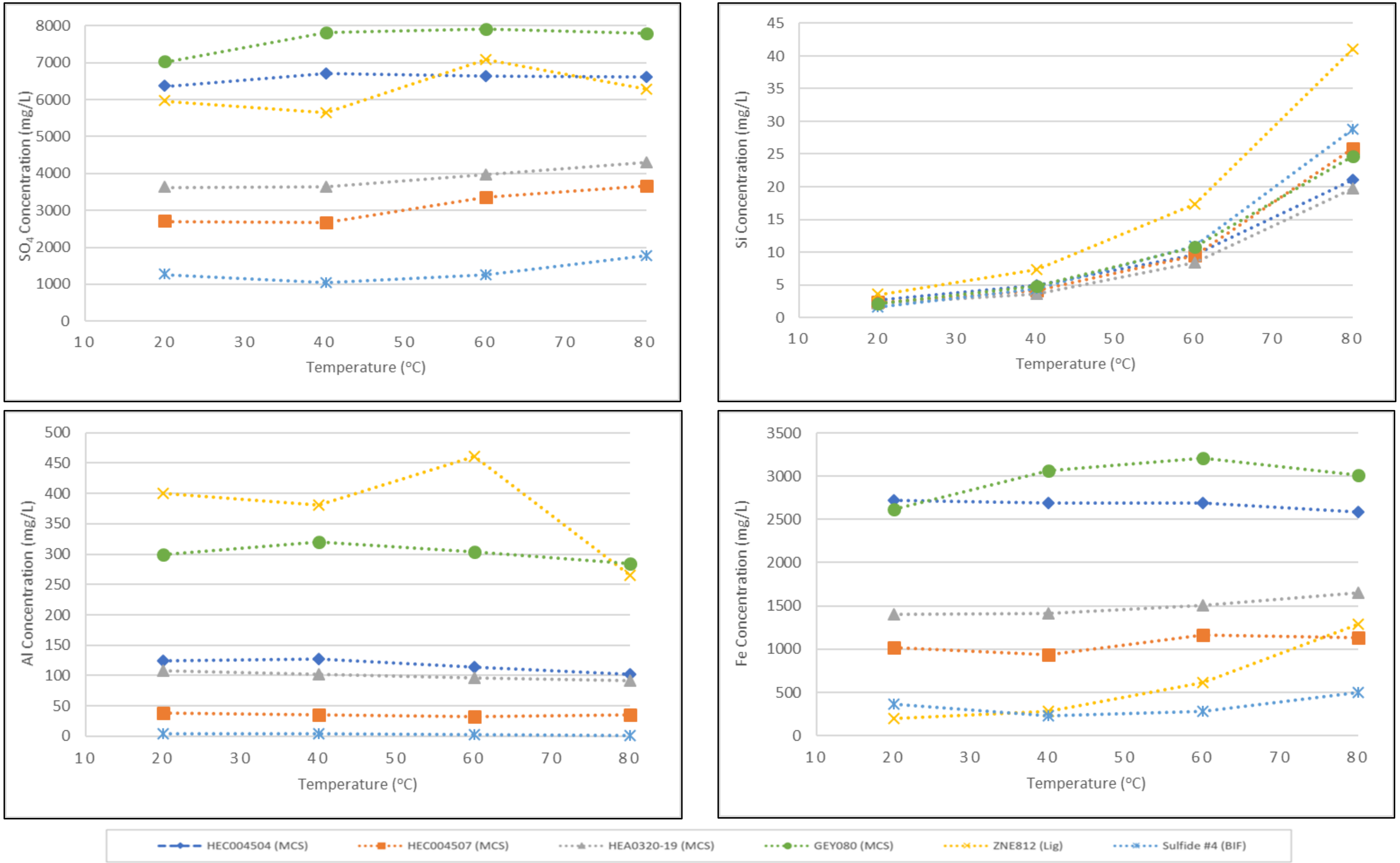

Fig. 2. Variation in SO_4, Si, Al and Fe concentrations with temperature

The plot suggests that SO_4 solubility is not significantly influenced by the leach temperature, although the profiles do show a tendency towards a higher dissolved concentration at higher temperatures.

For most samples, there is little variation in Al or Fe concentrations with temperature. Exceptions are:

- Al concentrations were variable for the lignite sample, showing increases and decreases over the temperature range; SO_4 (and Mg – not shown in Figure 2) show a similar trend for this sample).
- Fe concentrations show increases with temperature for the lignite and one of the Mount McRae Shale samples (GEY080). The Fe concentration trend for the lignite samples was similar to the Si trend.

Concentrations of Si increased with temperature for all samples. The highest Si concentration was measured in the leachate from the lignite sample.

The mineral phases inferred to control leachate chemistry were as follows:

- Fe and Al sulfates and hydroxysulfates. Jarosite was identified in the mineralogical assessment (Table 1). Other Fe and Al sulfates and hydroxysulfates may be present, not identified either due to low quantities or non-crystalline forms.
- A soluble silicate mineral (particularly at high temperature). A range of silicates were identified in the materials.
- Calcium and magnesium sulfate (gypsum and epsomite) – in the case of the lignite and sulfidic BIF samples. Gypsum was identified in the lignite sample (Table 1).
- For the lignite, it is also hypothesised that Mg could be sourced from an Al sulfate mineral, explaining strong positive correlations between Mg, Al and SO_4 concentrations.

Many trace elements were present in the leachates, with the highest concentrations leaching from the lignite sample. Concentration trends however were variable between solutes and from sample to sample. Correlations between trace elements and major ions suggest that trace elements may be present as impurities in the most abundant secondary mineral phases, and are released in response to dissolution of these phases. The current assessment focused on the solubility of major component phases only.

4. GEOCHEMICAL MODELLING

4.1 Thermodynamic datasets

Most thermodynamic datasets are collations of equilibrium constants applicable at standard temperature and pressure conditions (25°C, 1 atm.). To model thermodynamic equilibrium as a function of temperature, data for enthalpy are required so that equilibrium constants can be adjusted to the temperature of interest. Many thermodynamic datasets do not include enthalpy data for all aqueous species and solids represented. Clearly, the farther away the target temperature from standard conditions (25°C), the greater the degree of uncertainty associated with model outcomes – especially for cases where only a subset of the equilibrium constants are being adjusted as temperature changes.

Four thermodynamic datasets were assessed: i) HATCHES (Bond et al., 1997, NEA Version 20, released in 2013), ii) Wateq4f.dat and iii) minteq.v4.dat (two datasets distributed with PHREEQC; Parkhurst and Appelo, 2013) and iv) data presented in Baron and Palmer (1996). There is variability across the datasets; not only did equilibrium constants and enthalpy values differ, but the suite of species and solids represented within the datasets differed. Several instances were noted where no enthalpy data were included with the datasets – notably jurbanite and basaluminite (amongst the minerals) and $^{III}FeHSO_4^{+2}$,

$^{II}FeHSO_4^+$ (amongst the aqueous species).

Eremin et al. (2015) include a compilation of heats of formation for Al sulfates and hydroxysulfates. Using the data presented, it was possible to calculate heats of reaction for selected key dissolution reactions presented in the minteq.v4 and wateq4f datasets, namely -82.81 kJ/mol for jurbanite and -347.87 kJ/mol for basaluminite. These auxiliary values were added to the existing thermodynamic datasets.

4.2 Mineral solubility as a function of temperature

Mineral equilibrium controls were assessed by processing the measured solution chemistries using PHREEQC. The PHREEQC output includes calculated saturation indices (SI) to represent the degree of saturation with respect to possible mineral phases. Saturation indices close to zero suggest proximity to thermodynamic equilibrium and may be indicative of a solubility controlling mineral phase.

Leachates from lignite and sulfidic BIF samples are close to saturation with the widest range of minerals including: gypsum, $Fe(OH)_3$, jarosite, gibbsite and jurbanite. The variety of potential minerals likely reflects the slightly higher pH values for these leachates, when compared to the overall range observed in the test results. Mineral solubility controls are more likely to be encountered as solution pH increases.

Leachates from the Mt McRae shale samples (pH 1.5 to pH 2.5) indicated potential solubility controls by only jarosite and jurbanite, and only for a subset of solutions - typically those for the higher temperature tests (see Figure 3). Based on thermodynamic modelling, hydroxysulfates such as K-jarosite and jurbanite are expected to be less soluble as temperature increases.

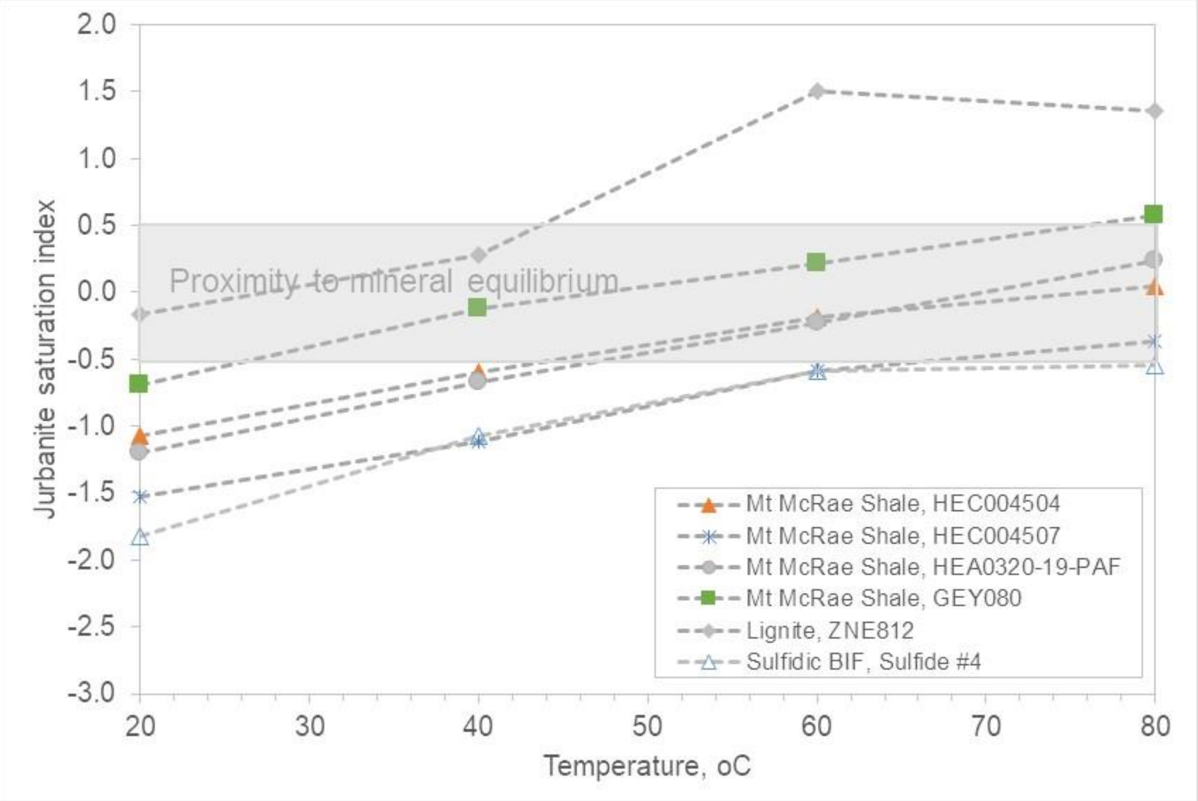

Fig. 3. **Calculated jurbanite saturation indices, as a function of temperature**

Due to gaps in thermodynamic datasets, a degree of uncertainty remains as to the role of the minerals identified. It should however be remembered that solubility controls may involve minerals not represented in any of the datasets, or, may take the form of solid solutions with variable compositions.

5. CONCLUSIONS

In general, the results indicated that temperature (over the range of 20°C to 80°C) did not have a strong, consistent, impact on leachate compositions, with the exception of dissolved Si concentrations. Leachate chemistry was dominated by acidity, Al, Fe and SO_4. Soluble mineral sources were inferred to be combinations of Fe and Al sulfates and hydroxysulfates (jarosites were identified in mineralogical studies), silicates, and - for lignite and sulfidic BIF only - gypsum. Dissolution of solutes from the lignite sample indicated strong correlations among Mg, Al and SO_4 concentration trends, and were considered indicative of a possible common mineral source.

Available thermodynamic datasets were incomplete with respect to enthalpy data, and therefore calculations at temperatures that differ from standard conditions (25ºC) are subject to uncertainty. Nevertheless, thermodynamic modelling was found to identify solubility controls that were broadly consistent with observation, providing confidence that modelling can be used to support predictions of seepage chemistry at conditions outside of current observational datasets.

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ALKALINE LEACHING OF PILBARA MATERIALS

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ABSTRACT

Tailings from iron ore operations in the Pilbara are typically conveyed to storage locations as a slurry. Relatively inexpensive additives (including sodium hydroxide, NaOH) may be used to improve ore beneficiation and reduce the viscosity of the tailings slurry. Whilst the rheological properties of the tailings may be more favourable after amending the slurry pH to alkaline values, consideration must be given to the effect of pH on contaminant leachability. There is a risk that the alkaline tailings slurry and contact with surrounding rock results in increased contaminant mobility, impacting groundwater quality.

Four waste rock samples and one tailings sample were subjected to simple leach extraction tests at the sample natural pH (i.e. deionised water leach) and at pH values of 8, 10 and 12 (pH adjusted using NaOH). All samples contained low sulfur (avg. <0.03%) and low acid neutralising capacity (<20 kgH_2SO_4/t).

Observed leaching trends were similar for the waste rock and tailings. Dissolved Si, Al and Fe concentrations increased at the most alkaline conditions, suggesting dissolution of silicates. The solubility of many trace elements showed analogous trends suggesting that these may be present as impurities within the soluble silicate phases. In contrast, Ca and Mg concentrations decreased with increasing pH, possibly due to decreased solubility of carbonates. Potassium, Ba, Li, Mn, Sr and Zn concentrations also decreased and may also be influenced by solubility of carbonate host minerals.

The results indicated that maintaining the tailings slurry pH below 10 lowers the risk of contaminant leachability.

Key words: Leaching, low sulfur, alkaline.

1.0 INTRODUCTION

Rio Tinto Iron Ore (RTIO) are investigating the merits of using relatively inexpensive additives in ore processing at their operations located in the Pilbara region of Western Australia. The additives enhance impurity separation, particularly clay minerals from iron oxide particles. In addition, the use of the additives is expected to improve the tailings rheology (reduced slurry viscosity), reduce water demand and reduce the overall volume of waste placed in the tailings storage facility or backfilled into mined out pits.

The additives include sodium hydroxide (NaOH) and will yield an alkaline slurry (pH between pH 9 and 10). RTIO recognise that alkaline waters contacting tailings and pit wall rock (where tailings water is released from backfill in pits) could increase contaminant mobility and impact groundwater quality. A study to evaluate contaminant leaching at various alkaline pH values was therefore completed to infer potential impacts on groundwater quality.

2.0 SAMPLE PROPERTIES

Four samples of waste rock (reverse circulation drill chips) and one sample of tailings were selected for testing. The waste rock samples represent the detritals (DET) and Joffre Member (JOF) lithological units. The three JOF samples selected represent different sub units within the Joffre Member; the hydrated (HYD), hydrated waste (HYW) and shale (SHL) sub units, each with differing chemical and mineralogical groupings. The rock samples represent the lithologies most likely to come into contact with the tailings. Sample preparation involved low temperature drying (ambient air), prior to splitting and crushing/pulverisation as appropriate.

Selected sample properties are summarised in Table 1. Acid base accounting (ABA) and net acid generation (NAG) test results showed that the samples contain low total sulfur and acid neutralising capacity (ANC), and that the samples are non-acid forming. [Note: the test methods were consistent with those in the AMIRA ARD Test Handbook (AMIRA, 2002) and the MEND Prediction Manual (Price, 2009).]

The samples are enriched with respect to As, Bi, Sb and Se (i.e. these elements were present at concentrations above crustal averages with geochemical abundance indices (GAI) of 3 or more). Quantitative X-ray diffraction (XRD) indicated that the samples comprise primarily iron oxide and oxyhydroxide, followed by silicate phases.

3.0 METHOD

The samples were submitted for the following leach tests:

- Deionised (DI) water leach extraction test.
- Alkaline leach extraction testing at pH 8, 10 and 12 using NaOH to adjust solution pH. Three stock solutions were prepared, one for each target pH interval (i.e. pH 8, 10 and 12) – with pH adjustment using 0.1 M reagent grade NaOH.

All leach extraction testing was carried out at atmospheric conditions on ‘as received’ samples at a 2:1 liquid to solid (L:S) ratio over a 12 hour contact period during which the slurries were tumbled. On completion of the test, the leachate was separated from the solids and the solution pH measured. The leachate was then filtered (at 0.2 µm) and submitted for analysis.

Since the pH was expected to change during the contact period, the pH was adjusted and stabilised at the target pH value before the test commenced as follows:

- The solids and stock solution (at target pH) were combined in a bottle at an initial L:S of 1.75:1.
- The pH of the mixture was monitored and adjusted (using 0.1 M reagent grade NaOH) to maintain solution pH in the target range, until the pH remained unchanged for 15 minutes. [The pH tended to decrease – interpreted as absorption of atmospheric CO_2 and/or buffering due to water/rock interaction.] The volume of NaOH added during the adjustment period was recorded.
- Once the solution pH had stabilised, stock solution was added to increase the L:S to 2:1, and the samples were then agitated for 12 hours.

The final pH values usually were within 1 pH unit of the target value.

An aliquot of each stock solution was submitted for analysis as blanks. Results indicated that most elements were below the limit of detection in the stock solutions. However, impurities comprising Si, Al and Mn were found to be present and were taken into account when interpreting the results.

Table 1: Sample properties

Group	Parameter	Units	Waste Rock Sample Strand (and Geological Tag)				Tailings
			DET	JOF (HYD)	JOF (HYW)	JOF (SHL)	
ABA, NAG and Class	Paste pH	pH Units	7.1	6.4	7.7	6.9	7.1
	Paste EC	µS/cm	482	601	657	349	609
	Total S	%	0.02	0.16	0.04	0.04	0.02
	ANC	kgH_2SO_4/t	2.3	2.4	3.8	1.5	3.4
	NAGpH	pH Units	7.6	7.3	7	6.8	7.4
	NAGpH7	kgH_2SO_4/t	<0.1	<0.1	<0.1	0.4	<0.1
	MPA	kgH_2SO_4/t	0.6	4.9	1.2	1.2	0.6
	NAPP	kgH_2SO_4/t	-1.7	2.5	-2.6	-0.28	-2.8
	Class	AMIRA	NAF-Barren	UC (NAF)	NAF-Barren	NAF-Barren	NAF-Barren
Trace element content (and GAI)[1]	As	ppm	17	20 (3)	39 (4)	207 (6)	37 (4)
	Ba	ppm	340	30	3210	190	60
	Bi	ppm	0.42	0.12	0.49	0.68 (3)	0.4
	Cr	ppm	246	48	77	81	31
	Cu	ppm	39	2.9	25	40	17
	Mo	ppm	1.85	2.33	0.76	6.36	1.86
	Pb	ppm	32	11	49	33	17
	Sb	ppm	3.4 (3)	2.1	5.3 (4)	14 (5)	2.3
	Se	ppm	2 (4)	1 (3)	<1	<1	<1
	Sr	ppm	33	32	116	90	150
Mineralogy (XRD)	Alunite	Hydroxysulfate %		0.8			
	Hematite	Oxides and Oxy-hydroxides %	17.9	55.7	6.7	8.2	32.5
	Goethite		11.5	17.7	32.6	49.4	41.8
	Gibbsite						0.6
	Anatase		1.2				
	Rutile		1.2				
	Quartz	Silicates %	20.1	0.3	0.6	6.6	3
	Kaolinite		22.4	9.2	24.9	18	13.4
	Chloritoid		6.4	0.8	7.5	3.1	2.1
	Chabazite			1.9			
	Ca-Montmorillonite				12.1	3.8	
	Non diffracting/ unidentified[2]	%	19.3	13.6	15.7	11	6.6

Notes: [1] GAI values for enriched elements shown in brackets; [2] Found by difference [100wt% – (sum of absolute estimates)]; EC – electrical conductivity; S – Sulfur; ANC – acid neutralising capacity; NAG net acid generation; MPA – maximum potential acidity; NAPP – net acid producing potential; NAF – non acid forming; UC – Uncertain.

4.0 RESULTS AND DISCUSSION

4.1 Major ions

Dissolved concentrations of SO_4, Cl, K and Si were present in all leachates and Al, Fe, Ca and Mg were above detection limits in most leachates. Dissolved mass generally represented less than 10% of the corresponding elemental mass present in the solids. Plots Ca, Si, SO_4 and Al concentrations as a function of pH are shown in Figure 1.

Concentrations of Ca, K and Mg are shown to decrease with increasing pH. This trend suggests that these elements are less leachable as conditions become more alkaline – possibly due to decreased solubility of source minerals such as carbonates (which may be present in trace quantities below XRD limits of detection). Saturation indices (SI) calculated using geochemical speciation modelling (PHREEQC) indicated that carbonates (such as calcite and dolomite) were below saturation at neutral/mildly alkaline pH values but were close to equilibrium in the pH 10 and pH 12 leachates.

Dissolved SO_4 and Cl concentrations increased with increasing pH for the JOF (HYD) sample. This sample contained 0.16% total sulfur (mostly present as alunite) and the increasing sulfate concentration may reflect dissolution of alunite. This conclusion is supported by strong calculated correlations between SO_4 and Al (Pearson = 0.95) and PHREEQC modelling which indicated that alunite was saturated in the DI water leachate, but undersaturated in the more alkaline leachates. The analogous trend observed for Cl, together with strong correlations with SO_4 (Pearson = 0.95) suggest that it may be present as an impurity within alunite.

Concentrations of Si, Al and Fe were relatively constant in the 6 to 9 pH range, but increased at pH 12 (the increase was most significant for DET sample – an increase of almost 8 times). The results indicate increased silicate mineral solubility at alkaline pH. This conclusion is supported by calculated SI values for silicate minerals (such as chalcedony) which showed near equilibrium conditions at neutral to alkaline pH values (up to pH 9), but undersaturated conditions at higher pH values.

Dissolved Fe and Al concentrations were analogous to that of Si, remaining relatively constant and low at neutral to alkaline pH values, but increasing significantly at pH 12. While it is possible that leachable Al and Fe may be sourced from dissolution of silicate minerals containing these elements, such as chloritoid (identified by XRD), calculated molar ratios and a decrease in Mg concentrations (Mg is expected to be a component of chloritoid) with increasing pH suggest that chloritoid is not the source. The trend was most obvious for the alunite-bearing sample, JOF (HYD), which leached the highest concentrations of both Fe and Al at alkaline pH. Al and Fe are likely sourced from alunite (with Fe is present as an impurity within the mineral) and/or less stable oxy-hydroxides.

4.2 Trace elements

Most trace elements leached at low to negligible concentrations at neutral to slightly alkaline pH values. Concentrations of As, B, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, and V increased at higher pH values. Examples of solute concentrations as a function of pH are presented in Figure 2 (showing Ba, Sr, Cu and Pb) and Figure 3 (showing As, Sb, Se and Mo). As shown in the plots, some elements including Sb and Mo show a gradual increase over the entire pH range, whilst other elements including Cu, Pb and As show a relatively abrupt increase at the most alkaline pH values. These trends, particularly the abrupt increase for the most alkaline conditions, are analogous to the trends shown by Si, Al and Fe and suggest that trace element release may be related to the dissolution of the same source minerals – where trace elements are present within the matrix of the source minerals. It is noted that the highest concentrations of Pb, Cr and Ti were observed for the alunite bearing sample, JOF (HYD).

Concentrations of a minority of elements, including Ba, Li, Mn, Sr and Zn, decreased with increasing pH. Whilst the trends for Ba concentrations do not appear to be inversely related to sulfate (i.e. formation of barite - $BaSO_4$), they are similar to those shown by Li and Sr concentrations and are analogous to trends shown by Ca, and Mg. This suggests that these elements may be present within carbonates (i.e. calcite and possibly dolomite which are less soluble at higher pH values, as discussed earlier). PHREEQC modelling indicated Mn and Zn trends may be influenced by the low solubility rhodochrosite ($MnCO_3$) and zincite (ZnO). SI values calculated for barite suggest that it may also contribute to observed dissolved concentrations for Ba.

The mass proportion of each trace element leached from the samples was generally low, around 0.1% or less (respectively), at neutral pH conditions (DI water leach). However, most trace elements leached at marginally higher proportions at pH 12, but the proportion generally remained below 0.5% (respectively). This suggests that the elements enriched within the samples (such as As, Bi, Sb and Se) are present in a form that is not readily leachable within the neutral to alkaline pH range.

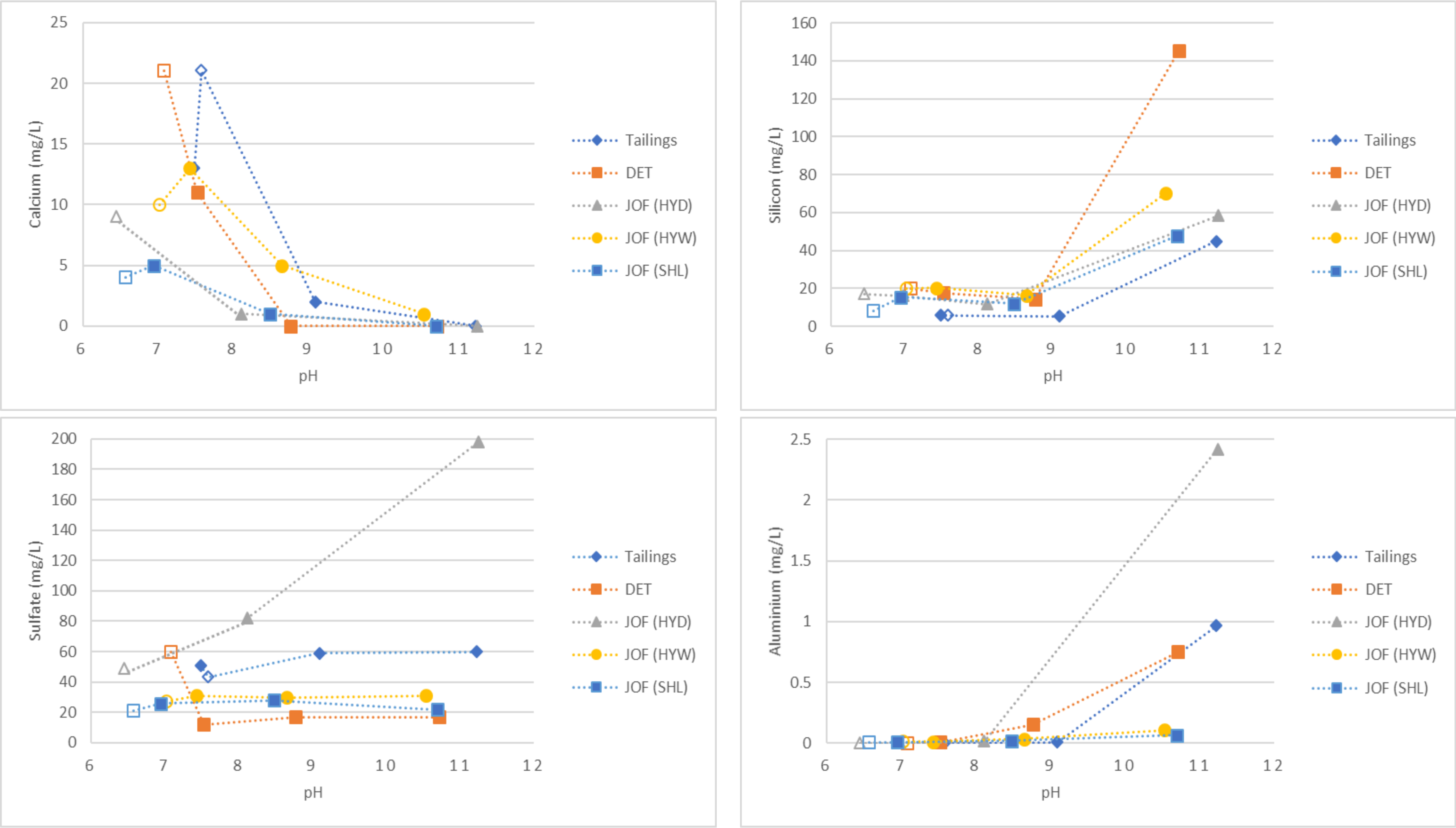

Figure 1: Leaching of Ca, Si, SO_4 and Al

Note: Results for deionised water leach are shown by hollowed out symbols.

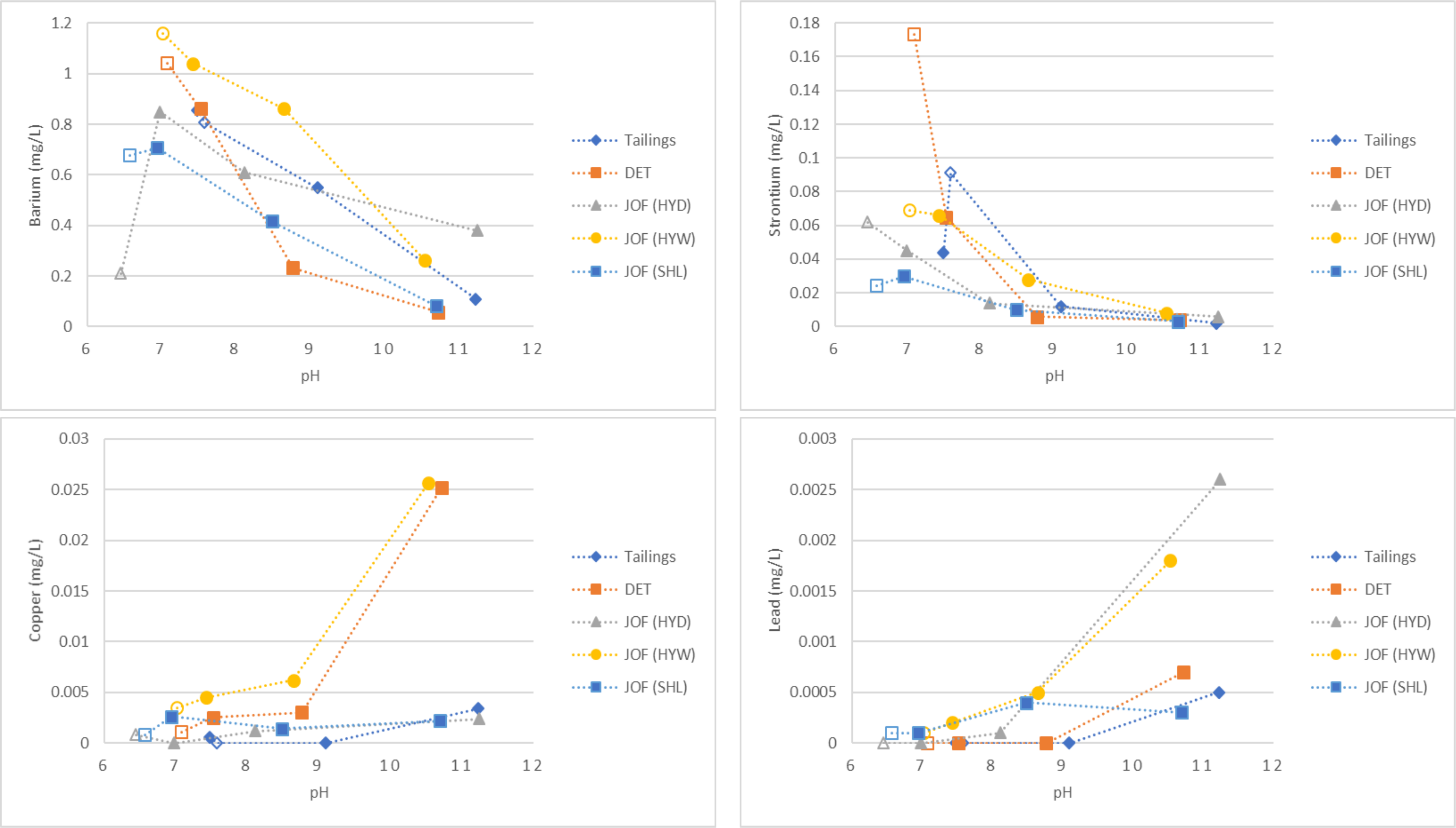

Figure 2: Leaching of Ba, Sr, Cu and Pb

Note: Results for deionised water leach are shown by hollowed out symbols.

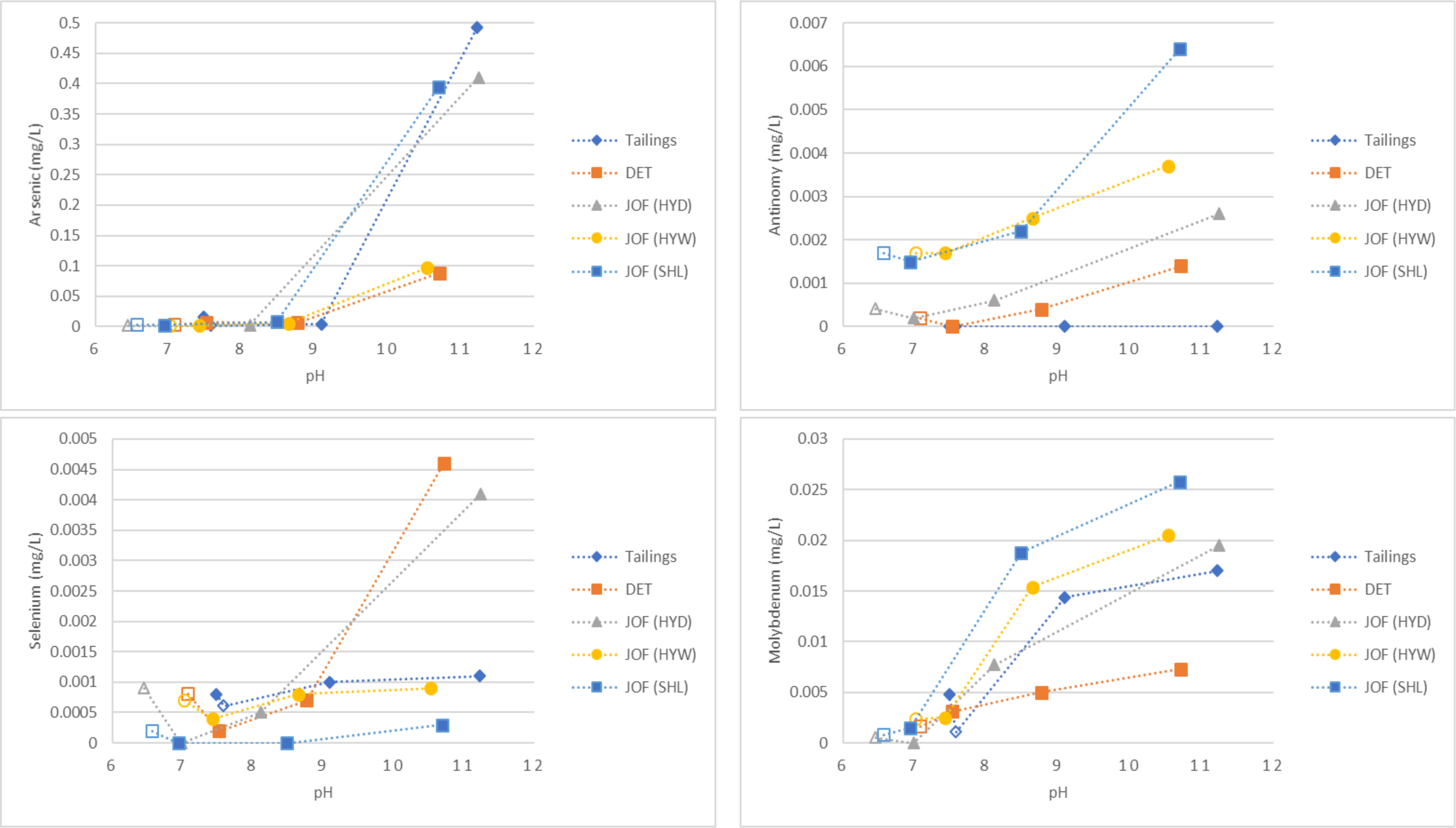

Figure 3: Leaching of As, Sb, Se and Mo

Note: Results for deionised water leach are shown by hollowed out symbols.

5.0 CONCLUSIONS

The test results indicated the following:

- Alunite solubility increased at alkaline pH as indicated by leaching trends and geochemical modelling for the alunite rich sample JOF (HYD). This sample leached the highest concentrations of Al and SO_4 (key components of alunite) as well as Cr, Fe, Pb and Ti (possibly present as impurities within alunite).
- High dissolved Si at alkaline pH suggests that there may be an additional silicate source under alkaline conditions.
- Many trace elements showed pH dependent dissolved concentration trends analogous to concentrations of the major elements Si, Al and Fe, suggesting that the trace elements may be present as impurities within the dissolving major element host phases.
- Dissolved concentrations of Ca and Mg decreased with increasing pH, suggesting solubility controls by carbonate phases (as indicated by decreasing solubility of calcite and dolomite). Concentrations of Ba, Li, Mn, Sr and Zn also decreased with increasing pH and may suggest precipitation of, or co-precipitation with, carbonate minerals.

Results of test work indicated that maintaining the tailings slurry below pH 10 would reduce the risk of impacts on groundwater quality.

6.0 ACKNOWLEDGEMENTS

Intertek/Genalysis laboratory in Perth who carried out the test work.

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GAS AND HEAT MODELLING OF A WASTE ROCK DUMP IN ORDER TO OPTIMIZE POTENTIAL MITIGATION MEASURES

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ABSTRACT

A sulphide-rich waste rock facility with elevated internal temperature has been investigated through field, laboratory and modelling methods. Advective transport of oxygen has been identified as the main mechanism that results in heat generation in the dump by supporting the oxidation of sulphide minerals.
Distribution of heat and gas through the dump has been monitoring over a period of time with thermocouples and air collection compartments installed in bores at multiple depths in the facility. From the monitoring results, a conceptual model of the multiphase gas, heat and water processes has been developed. Several aspects influence the airflow, gas consumption and heat generation of the dump. These include the geochemical character of the waste rock, water flow and transfer, heat flow, gas transport as well as certain geometrical features of the dump.

Due to the complexity of the interactions between the solid, water and gas phases, numerical modelling was performed to improve the conceptual understanding of the gas flow into and within the waste rock dump. The modelling allowed the mechanisms of heat generation in the facility to be explained and provides a means to identify, assess and refine potential mitigation measures such as interim and final covers.
Mitigation measures already implemented by the mine are actively monitored. The ongoing monitoring results will be used further to calibrate and validate the gas and heat model.

1.0 INTRODUCTION

The controlling mechanisms of acid mine drainage (AMD) escalate in complexity under increasing temperatures. Heat generation from pyrite and carbon oxidation in the waste rock dump enhances oxygen advective transport, mineral reaction rate, as well as generation of steam, sulphur and carbon gases. In turn, air convection[5] increases the transport of oxygen into the waste rock dump which further promotes pyrite oxidation.

This paper provides an overview of the typical mechanisms that control heat generation and airflow in a waste rock dump at high temperatures. Modelling was used to simulate the process and to investigate potential mitigation processes.

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[5] Definitions: Air flow signifies the collective movement of gases which may include oxygen, carbon dioxide, water vapour etc. along a pneumatic gradient. Convection specifically refers to air (or gas) flow related to temperature (and associated air pressure) differences. The advective transport of a gas (e.g. oxygen) refers to the passive transport of the gas as a result of air flow. Gaseous diffusion refers to the spontaneous movement of a gas along a concentration gradient.

2.0 OBSERVATIONS

Thermocouples and air collection compartments were installed in bores at multiple depths in the facility for monitoring purposes. As shown in Figure 1, the waste rock dump has an internal temperature in the centre of about 60 - 80°C which increases to 150 – 220°C towards some of the sides that do not have soil covers. Oxygen is not present deeper than 0 - 2 m at the top of the dump as it is expected that most air exits the waste rock dump through the top.

Carbon dioxide is generally low near-surface and increases with depth to values exceeding 5% atm (the maximum value recorded by the detector). It is produced from both the thermal combustion of carbon (in the presence of oxygen) or the neutralisation reaction of carbonate minerals. Carbon monoxide occurs at all levels within the dump at <30 ppm, although it is generally absent from the upper-most surface in contact with the atmosphere. Carbon monoxide is produced from the thermal decomposition of carbonaceous material in the absence of oxygen.

The greatest concentration of hydrogen sulphide (up to 140 ppm) typically occurs at depths midway between the upper and lower parts of the waste rock dump, with the concentration at zero closer to the top. Hydrogen sulphide will react with oxygen and even with sulphur dioxide which may explain why it is not present closer to the top.

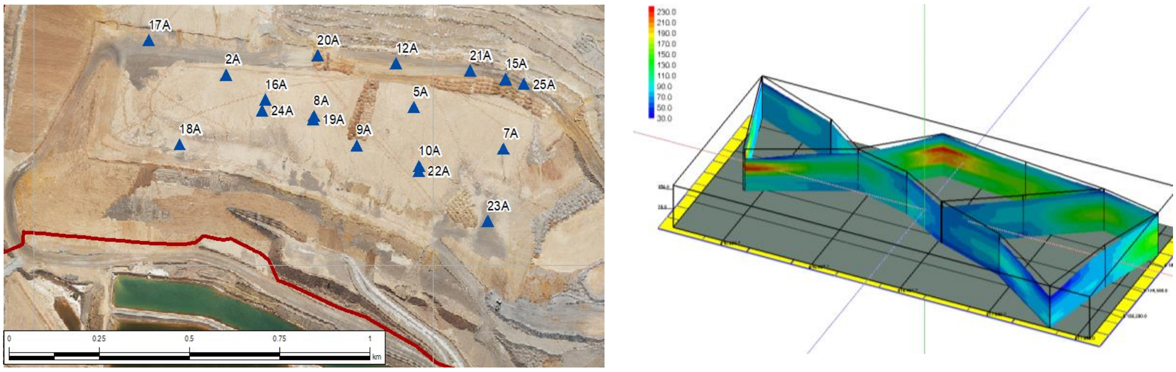

Fig. 1. **Snapshot of heat distribution throughout the waste rock dump before the implementation of mitigation measures**

3.0 CONCEPTUAL MODEL

A conceptual model of pyrite oxidation and oxygen supply from Lefebvre et al (2001) is depicted in Figure 2 showing how pyrite oxidation and heat generation influences the resupply of oxygen to the waste material.

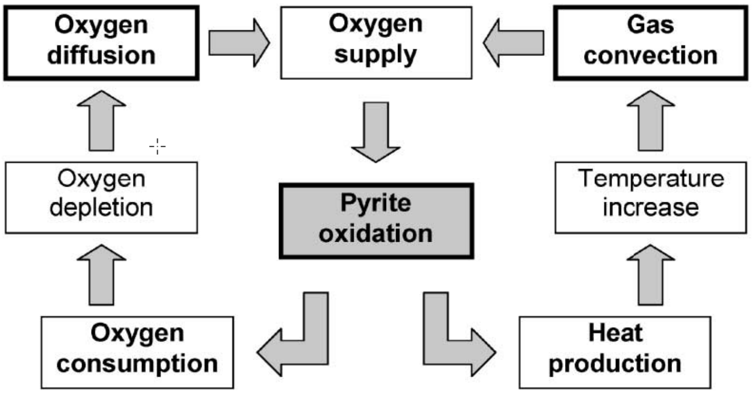

Fig. 2. **Conceptual model of pyrite oxidation and oxygen supply (Lefebvre et al, 2001)**

Several aspects influence the air flow, gas consumption and heat generation in a waste rock dump. The physico-geochemical processes in the waste rock dump are a function of the following:

- Geometrical features of the waste rock dump;
- Water flow and phase change;
- The geochemical character of the waste rock;
- Heat generation and flow;
- Air flow; and
- Oxygen transport (through advection and diffusion).

A conceptual model of physico-chemical processes for the waste rock dump is depicted in Figure 3 below.

- Steam emitted from the waste rock shortly after placement indicates that the waste rock is highly reactive and rapidly reaches elevated temperatures above ambient values. Background temperatures of the waste rock dump, where no oxygen was measured, varies between 60 – 80°C.
- Oxygen diffuses (flow from a high concentration to a low concentration) into the waste rock dump as the oxygen included in the freshly dumped material is consumed. Airflow through the waste rock dump results in some advective transport of oxygen into the dump.
- Pyrite oxidation results in the consumption of oxygen and simultaneous heat generation. The consumption of oxygen results in a gradient in the oxygen concentration promoting oxygen diffusion. Heat generation results in increased vapour movement, air convection and advection of oxygen into the dump. In the presence of water, oxygen can be consumed through the oxidation of pyrite as follows:

  $$FeS_2 + 3.5H_2O + 3.75O_2(aq) \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$
- Pyrite oxidation is an extremely exothermic reaction producing 1409 kJ/mole (or 1.7 x 10^5 kJ/g pyrite) of pyrite oxidized (Wels et al., 2003) or 411 kJ/mole of oxygen.
- The material only contains <5% organic carbon. The heat produced for the reaction $C + O_2 \rightarrow CO_2$ is 393 kJ/g for one mole of oxygen which is close to that of pyrite.
- Heat flow occurs through conduction as well as through gas and water movement. The thermal conductivity of rock is higher than for air and therefore heat loss will occur through both the top and base of the dump.
- External processes will influence the physico-chemical processes within the dump. These include changes in seasonal as well as daily climatic conditions. At the site wind direction, rainfall, humidity and temperature are seasonal. These changes will have some effect on the top and sides of the dump. Roughly about 85% of the yearly rainfall recharge will occur during the summer months and this should have a significant influence on vapour movement in the dump. Also notable is the 0.5 kPa barometric pressure difference between the top and bottom of the dump which will also change upon daily and seasonal changes of temperature.

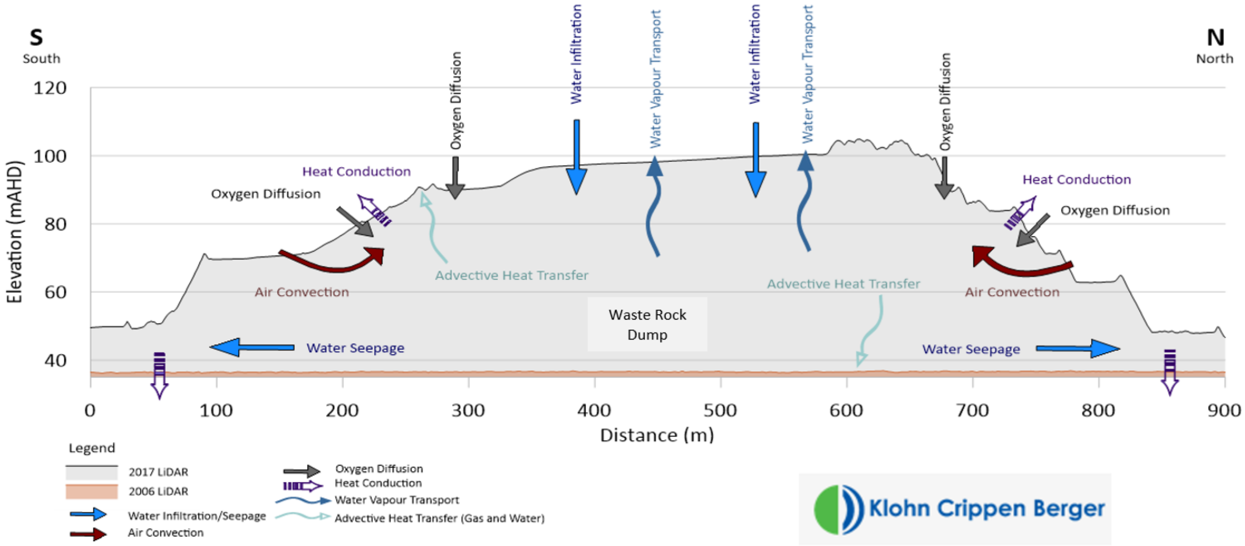

Fig. 3. **Conceptual model of physico-chemical prosseses**

4.0 NUMERICAL MODEL

4.1 Introduction

Due to the complexity of the interactions between the solid, water and gas phases, numerical modelling was performed to improve the conceptual understanding of the gas flow into and within the waste rock dump. The specific objectives of the multiphase numerical model were as follows:

- To understand the processes related to air convection and temperature generation at the dump. This will enable planning for further actions required such as further field testing required for the second phase of the multiphase modelling, as well as detailed capping design.
- A preliminary assessment was performed to assess the effectiveness of a soil cover and intermediate soil layers to minimize air convection.

4.3 Model Setup

Multiphase modelling was performed using the Geostudio 2018 suite of software for the multiphase modelling of water, heat and gas transport. An add-on package was used that enabled oxygen consumption to be coupled with the heat generation.

Model scenarios for one of the models performed on the waste rock dump, is listed in Table 1 below. Model Scenario 1 is a transient state model that incorporated the multiphase processes in the dump including oxygen consumption and heat generation. Model Scenario 2, is similar to the previous scenario except for the addition of soil layers (every 10 m), as well as a final soil cover to the waste rock dump.

Table 1. Model scenarios

Location	Scenario 1	Scenario 2
Model Type	Transient State (Multiphase)	Transient State (Multiphase)
Material	PAF Waste Rock	PAF Waste Rock + 0.1 m soil layers every 10 m + 1 m final capping
Oxygen Consumption	Oxygen consumption by pyrite oxidation	Oxygen consumption by pyrite oxidation
Heat Generation	Heat generation by oxygen consumption.	Heat generation by oxygen consumption.
Soil Capping	No Capping	Silty Clay Capping

A cross-section was generated through a part of the dump and divided into ~10 m thick layers parallel to surface. Two 1 m surface layers were assigned to the top of the model to refine the grid on the edge of the dump. A quadrilateral/triangular grid with a cell size of roughly 1 m in dimension was assigned to all regions except for the surface layers which had a 0.5 m cell size.

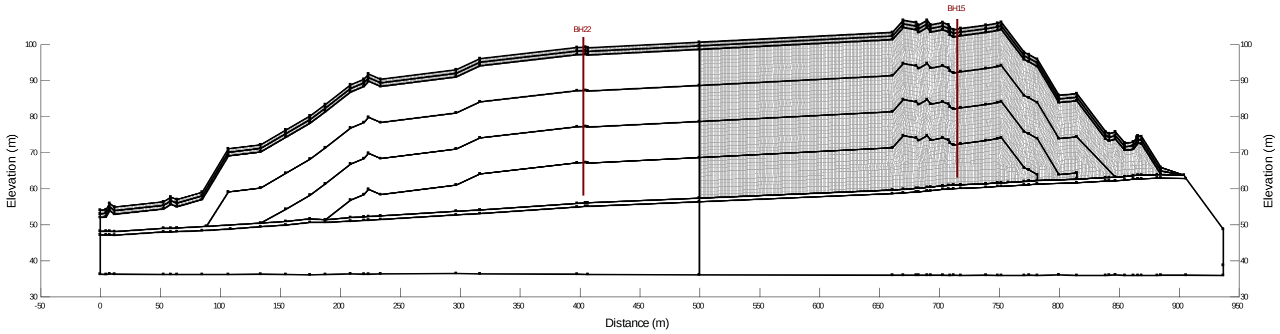

Fig. 4. Discretization of cross-section

The calibrated air permeability for the waste rock was at 4×10^{-9} m^2. In order to test the potential for soil covers to reduce oxygen advection, soil layers with a hypothetical permeability of 4×10^{-11} m^2 were assigned every 10 m in the model. The final clay capping has a hypothetical permeability of 2 orders lower. In the absence of site-specific values, the thermal conduction was calibrated to between 0.5 – 1 J/s/m/°C for the different models similar to the thermal conduction used for dry material by Lefebvre et al (2001).

The boundary conditions are summarized in Table 2 below. The steady-state water and air pressure results were assigned as initial conditions in the transient model. No oxygen was assumed to be present initially in the dump. As discussed previously, the background temperature in the dump is at 60 – 80°C and in the model an initial temperature of 70°C was specified. Rainfall recharge was assigned to the top and sides of the dump for all scenarios. The external air pressure at the top of the dump was at 0 kPa and at the toe at 0.5 kPa. The heat generation was related to oxygen consumption with the heat generated per mole oxygen consumed by pyrite at 1.258 kJ/Mg O_2 or 411 kJ/mole of oxygen.

Table 2. Boundary Conditions Assigned to the Model

Phase	Boundary	Value	Units
Water – Infiltration – Waste Rock	Surface	0.4004	m/a
Water – Infiltration - Cover	Surface	0.0787	m/a
Gas – Oxygen Concentration	Surface	276.7	g/m^3
Gas – Oxygen Concentration	Bottom	0	g/m^3
Air – relative pressure at the top of the dump	Surface	0	kPa
Air – relative pressure at the toe of dump	Surface	0.5	kPa
Temperature – constant	Surface	35	°C
Temperature – initial	Waste Rock and Bottom	70	°C
Temperature – heat generation	Material	411 kJ/mole	kJ/mole O_2

4.4 Model Results

The movement of heated air and water vapor towards the top of the dump initiate the process of air convection. In Figure 5 it is shown that there is a significant air inflow (and oxygen advection) from the side which will subsequently result in significant pyrite oxidation and heat generation. Heated gases will flow towards the top of the dump where it will be released into the atmosphere. Air convection will result in advective flow of oxygen, roughly 50 - 100 m deep into the dump from the batters (Figure 6). The temperature generated from the oxygen consumption reaches a maximum of over 200°C at between 10 – 20 m from the sides.

The oxygen consumption was calibrated to 2 x 10^{-5} kg/kg/s in order to reach the temperature and oxygen observed in the monitoring holes. This oxygen consumption rate is expected to be significantly higher than the rate measured in the laboratory at 30°C due to the elevated temperatures. The consumption rate measured in the laboratory (10^{-9} to 10^{-10} kg/kg/s) also did not include the reaction of carbonaceous material at elevated temperatures that produce a near equivalent amount of heat to pyrite per mole oxygen consumed.

The addition of soil layers and the final cover significantly lowers the oxygen concentration in the majority of the waste rock dump. The oxygen does not infiltrate deeper than about 5 m into the sides of the waste rock dump as depicted in Figure 7. Because of the flow of residual heat to the top, oxygen infiltration at the top remains low. Figure 8 shows that no significant additional heat is generated in the covered waste rock dump.

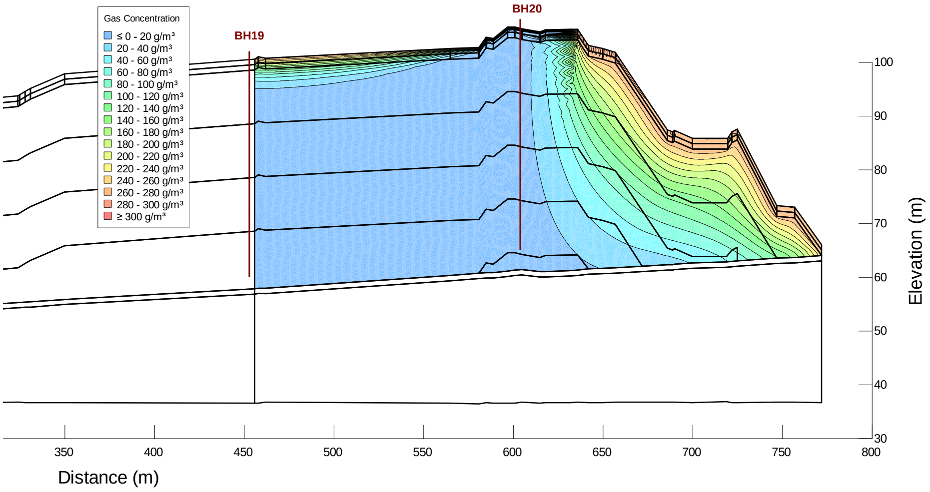

Fig. 5. **Sc1: Depth of oxygen infiltration into the waste rock dump after 10 years with no mitigation**

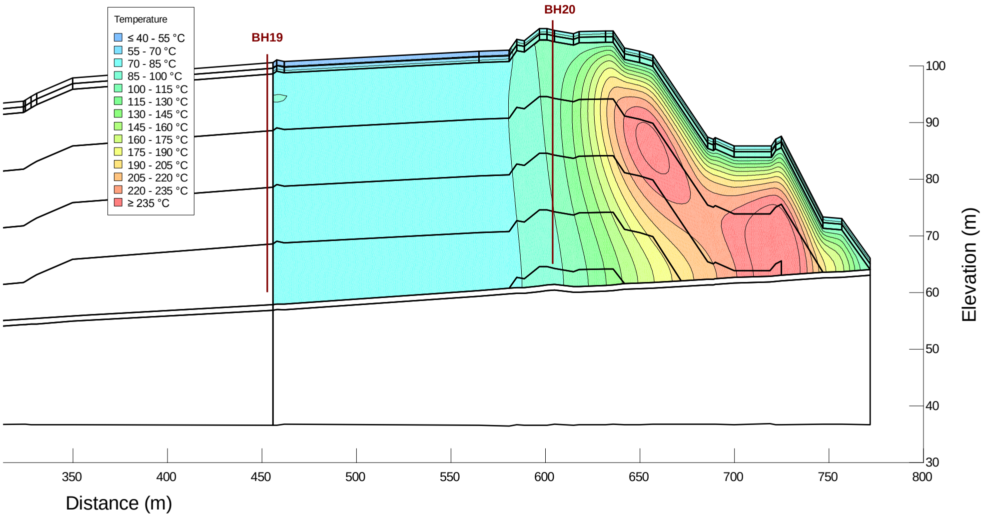

Fig. 6. **Sc2: Temperature in the waste rock dump after 10 years with no mitigation**

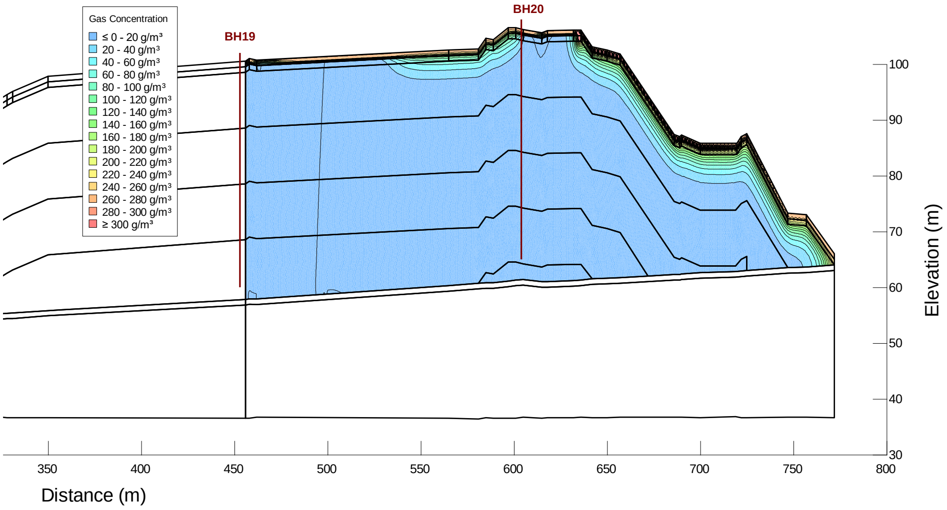

Fig. 7. **Sc1: Depth of oxygen infiltration into the waste rock dump after 10 years with interim soil layers every 10 m and a final 1 m soil capping**

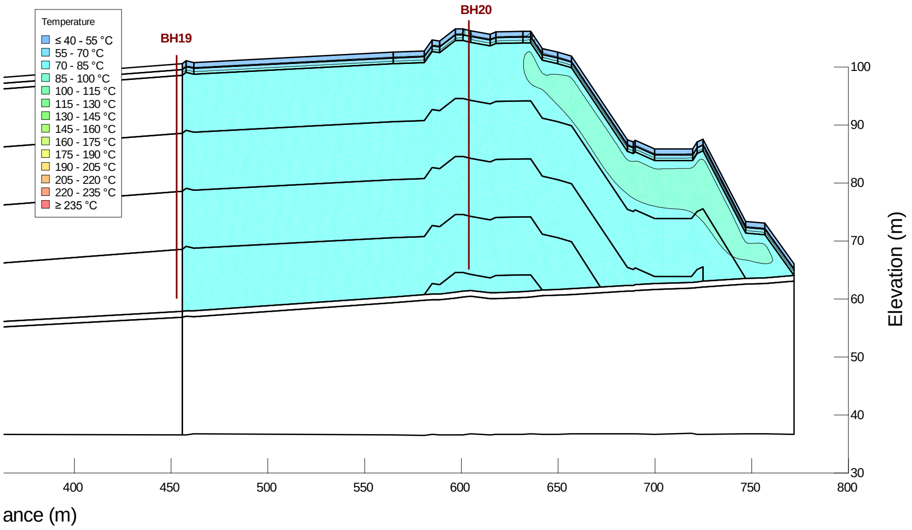

Fig. 8. **Sc2: Temperature in the waste rock dump after 10 years with a 1 m soil capping**

5.0 RESULTS OF IMPLEMENTED MITIGATION

The mine has covered some newly developed parts of the dump with soil layers every +-8 m. This resulted in no additional heat generated than the background temperature (60 - 80°C) in some newer parts of the dump as shown in Figure 9 below.

Existing parts of the waste rock dump closer to the sides covered with soil also showed a significant decrease in temperature over a two-year period as shown in Figure 10 below. The monitoring borehole showed a decrease in temperature from >160°C to <80°C in two years.

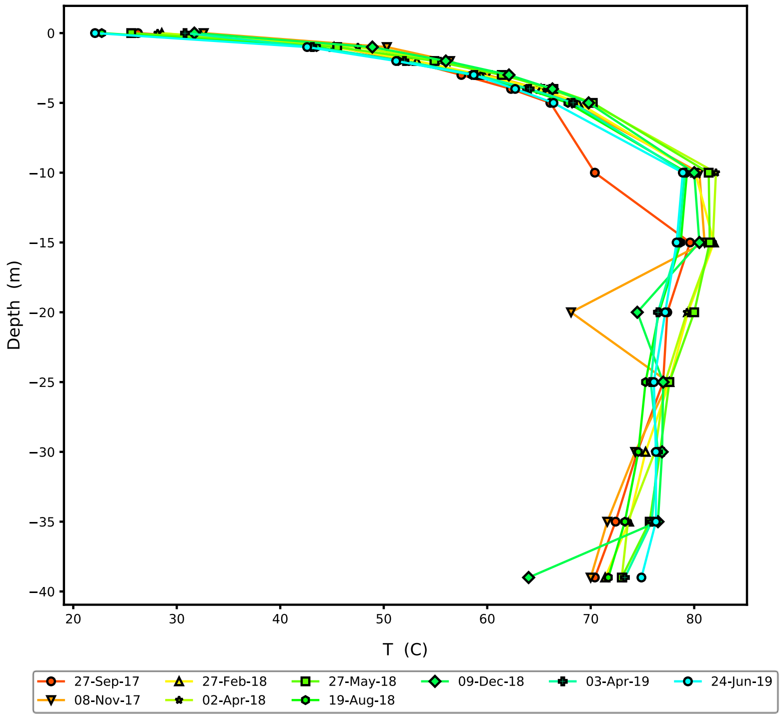

Fig. 9. **The temperature in a recently covered part of the waste rock dump (no increase in temperature after placement)**

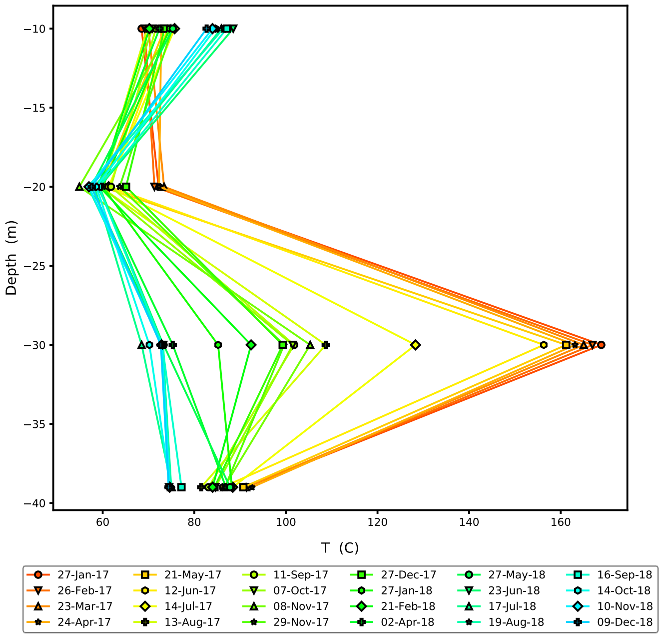

Fig. 10. **The temperature in a covered part of the older waste rock dump (significant decrease in temperature about 50 m from the sides after placement of cover)**

6.0 CONCLUSIONS

The numerical modelling improved the conceptual understanding of the multiphase processes related to air convection and temperature generation at the dump. The modelling confirms that heated air from in the waste rock dump migrate to the top and initiate the process of air convection. The convection draws air in from the sides with resultant oxygen advection 50 - 100 m metres into the sides dump. The temperature generated from the oxygen consumption reaches a maximum temperature of over 220°C on uncovered sides of the dump.

Modelling indicates that the addition of soil layers will significantly lower the convective flow of air through the waste rock dump. Monitoring data over a 2-year period, has shown that parts of the dump covered with soil layers, showed no additional increase in temperature above the background temperature. Existing parts of the waste rock dump closer to the sides also showed a significant decrease in temperature after the placement of soil covers.

It is expected that the reduced air convection and pyrite oxidation will not only improve the heat generation but also the water quality at the mine. The mine continues to monitor the temperature, gas and water quality at the dump and develop mitigation measures to reduce the potential for AMD.

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SETTING CUT OFF GRADES IN WASTE CHARACTERISATION SCHEMES: THE PERILS OF USING GRADE WEIGHT AVERAGING TO DETERMINE AMD RISK

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ABSTRACT

The majority of waste characterisation classification systems use discrete sulfide content-based cut-off grades to differentiate between wastes of different AMD risk. The use of a discrete cut-off grade approach reflects the assumption that AMD risk is directly proportional to sulfide grade when assessed on a grade averaged basis. However, many factors affect the validity of this assumption: the nature and distribution of sulfides and acid neutralising minerals in the host rock; sampling techniques during drilling; distribution of minerals by particle size as a result of mining activities; and, the approach to grade weighting and averaging during block-modelling.

Detailed assessments of the approach to applying cut off grades have been carried out at a number of sites where these factors and their impact on actual vs estimated AMD risk have been investigated.

Fragmentation analysis was carried out on samples of as-mined waste and involved detailed quantitative assessment of mineralogy across different grain size fractions. The results indicate that grain size differential distribution of sulfides and carbonates caused by mining induced fragmentation is a key factor influencing the validity of the cut-off grade approach. This is because the grade of the waste determined from drilling is an in-situ averaged property, but after mining, sulfides and carbonates have been shown to vary in concentration based on particle size due to differential fragmentation profiles. The geochemical properties of the waste as mined cannot therefore be assumed to reflect the bulk composition or properties of the waste determined by drillcore analysis coded into block models. Further, the composition of the fragmentation profile affects mineral reactivity, which is not normally reflected in grade weight averaging.

Our findings show that validation of grade weighted characterisation and modelling assessment systems using operational control techniques such as fragmentation analysis is key for managing AMD risk during mining operations.

1.0 INTRODUCTION

The waste characterisation process and degree of integration into mine planning has been incrementally improving over the last few decades. In recent times a notable and significant development associated with the significant increase in computing power and sophistication of computer software has been the development of detailed 3D waste models which have become increasingly widespread (Pearce et al 2012). The development and integration of waste models into mining models however has largely been facilitated by mine geologists and mine planners using approaches that were developed for resource development. It is important to note as such that the resource development approach is weighted towards the optimisation of the mining and recovery of ore and extraction of resources, and not waste management (Pearce et al 2019). As such by adopting an integrated (or assimilated) approach to consider waste management within standardised mine planning software, there is a fundamental assumption that the methods used to classify and model ore are explicitly the same as that for waste. A key factor employed using this approach is grade weight averaging.

The use of a grade weighted cut-off grade approach reflects an underlying assumption that, once mined, the waste material block has the same intrinsic properties as defined from the averaged value obtained from the block model. To test the validity of this assumption the authors have designed and carried out laboratory based assessment that seeks to identify the key factors that impact the validity of the approach, and suggest methods that may be used to supplement and optimise the approach. We have completed a study on the influence of the fragmentation of waste rock with respect to geochemical properties of the waste generated at a large nickel mine in Finland. The results have been used to assess the validity of using typical waste characterisation methods that assume that the properties of the mined waste product can be accurately defined from grade-averaged block modelling approaches, and that fragmentation effects from blasting/mining do not need to be considered.

2.0 FRAGMENTATION ANALYSIS

During the mining process blasting of ore and waste rock is considered optimal when the material is fine enough and loose enough to ensure efficient excavation and loading operations. The blasting optimisation strategy is usually focussed on minimising total mining costs and maintaining the optimal ROM fragmentation characteristics (Kanchibotla et al 1998). Importantly, because of the assumption that the mining model can adequately characterise the waste properties, the assessment does not consider changes to the properties of the waste as a result of blasting. These effects of blasting on waste properties has long been known as sulfide minerals can preferentially report to the fine fraction and as such this process has the potential to significantly increase the long-term costs of environmental management relating to acid mine drainage (AMD) risk (Elghali et al 2018, Pearce et al 2019).

Fragmentation analysis involves assessment of the particle size distribution of mined material at various stages in the mining process, typically after blasting has occurred. Because particle size has long been known to be a critical factor in the assessment of AMD risk of waste (Elghali et al 2018, Pearce et al 2019). materials, an opportunity was identified to explore the potential to utilise the technology to supplement waste characterisation and management.

3.0 METHODOLOGY

3.1 Sample Preparation

All testing was undertaken at the Geochemic Ltd laboratory facility located in Wales, UK. Testing was undertaken on waste rock samples obtained through screening of 100mm diameter sonic drill core intervals into representative grain size fractions. Samples were recovered from a sonic drilling program that was undertaken on existing waste rock dumps at the mine that represents “as mined” waste materials.

In total 30 separate sample intervals were considered. All of the samples were dry sieved into nine sub samples by fraction size, with the sieve aperture sizes being 10mm, 4mm, 2mm, 1mm, 0.5mm, 0.25mm, 0.125mm, 0.063mm. Waste rock larger than 10mm was then sieved at 22mm and 40mm. In total 270 samples were analysed.

3.2 Characterisation of Samples

A series of geochemical characterisation tests were selectively undertaken on the sieved fractions from the 270 samples to determine key properties . The tests included the following:

- Elemental composition through Energy Dispersive X-Ray Florescence (ED-XRF) (Panalytical MiniPal-4)
- Total Carbon and Sulphur determined through high temperature combustion (Perkin Elmer 2400)
- Acid Neutralising Capacity (ANC) in accordance with EN 15875:2011
- Automated modal mineralogy through SEM-EDX mapping, and liberation analysis
- Oxygen consumption testing

4.0 RESULTS

4.1 PSD

The results of PSD analysis indicate that the material is dominated by coarse textured particles, on average:

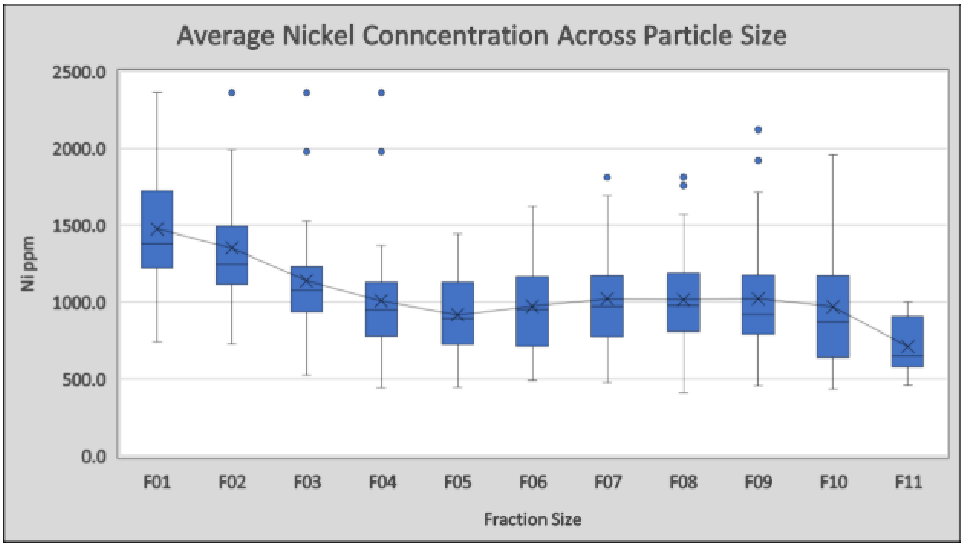
- 60% of the mass is dominated by >22mm size fraction
- 25% of the mass is dominated by 2.3mm-22mm size fraction
- <15% of the mass is <2.3mm size fraction

The results indicate that as a result of mining process (blasting/excavation/placement), overall fragmentation results in a relatively low level of fines being produced.

4.2 Nickel content

Nickel is present in the deposit in both silicate and sulfide phase, detailed SEM microprobe analysis indicates that the nickel is found predominately as pentlandite with ~300ppm being found in the silicate phase (mainly within olivine).

Figure 1 shows results for nickel content by grain size as a box and whisker plot, it is clear that nickel concentrations are lowest in the largest particle size F11 (>40mm) and highest in the smaller grain sizes F01-F03 (<0.25mm). 270 samples were assessed therefore the data set is large enough to demonstrate that there is a consistent preferential concentration of nickel into the fine fractions, and that the >40mm fraction has significantly lower nickel content. As nickel concentrations are significantly higher than 300ppm (representing underlying silicate content) the “upgrading” noted represents increased pentlandite content, which has been confirmed from microprobe analysis (Pearce et al 2019). Overall this means the waste can be characterised as having a small fraction of finer textured higher grade nickel material (<0.25mm), a larger fraction of coarser textured moderate grade nickel material (>0.25mm-40mm), and a significant fraction of very coarse textured low grade nickel material (>40mm).



Particle size referencing system	
Fraction ID	Particle Size
F01	<0.063mm
F02	0.125-0.063mm
F03	0.25-0125mm
F04	0.5-0.25mm
F05	1mm-0.5mm
F06	2-1mm
F07	4-2mm
F08	10-4mm
F09	22-10mm
F10	40-22mm
F11	>40mm

Fig. 1. **Nickel content by grain size (Anderson 2019)**

Figure 2 shows the results of sulphur analysis by grain size, it is clear that compared with nickel there is not as strong “upgrading” by particle size. The majority of the sulphur is present as the iron sulphide pyrrhotite in the material which indicates that although the nickel sulphide pentlandite is found preferentially in the fines, this relationship does not hold for iron sulphides.

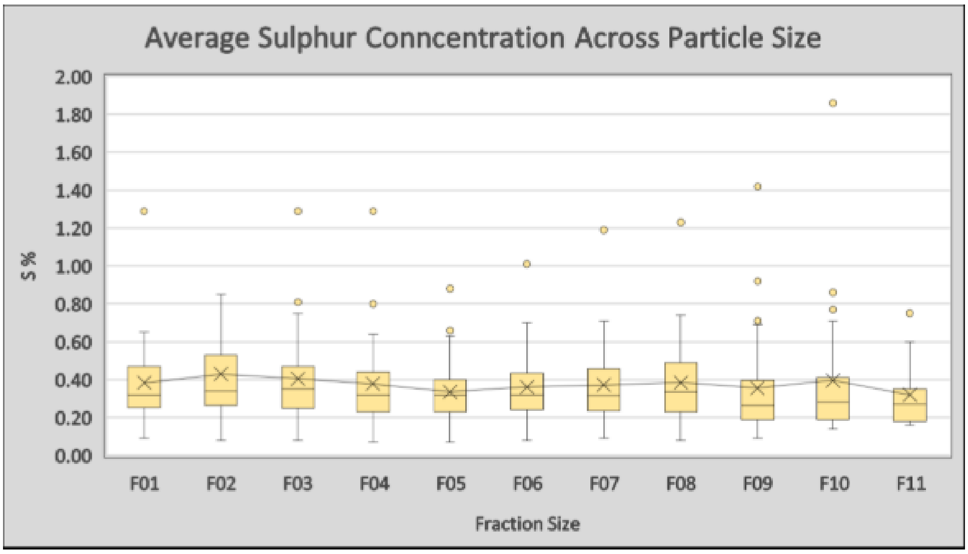


Fig. 2. **Sulphur content by grain size (Anderson 2019)**

4.3 Comparison of as mined waste vs block model

Due to the differences in nickel grade noted between particles sizes in the waste rock analysis, a comparison was made to compare the results to the waste block model within the current mining model. Figure 3 shows the results from nickel and sulphur analysis from the life of mine waste block model (BM) where n>100,000 samples, and waste rock storage facility sampling (WRD) where n=30 and material sampled was <22mm waste fraction. Materials were recovered from a sonic drilling program into constructed waste rock storage facility.

The data in Figure 3 clearly shows that concentrations (and distribution) of nickel in the as placed waste (<22mm fraction) are higher than the block model estimates. This data is noted to correlate with the smaller data set shown in Figure 1 which indicated that fragmentation is resulting in concentration of nickel sulphides within the finer fractions as result of mining. It is noted that the number of samples in the waste rock sampling are significantly lower than the block model thus indicating the potential for bias in the data set. To resolve the potential for bias of data an assessment of sulphur grade was made in the samples with the data shown in Figure 4. The sulphur data indicates that there is less variability in the result, and less evidence for “upgrading” in the finer fraction which matches the observations noted in Figure 2. As such it is concluded that the increase in nickel noted in Figure 3 is not likely an artefact of a bias but is more likely to be reflective of a real difference in nickel sulphide content (pentlandite) as indicated by the fragmentation analysis shown in Figure 1. The data clearly indicates that a grade weighted approach to determination of nickel sulfide content is likely to significantly underestimate the true concentration of nickel within the more reactive finer fraction of waste rock.

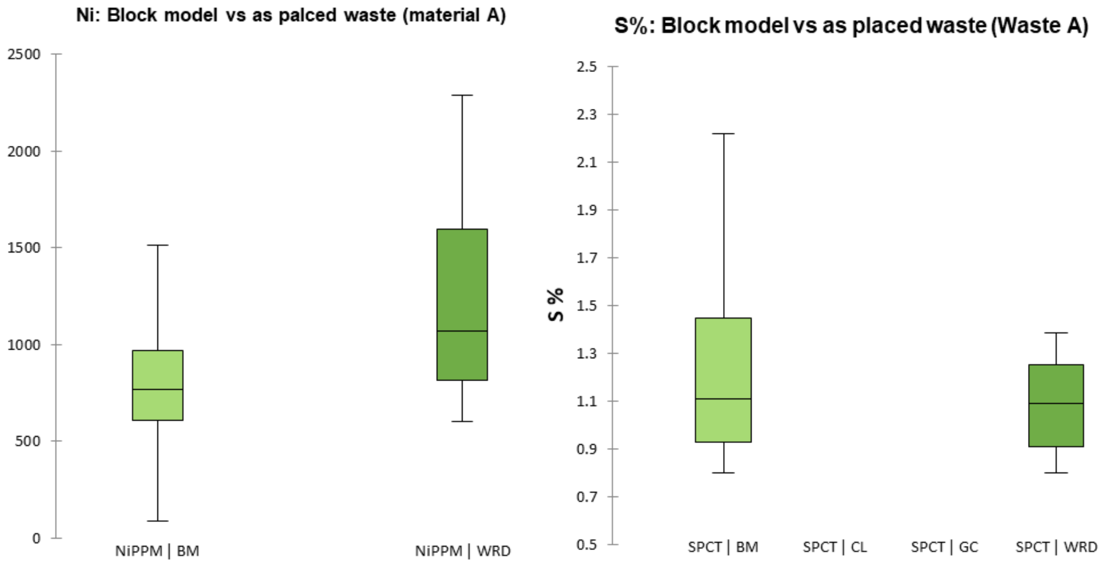


Fig. 3. **Block mode (BM)I data vs waste rock (WR) data (<22mm fraction)**

4.4 Carbon and Sulphur analysis

Figure 4 shows the result for one sample selected for detailed carbon and sulphur analysis. Previous assessment has indicated that the majority of carbon is present as carbonate (Pearce et all 2019) as such carbon content is a good proxy for carbonate content. It is clear that the carbonates have a strong association with particle size that is even more pronounced than the nickel sulphide distribution. A critical observation from the distribution is that the relative concentration of carbonates to sulphide content increases significantly with decreasing grain size. This means that from an acid base accounting perspective the net acid producing potential (NAPP) shows significant variability with finer grain sizes having strongly negative acid forming potential. Given that the finer fraction is generally accepted as being more reactive the finding that carbonate content is significantly higher is likely highly relevant from the perspective of consideration of long term seepage water chemistry. This is because significantly greater buffering is provided than would be indicated from grade averaged data from drill core assay/block modelling data. As coarser fractions are likely to have significantly lower sulphide oxidation rates the net impact on acid base accounting of the carbonate distribution is likely to be significant. Results from oxygen consumption tests confirm this as rates were determined as follows:

- <2.3mm = 10kg/H_2SO_4/t/yr
- 2.3-22mm = 0.6 kg/H_2SO_4/t/yr

Taking the sulfide distribution by grain size and by mass distribution, sulphide oxidation rates by grain size, and carbonate distribution by mass and concentration by grain size into account this means that the acid base accounting profile of the material likely to be very different to that predicted from grade weighted block modelling. There are also obvious implications for predictive modelling that is carried out on the basis of grade weighted data.

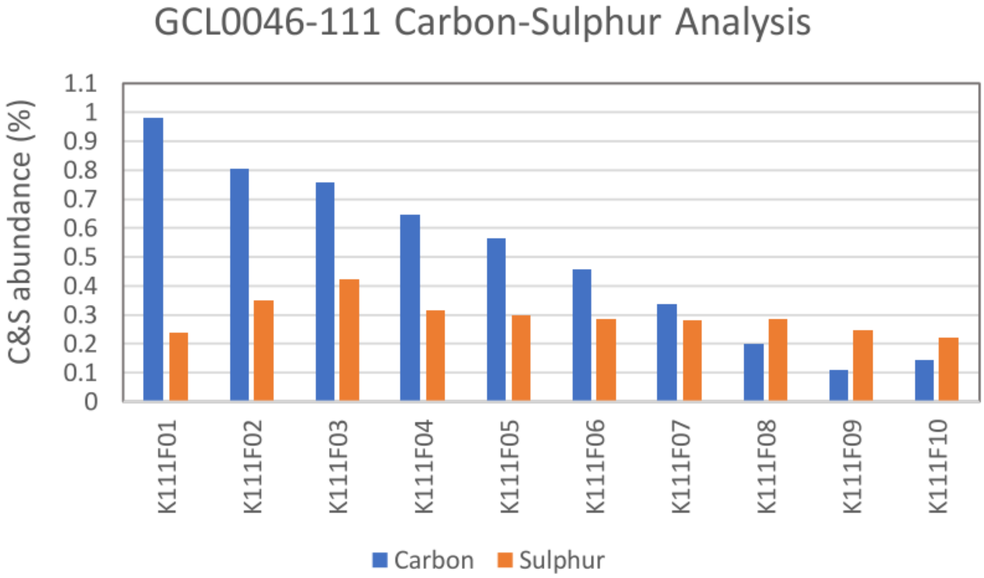


Fig. 4. **Carbon and Sulphur analysis by particle size (Anderson 2019)**

Figure 5 shows the results of acid base accounting data determined from sulphur and carbon data plotted as a function of grain size. It is apparent that there is huge variability in acid base accounting classification values between grain sizes, in general the finer the size fraction the more highly NAF the sample. The data clearly shows that a grade weighted approach to acid base accounting likely carries a very high degree of error when the as mined waste material is considered by particle size.

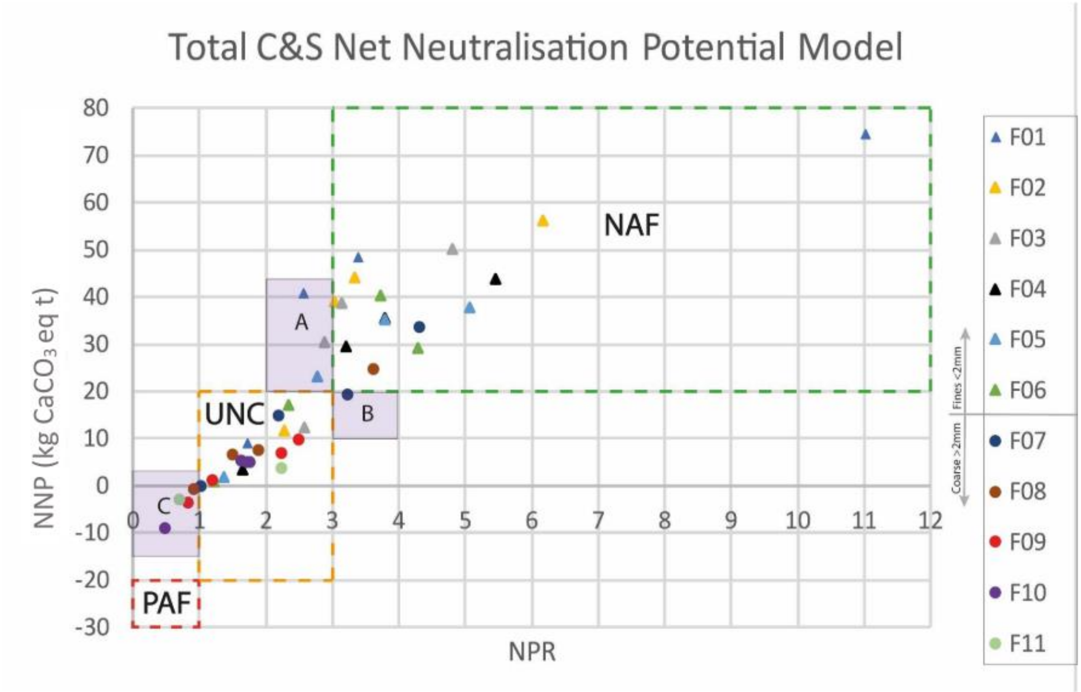


Fig. 5. **Acid base accounting by particle size (Anderson 2019)**

5.0 KEY FINDINGS

The use of grade weighted average block models to assess waste properties and generate waste schedules has been increasingly used across industry over recent times and represents an important step forward for waste management planning, AMD risk reduction and project cost optimization. However this research demonstrates that the approach should be viewed with caution. Classifying materials based on bulk grade weighted averages without assessing the actual properties of the as mined waste product may result in both underestimation, or overestimation of potential AMD risks due to effects of grain size fraction on geochemical properties. Fragmentation analysis has been identified as a potential means to assess the relative change to AMD risk profile of the as mined waste.

The results indicate that preferential concentration of metal sulphides into finer fractions occurs as a result of fragmentation (from blasting/mining). These “enriched” finer particle sizes may be in some cases even be considered “ore” because of the significant upgrading in metal suphide content and could represent a potential resource for recovery. The implication of this study is that in some cases not insignificant quantities of ore grade material is being discarded into waste facilities. Further assessment of the geochemical properties of this finer fraction indicates that this fraction represents the most significant component of the overall risks related to AMD and thus long-term environmental liability. As such a dual benefit can be identified in separating this material into a separate waste stream. This would both remove the high-risk AMD source from the main waste stream (lowering both risks and costs of managing the bulk waste stream) and also presents an opportunity to direct this material to processing to recover metals and generate revenue from a “waste” product.

The study also highlights how the fragmentation process can significantly impact consideration of acid base accounting carried out on grade weighted average values, as carbonates and sulphides may have a significantly different fragmentation profile. In this case carbonates are concentrated in the more reactive fines fraction which likely reduces the risk of acidity production. However this may not be representative of all sites and if the reverse pattern was true then acid production risks would increase significantly.

Our study provides evidence that the application of established fragmentation-based technology and processes, currently used to for develop mining plans for ore zones, to the development of the mining plan for waste zones, provides many opportunities to significantly reduce environmental risk and long-term liabilities of mine waste, reduce operational costs, and improve sustainability metrics of mining operations.

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DEVELOPMENT OF LEADING PRACTICE WASTE GRADE CONTROL AMD CLASSIFICATION METHODS BASED ON DEPOSIT SPECIFIC MINERALISATION CHARACTERISATION AND MODELLING

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ABSTRACT

Barani and Ramba Joring are deposits located at the North Sumatra Martabe gold mine. Waste materials produced from the deposits are stored in an integrated waste storage facility (IWSF). The mine is an epithermal deposit of a high sulfidation system, but due to a very significant change in hydrothermal solution in all deposits, there are several types of mineralisation that are controlled by structure and lithology. AMD management commenced with acid base accounting (ABA) geochemical analysis system conducted for both deposits. The program has since been expanded to include implementation of a detailed waste grade control drilling and reconciliation program fully integrated into waste scheduling and mine planning operations, and is considered to be an example of leading practice in this area.

The Barani pit is dominated by quartz veins and is classified as low sulfidation system, it was analysed using the ABA method which showed that 75% of material has a total sulfur content <0.15% indicating a low risk of AMD. However, the presence of low level acid generating sulfate minerals, and limited carbonate content has identified that ABA is not a good guide for AMD classification and modelling. Detailed grade control drilling and reconciliation utilising the paste pH and ANC tests methods along with particle size based assessment has been implemented to optimise operational AMD control.

Ramba Joring is dominated by vuggy silica consisting of mineralisation associated with silica-alunite and massive-vuggy silica alteration zones. The deposit has a higher sulfur grade than Barani (average grade of 1%), however detailed testing using CRS and mineralogical analysis identified the abundance of natroalunite to interfere in sulfide sulfur estimates resulting in the ABA method to significantly overestimate AMD risk. Validation using kinetic testing demonstrated the NAG test to be a suitable method to optimise operational AMD control when implemented into grade control drilling.

1.0 INTRODUCTION

The process of characterising waste rock and incorporating classification systems into mine models such as geological block models and resource and reserve models for the purposes of mine planning has evolved significantly over the last decade. This has come about both from increased focus on mine waste characterisation but also because of the significant increase in computing power and sophistication of software accessible now available to carry out waste block modelling (Pearce 2012). Although this progress is undeniably a positive step towards improving waste management, the process of estimation through modelling prior to mining activities can only be considered a front end study. When it comes to ore extraction and mine planning and operational management, it is well established that the front end modelling of ore reserves is subject to significant limitations on accuracy. The “accuracy” of reserve models are inherently deposit specific and depend on many factors such as the extent of drilling carried out, resolution of models (block size), the complexity of the ore body etc. As such it is standard practice that during operations a process of model validation is likely to be required, which for the most part is completed using programs of grade control drilling and modelling. This exercise is typically carried out both to increase the density of sampling within the deposit being mined, improve the resolution of modelling (block size), and to allow reconciliation against the reserve model. The results of validation are then used to determine if adjustments need to be made to estimates made from the reserve model with regards to mine planning and ore/waste management plans. The value of this process for mine planning is clear for management or ore extraction, however the adoption of these processes as part of the management and extraction of waste rock is less commonly implemented to the same degree of rigour.

This paper outlines a case study where a very comprehensive waste grade control drilling, modelling and reconciliation program has been developed for waste rock management under the general principal that waste should be mined in the same way as ore. The study is presented as an example of “leading practice” for the practical implementation and integration of the process into a modern mine planning environment.

2.0 SITE BACKGROUND AND CONTEXT

The Martabe gold and silver mine is situated in northern Sumatra and comprises several deposits in steep terrain that are required to be developed in the optimal sequence for the best possible Net Present Value (NPV) return on the project. In addition, the waste from the excavations is a by-product to be scheduled and used for construction of the tailings storage facility (TSF). These plans need to be aligned to ensure the tailings can be contained relative to the production rate (Grohs and Pearce 2019). The TSF embankment construction includes potentially acid forming (PAF) waste that needs to be progressively sealed and rehabilitated to meet the closure requirements of the future.

The mine is situated approximately 3 kilometres north of the township of Batangtoru in a seismically active zone between the off-shore subduction zone and the trans Sumatran fault. The mining operation currently includes three open cut pits with a fourth in development stage, an integrated TSF and dual purpose valley-fill type waste rock storage facility (WRSF) and TSF embankment. Mine waste is used in construction of the WRSF / TSF embankment, including PAF waste rock, which needs to be scheduled for optimal use in construction activities in a manner that mitigates future acidic and metalliferous drainage (AMD) risks (Pearce et al 2017).

2.1 Mine planning overview

The waste rock varies significantly both in geochemical and physical properties between the pits, and within each pit, presenting challenges for mine planning and execution of an optimal progressive mine closure strategy (Pearce et al 2017, Grohs and Pearce 2019). As such a number of detailed long and medium term practical mine planning and management practices have been developed at the site to guide operations.

The long term planning method requires consideration of waste delivery from existing and future pits to ensure that the progressive closure strategy is sustainable over life of mine operations. This requires that LOM planning considers pit optimisation in terms of mining for waste delivery as well as ore.

Short term planning practices include execution of a detailed program of waste grade control drilling, sampling, modelling and validation within all mine pits simultaneously to produce an integrated detailed waste grade control model that is reconciled monthly with the LOM reserve waste model. The validated waste grade control model is then used to inform a rolling three month forward waste delivery and placement plan to guide TSF construction (build plan). Placement of waste material at the TSF is then subject to detailed validation testing to confirm placement is in accordance with the material placement specification and sequencing within the embankment.

2.2 Mine deposit geology and geochemistry

The Martabe site is characterised as an epithermal deposition (e.g. Foley et al 1987) of a high sulfide system, which is characterized by the presence of leaching or sulfuric acid leaching and interaction with the wall rocks, shown by the vuggy texture, and occurrence of breccia . The alteration zones in the Martabe area are distinguished into four types, massive silica-vuggy silica at the centre, followed by the advanced argillic dominated by quartz-alunite and quartz-dickite-kaolinite, and then to the outside it is occupied by Argillic (Illite-Smectite) and the latter is a propylitic alteration that consists of chlorite-calcite and trace epidote (Mandradewi et al 2014) This alteration pattern demonstrates the process of progressive neutralisation of the hydrothermal acid solution from the centre towards the outside through interactions with the host rock and groundwater and decreased temperature.

The change of hydrothermal solution is very significant in all deposits in the area, thus causing several types of mineralisation which are usually controlled by structures that can be differentiated based on texture and alteration type that are related to the composition of hydrothermal solutions as mineralisation carriers. The mineralisation in Barani which is located in the southeast is characterised by quartz veins with little vuggy silica, while Ramba Joring is dominated by vuggy silica. Both ore and waste contain sulfide which is high and increases according to the depth. The sulfide is present in rock masses both as dissemination and filling in the cavity/massive vein systems, usually pyrite.

Analysis of mineralogy that has been carried out has identified the primary sulfide pyrite as being the main source of acid generating potential in both Barani and Ramba Joring. In addition to primary sulfides, sulfate minerals are identified which differ between the pits based on differences in mineralogy. In Barani, acid forming secondary sulfates have been identified that include minerals such as jarosite. Large scale kinetic tests have demonstrated the ability of the acid sulfate minerals to rapidly dissolve in the presence of water and release acidity and metals into solution. In Ramba Joring the main sulfate mineral identified is alunite which after large scale kinetic testing has been identified to be less soluble and produces low levels of acidity or metals on contact with water or after weathering. Acid neutralising minerals have been identified to include calcite and ankerite present mainly in argillic alteration type materials, and a large number of clay minerals present include kaolinite, dickite, Illite and smectite depending on the level of alteration (with argillic material having the highest content of clay).

3.0 WASTE CLASSIFICATION AND MODELLING APPROACH IN RESERVE MODEL

The assay database used to construct the reserve models used for mine planning includes tens of thousands of results of analysis from exploration, resource and infill reserve drilling campaigns. This includes standard parameters such as sulfide sulfur using SCIS (sodium carbonate insoluble sulfur) method, total sulfur (Leco), calcium (ICP), and key metals (copper, arsenic, lead by ICP). From these parameters initial waste block models were created using acid base accounting (ABA) approach. The maximum potential acidity (MPA) is derived from wt% SCIS (assumed to be sulfide S), and the acid neutralisation capacity (ANC) based on the wt% Ca (assumed to be calcite). The net acid producing potential (NAPP) is then determined from deducing the ANC value from the MPA value and values coded into the model based on cut off criteria for waste classes.

Although the initial model created in the reserve model based on SCIS and Ca were useful as a general guide to volumes of materials with high/low AMD risk, it was found from detailed assessment that the deposits of Barani and Ramba Joring are complex and differ with respect to key mineralogical aspects that relate to AMD risk assessment. This means that identification of appropriate geochemical testing methods to further characterise the materials, and methods to classify materials within the mining block models has been a key priority for the site operations. Extensive geochemical testing carried out on samples from the drill hole assay database (used to create the waste block model within the reserve model) indicated that the ability to characterise and model the waste materials is impacted because of differences in mineralogy with respect to AMD risk.

- In Ramba Joring it has been found that the direct method of sulfide sulfur analysis using SCIS method is not accurate in estimating sulfide content. The SCIS method involves chemically removing the sulfate sulfur by boiling a sample in sodium carbonate solution and analysing the residue which is interpreted to be sulfide sulfur. In general, most sulfates are readily soluble in sodium carbonate solution, while most sulfides are insoluble in sodium carbonate. However sulfates of alunite ($K_2(Al_2OH)_6(SO_4)_4$) are only partially soluble (e.g. Alpers et al 1989). As such the SCIS method on material containing these minerals will result in erroneously high estimations of sulfide sulfur. Detailed testing using alternative methods of sulfide sulfur analysis such as mineralogical approaches (XRD), alternative sulfide sulfur methods such as chromium reducible sulfur (CRS) and the NAG test indicated that the alunite content was significantly impacting the ability of the SCIS method to determine true sulfide content. Based on results of testing it was determined that the alunite content determined from mineralogical data present in the reserve model (ASD data) could be used to adjust the SCIS value reported in the assay database. However this approach was associated with a high degree of error and so can be considered qualitative in nature, and as such it was concluded that the only reliable means to classify materials from this deposit would be by using a grade control program during mining.
- In Barani the presence of soluble acid generating sulfate minerals was identified through detailed testing using ANC tests where reporting of negative ANC values allowed the identification of the acid salts. Due to the low concentration of these minerals, it was not possible to use ASD data in the drill hole assay database determine the presence of the acid salts in the reserve block model. In addition comparison of sulfide sulfur and total sulfur (present in the drill hole assay database) was also not able to be reconciled with the presence of these minerals due to the presence of non acid forming sulfates (gypsum). As a result it was concluded that the only reliable means to classify materials would be by using a grade control program during mining.

Table 1 highlights key modelling parameters used in the reserve model and identified limitations of using data from drill hole assay database used to form the reserve model:

Table 1. Reserve modelling parameters

Reserve model parameter	Barani	Ramba Joring
Total sulfur	Total sulfur of limited benefit due to poor link with acid sulfate content (once sulfide content deducted)	Total sulfur of limited benefit for AMD classification due to inaccuracy of sulfide sulfur determination due to high alunite content
MPA (derived from SCIS)	Provides accurate estimate of sulfide content and acid forming potential from sulfide oxidation	Sulfide sulfur analysis impacted by alunite content, if used for ABA overestimates acid forming potential
Alteration mineralogy by ASD	Jarosite minerals present at levels too low to detect by ASD	Alunite minerals present at high enough levels to detect and characterise using ASD data. Alunite zone created as wireframe in model based on ASD data.
ANC (calculated from calcium)	Presence of acid salts means estimation of ANC not possible using parameters in drill hole assay database	Where present calcium linked to carbonates so provides accurate estimate of ANC
NAPP (MPA-ANC)	Modelled NAPP does not identify materials with acid sulfate risk	Modelled NAPP has high degree of uncertainty due to impact of alunite on SCIS data

It is important to note that in the case of Ramba Joring mineralogy is able to be modelled in the reserve model only because Analytical Spectral Device (ASD) data using near-infrared spectroscopy has been included in the reserve model dataset. As such zones where waste mineralogy is dominated by alunite can be included as a discrete domain in the reserve model (after wireframe modelling of ASD data has been integrated). This finding therefore also demonstrates the value that ASD data can provide when used as part of waste characterisation and modelling within reserve model as without it modelling the alunite zones would be significantly more difficult. The identification of this mineralogical control factor is key because it presents an opportunity to reclassify materials within the reserve model that using SCIS data alone would be determined as high risk. This has considerable influence on the LOM waste materials delivery plan as the lower risk material has been identified as a critical material for use as part of the outer growth medium profile of the TSF construction. As such identification of this material is critical and may allow this zone to be significantly thicker than would otherwise be possible.

A practical independent validation check of the material classification adopted in the reserve model based on AMD risk has been achieved through a number of studies that include:

- QA/QC analysis using the chromium reducible sulfur method (CRS), XRD and NAGpH testing was completed to provide comparative analysis data to compare sulfide sulfur (SxS) data obtained from the SCIS method. The results indicate that for grades of <3% SxS, where alunite is present >10%, then CRS results are <0.15%, NAGpH >3.6 and NAG acidity <5 kg/t H_2SO_4. Taken together the results indicate that the alunite rich material has very low to negligible sulfide content and has a low potential to release significant acidity.
- Kinetic testing assessment using IBC leach tanks to assess samples of Ramba Joring material over a range of sulfide sulfur grades and alunite contents was initiated to

provide data on drainage chemistry and AMD risk. The results to date indicate that material that was indicated from SCIS data to have sulfide grades of between 0.5-2%, and where alunite content from ASD data was >10% and where NAGpH values of >4 were recorded, has a very low release rate of acidity or mobile metals.

- Oxitop testing indicates that samples of material which reported SxS results of between 0.5-2%, and where alunite content from ASD was >10%, have low oxygen consumption rates <0.5 kg/t/yr O2. This data indicates that reactive sulfides are not present at appreciable levels.

4.0 WASTE CLASSIFICATION AND MODELLING APPROACH IN GRADE CONTROL MODEL

Based on the validation work carried out for the reserve model parameters, practical grade control validation criteria have then been developed that can be demonstrated to both accurately determine AMD risk and are able to be practically implemented into grade control drilling modelling. The practical implementation of AMD parameters into grade control modelling is an important and often overlooked point as in many cases geochemical validation criteria area developed based on geochemical test outputs that are not able to be successfully modelled as part of integrated ore/waste grade control modelling. For example, although NAGpH has been identified as a suitable test to identify lower risk alunite material (where sulfur is present as alunite not sulfides) a pH value is not strictly suitable for estimation modelling purposes as model estimation uses variography to average values between samples but pH being a log value cannot be averaged. Based on assessment of appropriate values for model estimation purposes, NAG acidity and ANC values have been selected for GC model estimation purposes as these inputs are compatible with the integrated ore/waste GC model.

In recognition of the influence of deposit mineralogy over the ability to create accurate waste models in the reserve modelling process, a specific testing schedule tailored to each deposit was determined as part of development of grade control assessment. An overview of the use of typical laboratory geochemical testing methods for grade control in each deposit based on comprehensive validation testing, and field scale kinetic testing is provided in Table 2.

Table 2. Classification testing overview for grade control program

Classification test	Barani	Ramba Joring
Sulfide sulfur	Provides accurate estimate of sulfide content and acidity potential from sulfide oxidation	Provides comparable means to compare against reserve model data
Paste pH	Found to overestimate contact pH compared to kinetic test data	Not used as NAGpH used as main acid forming determinant
Rinse pH	Provides more accurate estimate of pore water pH than paste pH	Not used as NAGpH used as main acid forming determinant
ANC	Reporting of negative ANC values allows estimation of acid salt content	Not used as NAGpH used as main test for classification

NAGpH	Not used in Barani	Provides accurate estimate of overall acid forming potential of material

4.1 Application of ore grade control principals to waste rock management

Due to the varying nature of the deposits and need for immediate placement to final profile in the TSF construction, a waste grade control philosophy has been implemented resulting in waste being defined similarly to ore control through detailed sampling, modelling and classification for optimum construction placement and AMD risk management. The operational waste management practice developed at the site includes detailed grade control drilling which comprises an integrated operational program carried out in both waste and ore zones. Sampling in waste zones for AMD analysis is carried out at 12.5-25m centres and composite samples are taken over 1m depth intervals for laboratory analysis. This results in generation of >1,000 samples per pit, per month, for AMD analysis. The GC waste block model is then constructed using this extensive testing data such that the block size is able to be constructed at a higher resolution (12.5m) than the RM (25-50m).

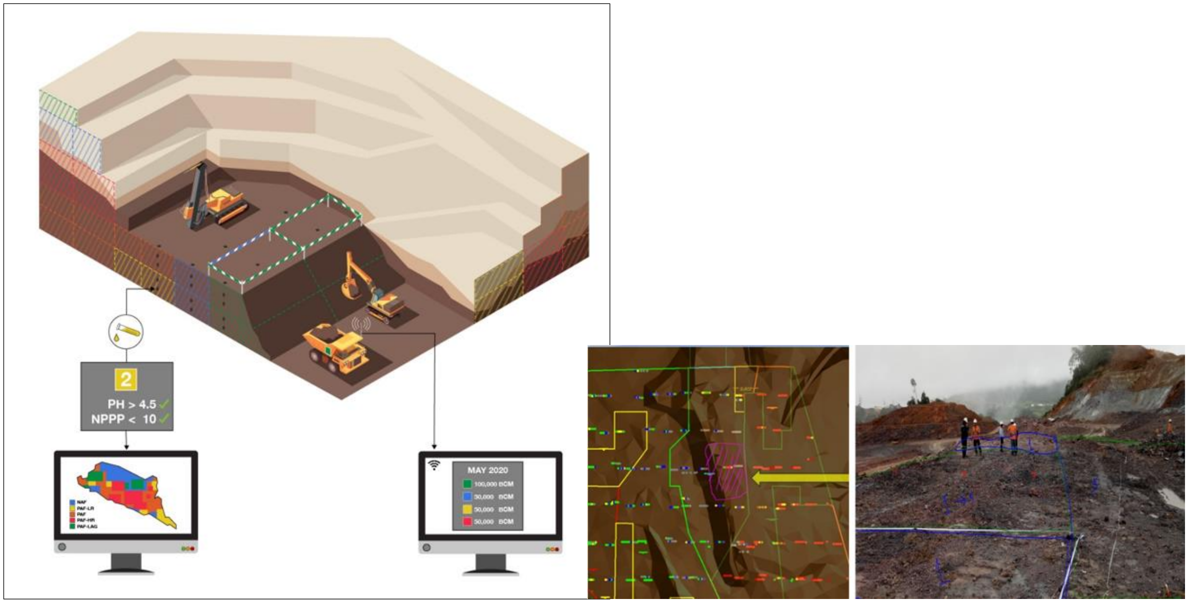

Fig. 1. Grade control assessment concept used as part of short-term planning

Full reconciliation between the waste grade control and reserve waste model is also carried out monthly to provide constant feedback on variance in predicted vs actual waste volumes and quality, and to validate the reserve AMD model. Reconciliation refines the rolling three month waste schedules for placement within the embankment to ensure specific elements of the closure strategy can be realised.

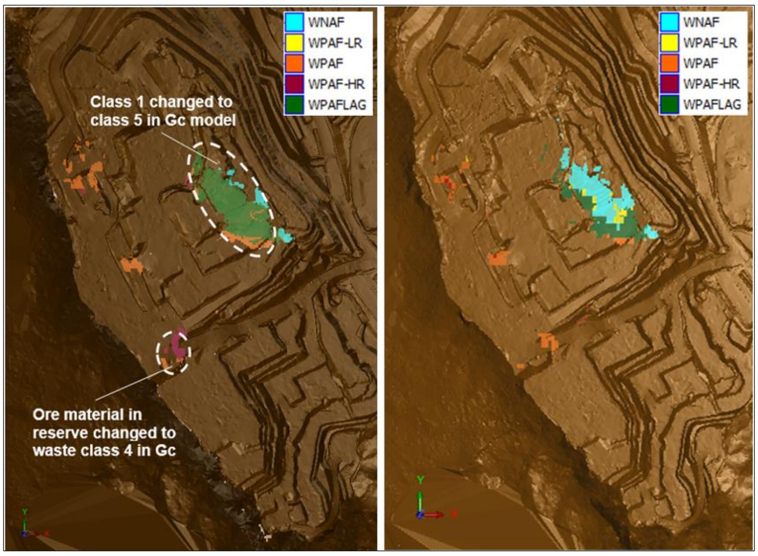

Fig. 2. Conceptual figure showing reconciliation between grade control (LHS) and reserve block models (RHS).

Figure 2 shows a comparative graphic reconciliation between the grade control block model based on ore control RC close spaced drilling on the left and the long term planning Reserve model block model based on exploration diamond drilling and resource development RC drilling on the right. The monthly variance is determined from these comparisons. Note the variations in classification between the reserve model and more detailed grade control model is tracked for further long term planning improvement.

5.0 CONCLUSIONS

The use of integrated front end block modelling that includes both ore and waste zones as part of mine planning has gained widespread recognition in the industry as providing an important tool to be used as part of LOM waste management. In addition the tool has been demonstrated as a key enabler of the optimisation process when it comes to the LOM planning process. However, these models are only as accurate as the data used to compile them, and as this study demonstrates are in many cases impacted by many factors including the resolution of the models and the deposit specific nature of mineralogy (with respect to estimation of AMD risk). With respect to the ore extraction process the uncertainties associated with front end modelling (i.e. resource/reserve models) has long been known, and as such detailed grade control programs are often required to be implemented during operations. This study demonstrates a case study where the practical implementation of an intensive and integrated waste grade control drilling, modelling and reconciliation program has been successfully implemented on an active mine site, at a scale analogous to that carried out for ore zones. When taken in totality the authors consider this program to be a potential example of industry leading practice in the area of waste rock operational management and planning.

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CHARACTERIZATION, MANAGEMENT, AND MITIGATION OF AMD FOR LINEAR INFRASTRUCTURE PROJECTS: RECENT CANADIAN EXPERIENCE

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ABSTRACT

The generation of acid and metalliferous drainages (AMD) is not exclusive to mining activity. The construction of linear infrastructure can produce large quantities of waste rock and produce rock-cut exposures of material with high AMD risk. Past examples of infrastructure construction without adequate characterization and mitigation have produced highly visible and on-going AMD generation with attendant costs of management and mitigation. These examples prompted the initiation, in British Columbia, of a regulatory protocol to require the characterization, prediction, and mitigation of AMD risks. This paper presents a set of case studies of infrastructure AMD programs on infrastructure projects conducted in British Columbia. The projects are at various levels of completion and are of differing levels of complexity with regards to geology, logistics, and engineering. The case studies show that the principles and practices developed on mine sites to deal with AMD are equally valid on linear infrastructure projects.

1. INTRODUCTION

Acid and metalliferous drainage (AMD) can occur in any situation where sulfide-bearing rock is exposed to oxidizing conditions and so is not restricted to mine sites. Highway and other linear infrastructure projects can involve the excavation of large quantities of rock that may have the characteristics leading to AMD conditions with the resulting impact on the receiving environment.

In recent years, Klohn Crippen Berger (KCB) has been engaged in the development and execution of AMD characterization programs for geological materials associated with highway projects in British Columbia (BC). Where necessary, these programs have been followed by the development of material management and AMD mitigation programs (as warranted). This paper summarizes the findings from a selection of these studies and illustrates the validity of the mine-site approach to the infrastructure projects.

1.1 The Instigation: Pennask Summit

Highway 97C was built in the 1980s through the interior mountains of British Columbia. In the course of construction, a zone of pyrite mineralization was exposed in a rock-cut. Since this time, the exposed rock has produced AMD, first noted in 1992 (Morin and Hutt 2003), that ultimately flows to Pennask Creek, a world-class salmon basin. The resulting deterioration prompted the successful prosecution of the predecessor of the BC Ministry of Transport and Infrastructure (BCMOTI) under environmental protection regulations.

1.2 The Regulatory Situation

To prevent similar occurrences as Pennask Summit, the BCMOTI has implemented regulations that require the evaluation of the rock and other geological materials for AMD as part of the design and execution of highway projects. The regulations have evolved through the years with the current guidance being technical circular 04/13 (BCMOTI, 2013). This document defines what is required for an AMD assessment in British Columbia. The technical circular does not dictate an exact procedure but relies on the professional judgement of a qualified person and follows the accepted practices of a mine site AMD assessment.

2. CASE STUDIES

The general characteristics of the projects examined in this paper are presented in **Table 1** with locations shown in **Fig. 1**. The first project is examined in a little more depth that the following project to define the common aspects of the projects.

Table 1. Characteristics of Projects Discussed

Project Name	km	Screening	Detail	Other	Management	Highway Project Status
Hoffman Bluff to Jade Mountain	12	x	x	x	x	Planning Stages
Illecillewaet	2.5	x	x	x	x	Construction Underway
Malahat	4.9	x	x		x	Project Complete
Bruhn Bridge approach	2.0	x				Planning Stages
Highway 14	1.6	x				Ongoing Geotech

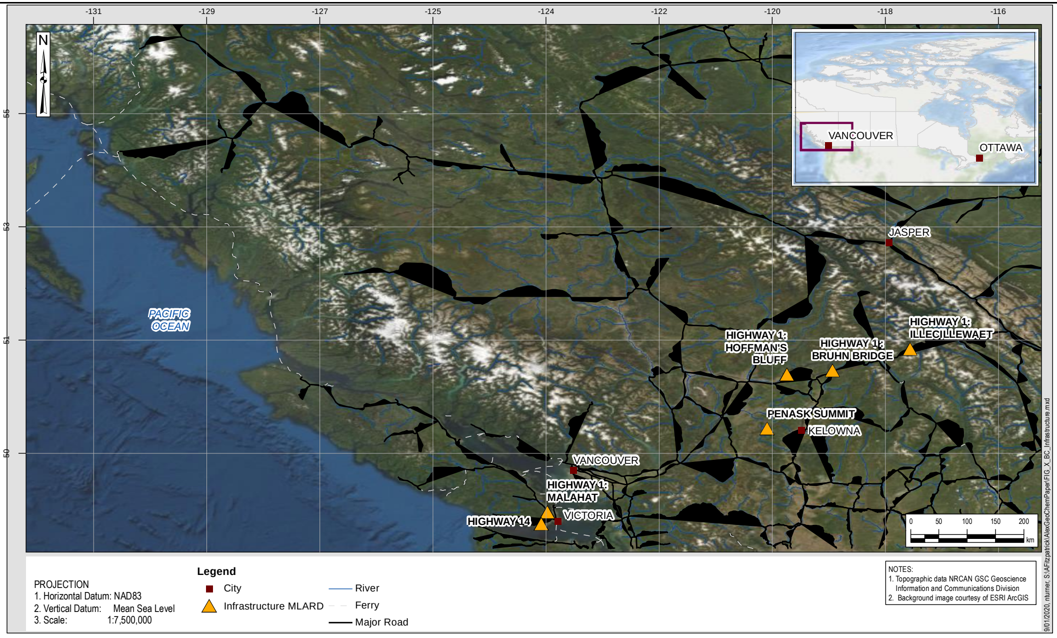

Fig. 1. Project Locations

2.1 Highway 1 Hoffman Bluff to Jade Mountain

The proposed Hoffman Bluff to Jade Mountain project entails 12 km of road widening of Highway 1 and realignment in the interior of BC.

The first step in this (and any) project was the review of available geological and mineral occurrence data. Two occurrences of sulfide mineralization were noted as occurring with 10 km of the project area.

A prior third-party investigation of the area included the collection and characterization of six samples by an acid base accounting (ABA) suite. This program showed three of the samples to have a potentially acid-forming (PAF) character.

2.1.1 Phase 1 Screening Investigation

The KCB screening level characterization program consisted of grab sampling over the project alignment focusing on the area identified most likely to be at risk for AMD by geological unit and where rock is planned to be excavated. These samples were tested by an ABA Suite, whole rock analysis by X-ray fluorescence (XRF), elemental abundance, and X-Ray diffraction (XRD) analysis.

The metal leaching potential of the rocks was investigated by shake flask extraction (SFE) testing on samples with elevated concentrations of cobalt, molybdenum, and/or nickel as compared against crustal means. An elevated concentration is defined as a measured value that is above some multiplier (3x to 5x) of the mean crustal value. The mean value used for each site is based on the concentration dataset that most closely matches the lithological character of the sample or exposed geological units, in this case, a mixture of metamorphosed sedimentary and volcanic rocks.

The testing suite revealed two distinct zones of PAF material including and the presence of pyrite. The PAF conditions are related to the absence of carbonate material rather than especially elevated levels of sulfide-sulfur.

The SFE testing generated leachates that were in excess of freshwater aquatic life characteristics for aluminium and cadmium. The “elevated” elemental concentrations did not produce corresponding elevated leachate concentrations.

2.1.2 Phase 2 Detailed Investigation

The presence of distinct PAF zones required detailed investigation. This entailed the sampling of three diamond drill cores in the PAF zone (drilling was also in support of geotechnical investigations for the site).

The phase 2 samples were tested using both static testing (as per phase 1) and kinetic analytical suites.

87.5% of the samples in these zones as classified as PAF. As was the case for the phase 1 testing, the PAF condition was a result of low neutralizing potential (NP) rather than a high sulfur content.

A subset of samples was assessed through Net Acid Generation (NAG) testing, SFE, Optical Petrography, and XRD. Two samples were selected for humidity cell testing.

The mineralogical investigations revealed the presence of 0.2-2 wt.% pyrite in the tested samples. SFE testing revealed leachate extractions exceeding criteria for one or more of pH, sulfate, aluminium, manganese, and zinc and the NAG leachate showed exceedances of pH, sulfate, aluminium, cadmium, chromium, copper, iron, lead, manganese, silver and zinc.

The humidity cell (operated for 24 weeks) leachates showed exceedances for many parameters. Common and persistent exceedances for the two cells that became acidic were for pH, aluminum, zinc, and cadmium.

2.1.3 Other Investigations and Material Management Plans

A water quality model (WQM) was developed for the receiving environment downstream of the cut face of the PAF zone. This suggested that that the cut face of the PAF zone would not generate a load that would cause downstream water quality criteria (WQC) exceedances.

The developed material management plan for the project presented two options:

- Blending of PAF and not potentially acid-forming (N-PAF) excavated rock for other sources to achieve an acceptable blended neutralizing potential ratio (NPR); and
- Isolation of PAF rock to reduce contact with water.

Both options are based on geochemical properties and the cut/fill quantities of the project.

The blending calculation was a sensitivity assessment and established that a maximum mixing ratio of 3 in order could achieve an NPR of 4 or greater

The second option is to isolate the PAF material. It was proposed to isolate the material by placing the material in the road prism and away from drainage surfaces, with defined minimum setbacks to limit the interaction with water and/or oxygen. An example of a typical cross-section is illustrated in **Fig. 2**:

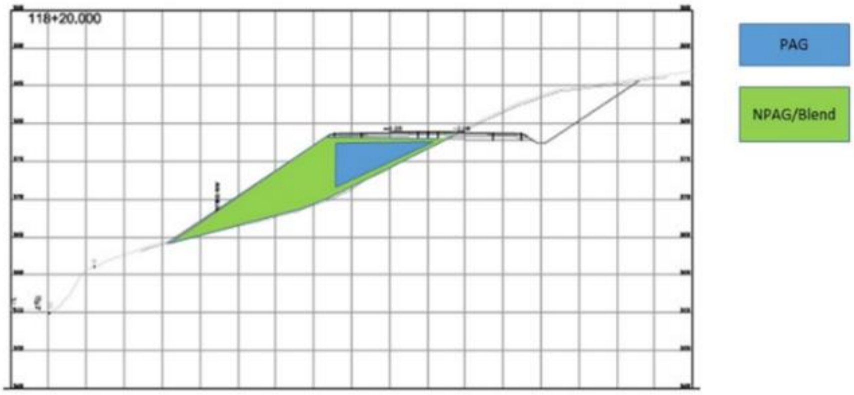

Fig. 2 Example of PAF Isolation

This project remains in the planning stage, but the AMD material management concept is been carried forward in the current project plan.

2.2 Highway 1: Illecillewaet 4-Laning Project

The Illecillewaet project began with a review of an AMD investigation by a third party and then proceeded to a detailed investigation involving a field investigation including a drilling and sampling program. The results of both investigations provided input terms to a water balance model which in turn formed part of the basis for the material management plan.

The site itself has complex geology which includes five lithological units (phyllites of variable composition) and multiple phases of structural deformation. Near the project are multiple lead-zinc mineral prospects.

2.2.1 Review of previous investigations

The third-party investigation of the Illecillewaet project alignment was completed opportunistically as part of a geotechnical investigation, so the sampling coverage had a different set of priorities than what was required for the final project alignment. The third-party investigations followed the same two-phase approach outlined in the preceding section. The second phase of investigation included humidity cell testing, surface water quality testing and a simple dilution model to forecast the effect of rock cuts and excavated material on downstream water quality.

The investigation revealed the presence of zones of PAF risk material and zones of elevated (>5x mean shale abundance) of barium, cadmium, chromium, cobalt, copper, and silver. The shake flask extraction testing revealed leachates with aluminium, cadmium, selenium and zinc concentrations in excess of environmental water quality criteria.

The humidity cells (operated to 10 weeks) all remained at near-neutral conditions. HC leachates exceeded WQ criteria for aluminium, cadmium, selenium, and zinc.

2.2.2 KCB Investigations

Gaps in the third-party investigation (due to the nature of the sampling) lead to recommendations for further investigations. The investigations were additional site investigation, sampling, and analysis, development of a WQM for the receiving environment and additional surface water quality sampling.

The site investigation along the existing road cuts identified distinct zones of pyrite within specific geological units and the presence of two sphalerite bearing veins (**Fig. 3**b). A systematic surface sampling at set intervals along the outcrops was made. Sampling from drill core from a geotechnical program was also undertaken. Water quality sampling at key locations was also undertaken by the client.

The testing of the samples (by the standard analytical suite including select SFE, XRD testing) revealed samples to mostly be in the Not-Potentially Acid Forming category due to sufficient NP being present to neutralise the acidity that may arise from sulfide oxidation. Concentrations of sulfur ranged from >0.01% to 2.25% with a mean of 0.59%. There was no appreciable association of sulfide with lithology. There was also no appreciable association of NP to lithology.

Linear sampling of the existing outcrop allowed elemental concentration profiles to be produced (**Fig. 3**a). These clearly show the discrete nature of the elevated concentrations along quartz veins. The higher element contents in samples were also accompanied by elevated SFE leachate concentrations. The water quality samples taken in the field near to these veins also had elevated metal concentrations.

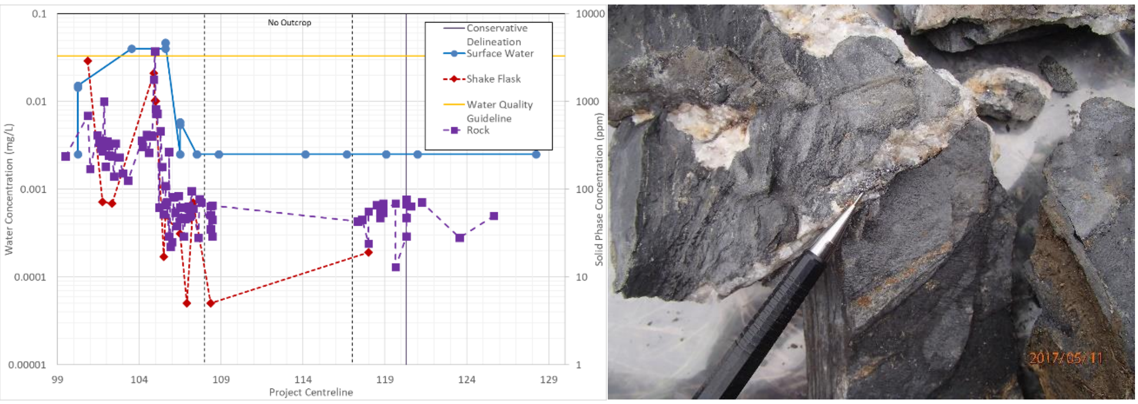

Fig. 3 **Project Chainage Distribution of Composite Zinc Concentrations (a) and Sphalerite Bearing Quartz Vein**

The water quality model developed for this project was significantly more complex than that of the Hoffman Bluff project as it involved multiple sources, catchments, and AMD zones. A schematic of this is shown in Fig. 4. The model was developed earlier than the field investigation and was primarily populated with the data from the 3rd party investigation.

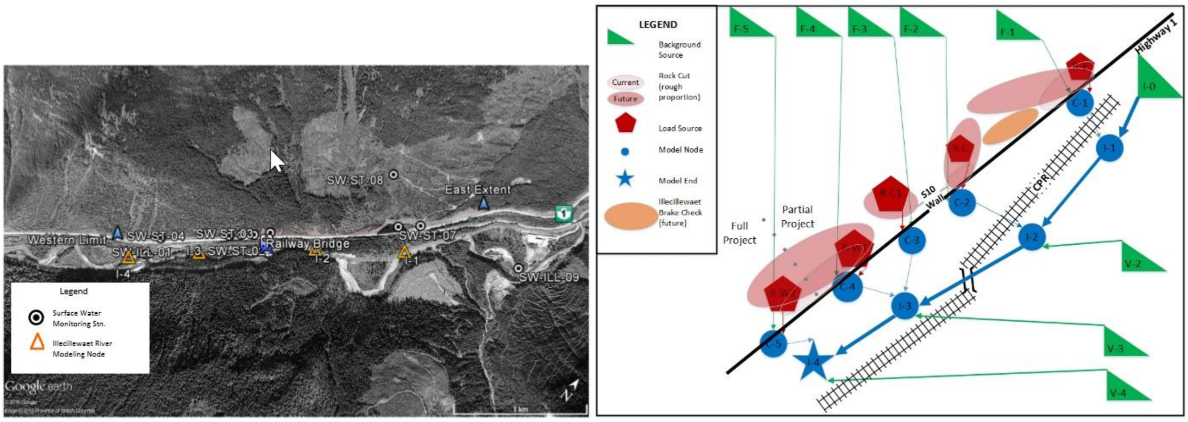

Fig. 4 Illecillewaet Site and Relationship to WQM (a) WQM Schematic (b)

The WQM was run with variable precipitation and flow regimes to assess the potential for water quality exceedances. Elements with persistent exceedances at nodes near sources were sulfate, cadmium, and selenium. All three exceedances were traceable to cadmium- and selenium-bearing sphalerite reacting under neutral conditions.

2.2.3 Material Management Plan

The results of geochemical characterisation, the material balance for the site and the water balance/water quality model defined and constrained the AMD material management plan. The investigations indicated that the presence of lead-zinc sulfide mineralization and the consequent risk of neutral leaching of cadmium and selenium as a key risk to be accounted for in the material management plan.

The management plan took the same approach as at the Hoffman Bluff project where management of AMD risk waste rock is managed through isolation or blending. The isolation case was a preferred option and specific locations for isolation in road fill prisms were identified and quantified. The designated locations were found to have sufficient capacity to house the identified high-risk material. There was also a significant surplus of space that could provide for the isolation of additional excavated material under a conservative definition of AMD material.

Sufficient low reactivity material was present for blending to be considered but the challenges associated with staging and stockpiling such that sufficient stocks made meant that the encapsulation option was preferable for practical and risk-mitigation reasons.

There is little practical mitigation available for the load of neutral leaching metals that might be generated from increased rock-cut exposure but the existing water quality near the sphalerite bearing veins is already exceeding WQ. The model forecasts that dilution capacity in the Illecillewaet River would reduce concentrations in the river to below WQC. A water quality sampling program was proposed to confirm this.

This project began construction in 2019 with the tender documents including the recommendations for the AMD material management and monitoring as outlined from the findings of the investigation outlined above. The exact implementation of the program is the responsibility of the construction contractors.

2.3 Highway 1: Malahat

The Malahat project is discussed to illustrate the logistical difficulties that can occur in the characterization and management of PAF wastes in the context of transportation construction. The details of this project are excluded for brevity. The project alignment had been investigated at a screening level two years prior to construction. Zones of potential

PAF material in the project alignment were identified and a recommendation for future detail investigations was made.

With the initiation of construction planning, a combined management and detailed investigation plan was required. A key component of this was the requirement for a rapid analytical turn-around in order to be able to classify excavated material. There were also designated zones of disposal for the PAF material. The nature of the highway (it is the only feasible transport route from Northern and Central Vancouver Island to Victoria) is such that there was a priority on the final placement of excavated rock.

The execution plan proposed that rock to be blasted should be sampled prior to the blasting. However, the blasting schedule was in a state of constant change so that most sampling was conducted after blasting. The analytical turn-around times then became a bottleneck for the general management of excavated project material. In one instance, material that turned out to be PAF (due to high sulfide) was placed in a non-designated location since it required final placement earlier than analytical results being available. As it turned out, this material was placed in a zone that was above the expected water line and was mixed with other material with high NP values so that any AMD risk was minimized.

This project illustrates that the recognition of AMD as an issue is not universal as in the mining industry and that its importance must be reinforced to site personnel at all levels.

2.4 Highway 1: Bruhn Bridge Approaches, Highway 14: Connie Road to Glinz Lake Road

The Bruhn Bridge Approach and Highway 14 projects represent AMD characterization programs that did not need to proceed beyond a screening phase.

The two projects were sampled over their project alignments by piggybacking on geotechnical investigation programs based on distance as well as geological variability.

These samples were tested by an ABA suite, whole rock analysis, elemental analysis. The Bruhn Bridge project samples were also tested by SFE and Net Acid Generation testing. This was not done on the Highway 14 samples since the geology (tholeiitic basalt) suggested that minimal sulfur would be present,

The testing on both projects showed the material along to be N-PAF. For Bruhn Bridge, this was due to abundant NP and in the case of Highway 14 it was due to the absence/low quantity of sulfur.

At Highway 14 no elevated levels of elements were found except for elevated gold and a single instance of elevated cadmium.

The lack of identified PAF material, the absence of elevated elemental contents, and the absence of significant leachate concentrations (Bruhn Bridge) negated any need for further investigation nor was a PAF material management plan needed.

The Bruhn Bridge project remains at the planning stage and the Highway 14 project investigation is ongoing for geotechnical aspects.

3. CONCLUSIONS

The characterization programs and the developed material management plan follow the general pattern of AMD investigation and management plans that are undertaken at mine sites. The nature of infrastructure construction is such that additional challenges of scheduling and logistics are imposed. The acceptance of AMD as an issue in the highway construction industry is not universal as it is the mining industry and the requirement for knowledge transfer must also be considered in these projects.

An early linkage between geotechnical and geochemical investigations is also beneficial so that sampling programs can be optimized for both geotechnical and geochemical purposes.

The linear infrastructure projects discussed are all Canadian and have specific geological conditions, but the general processes of investigation have an application to future Australian linear infrastructure projects. This includes specific projects such as the Inland Rail project or more generally projects crossing regions of acid sulfate soils that commonly occur in Australia. The projects discussed have also been along existing corridors so there was not an opportunity for AMD avoidance, new project alignments may have opportunities for AMD avoidance.

4. ACKNOWLEDGMENTS

The contributions of past and present employees of KCB, employees of contractors and clients and of the BC Ministry of Transport and Infrastructure to the projects discussed in gratefully acknowledged.

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IDENTIFICATION OF GEOCHEMICAL PROCESSES CONTROLLING METAL MOBILITY IN A NATURAL LAKE IMPACTED BY MINE WASTE AND AMD FROM ANCESTRAL MINING IN HUANCAVELICA, PERU

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ABSTRACT

Huancavelica district was one of the world's district producer of mercury in the ancestral mining in Peru. The extraction of this element from cinnabar and associated sulphurous minerals caused the accumulation of mine waste and generation of Acid Mine Drainage (AMD) which in the surrounding area of a natural lake and impacted the ecosystem with metal release contamination.

The present paper has the objective of identifying the geochemical processes governing the mobility of toxic metals in the natural lake impacted by ancestral mining. For this reason, the monitoring program included, 10 lake water samples inform the surface and variable depths; one groundwater sample located in a wetland upstream of the lake; three surface water samples from downstream locations; three composed sediment samples from the lake bottom and three composed mine waste samples located in the surrounding piles. Water samples were analyzed for pH, major cations, anions, and trace elements, having as a result: acid pH(~3), high concentration of Al (1-5 mg/L), Cd (0.01-0.1 mg/L), Mn (0.2-1.6 mg/L), Pb (1-8 mg/L), Zn (1-5 mg/L) and Hg (0.0002 mg/L). Additionally, mine waste and sediment samples were analyzed for trace elements, acid base accounting test (ABA) and synthetic precipitation leaching procedure (SPLP) to predict potential mobility of trace elements into the groundwater and lake, having as a result that both materials generated AMD.

Research results suggest the pH in the lake layer surface is higher than the deepest layer due to oxygen availability. The geochemical analysis of metals cycle showed that the leaching of metals occurs from mine waste and sediments to the groundwater and lake water. This metals release is amplified for the acid pH environment and O2 availability. Finally, due to the carbonated geology in the downstream riverbed, the pH reached values of near 6 with the consequent decrease of total metals and secondary minerals precipitation.

1.0 INTRODUCTION

Mining activities can generate large volumes of waste rock that are commonly stored in large unsaturated piles on the land surface at the mine site potentially impacting surrounding environments (Amos et al, 2014; Candeias et al., 2015; Fetter et al., 2017). The plluted seepage from waste rock dumps can drain directly into the local runoff or can be dispersed longer distances into rivers via rainfall and hydrological processes (Li et al, 2019, Oliveira et al., 2018; Sanchez-Pena et al., 2018).

In this project, samples of mine waste, sediments, and water from the surroundings of an ancestral mining site in southern Peru were analyzed to understand the geochemical processes controlling the mobility of elements in a natural lake. This paper presents the geochemical characterization of the samples, the conceptual model as a summary of the results and finally the geochemical modeling to understand the mineral dissolution and precipitation.

2.0 DESCRIPTION OF THE STUDY AREA

2.1 Historic and geologic settings

Huancavelica is located 450 kilometers southeast of Lima, it has been known as one of the world's most abundant sources of mercury since the Spaniards gained control of the Peruvian mines around the 1500s. Since then, an estimated 36,000 tons of mercury was mined from the region's cinnabar ore until the mines were closed in 1974 due to diminishing production (Cooke, 2009).

The outcrops of the area include sedimentary rocks of the Chúlec-Pariatambo and Churumayo formations, and volcanic-sedimentary of the Tantará Formation (Romero and Torres, 2003). Mineralization occurs in a vetiform structure in strata of limestone and limestone conglomerates. The vein contains silver sulfosal, copper and iron oxides (goethite), the bargain is mainly made up of white and gray tabular barite, and white leaf shaped barite (INGEMMET, 2011).

2.2 Hydrology and drainage sources

The climate of Huancavelica is varied, cold, glacial and with great atmosphere dryness in the high mountain. At higher altitude the climate is cold, very dry, with strong variations in temperature between day and night, frequency of frost, and presence of ice and hail.

The average annual temperature of this zone is 9.2 °C, the absolute maximum being 20.8 °C in the month of October. The Precipitation in the area reaches up to about 750 mm per year, especially in rainy season (November to March months).

2.3 Mine waste distribution and drainage

Mine waste dump at the site consists of significant amounts of waste rock (≈200 000 Tn). The superficial material was homogenous in grain size and composition.

The total area of mine site is around 8,000 m2. The maximum height of the dump is less than 20 m. Cut back erosion along exposed unoxidized mine waste and an oxidized upper zone of the mine waste was generally 20– 30 cm deep. A small arm of mine waste extending to the surrounding wetlands and lake, presumably related to cycles of mine wastes discharge. The surface of the mine waste dump has small gullies eroded by ephemeral flow from seeps and other surface water.

3.0 METHODOLOGY

Surface water, groundwater, lake water, mine waste and sediment samples were collected for this study (Table 1 and Fig. 1). Water sampling included sampling of diverse drainage environments around the site the lake water (different depths), groundwater from wetland area, and surface water including the stream lake discharge and downstream.

Mine-waste samples included bulk composite surface samples of oxidized and unoxidized mine waste at depth, and composite samples of lakeside material.

Sediment samples were taken from the lake bottom.

1. Table 1. Location of water, mine waste and sediment samples

Type Sample	Sampling ID	UTM Coordinates (WGS 84)		Description
		East (m)	North (m)	
Lake water	LK-01-SUP	8580047	503599	0.5 m depth
	LK-01-MED			3 m depth
	LK-01-INF			6.5 m depth
	LK-02-SUP	8580100	503581	0.5 m depth
	LK-02-TCN			3.5 m depth
	LK-02-INF			8 m depth
	LK-03-SUP	8580220	503528	0.5 m depth
	LK-03-INF			4 m depth
	LK-04-SUP	8580268	503501	0.5 m depth
	LK-04-INF			1.3 m depth
Groundwater	BF-SB-06	8579969	503690	Wetland upstream lake
Surface water	SW-SB-01	8580322	503421	Discharge stream of lake
	SW-SB-09	8581031	503212	Downstream of lake
Mine Waste	GQ-SB-07	8580226	503650	Lakeside material
	GQ-SB-08	8580249	503668	
	GQ-SB-09	8580181	503612	
Sediment	SED-DB-01	8580173	503603	1.0 m depth
	SED-DB-02	8580171	503594	1.8 m depth
	SED-DB-03	8580165	503569	9.0 m depth
	SED-SB-04	8580159	503545	5.0 m depth
	SED-SB-05	8580114	503639	2.3 m depth
	SED-SB-06	8580112	503625	5.8 m depth
	SED-SB-07	8580098	503606	9.2 m depth
	SED-SB-08	8580090	503582	8.0 m depth
	SED-SB-09	8580303	503458	1.5 m depth

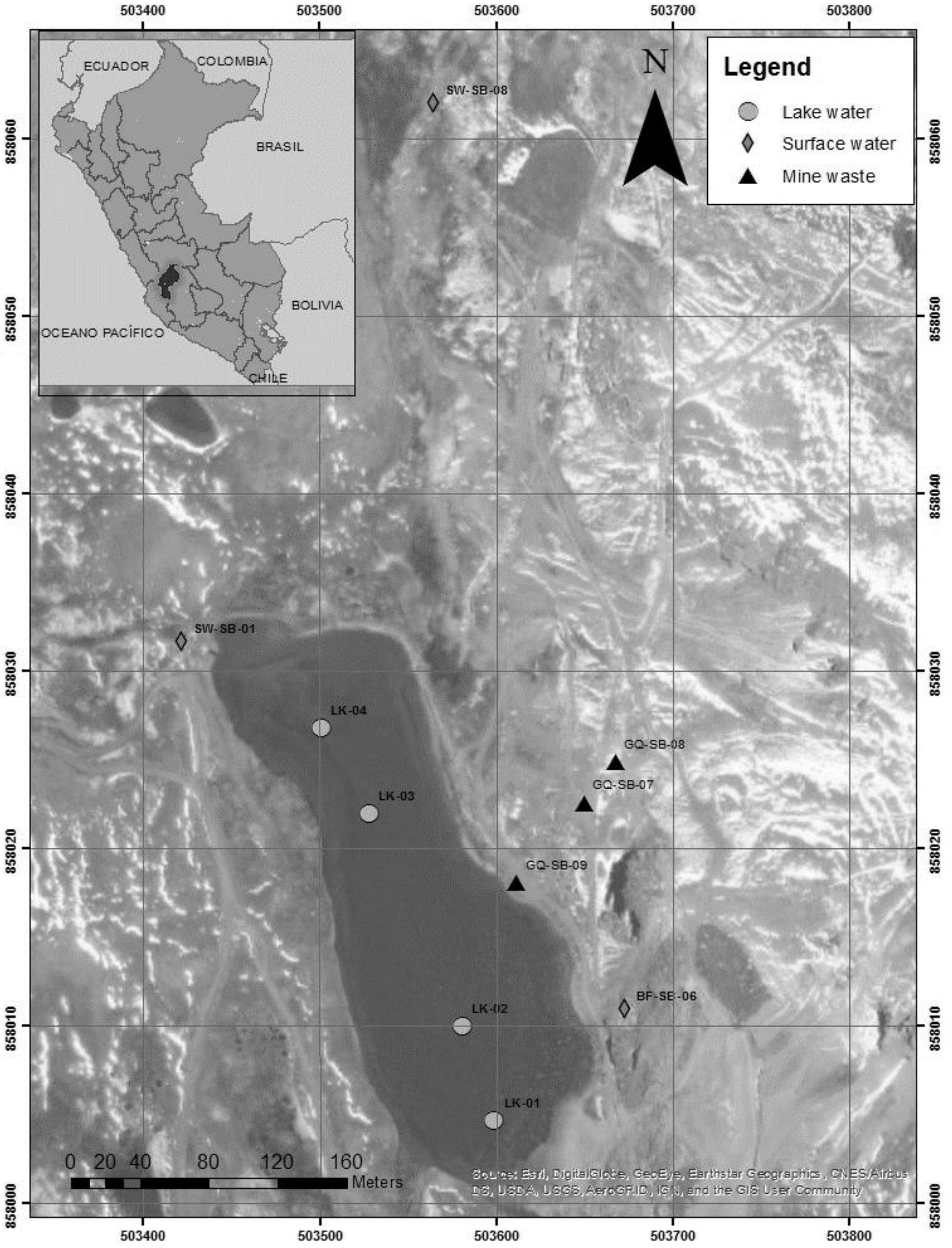

Fig. 1. **Location map**

3.1 Mine waste and sediments

Mine wastes and sediments were analyzed for major element content, chemical characteristics, mineralogy, the capacity to generate acid mine drainage (ABA) and the mobilization of metals in the soluble way (SPLP).

The morphology of the mine waste and bottom sediment at the macro and micro levels were obtained by microscopy. X-ray diffraction (XRD) analyses of the samples were performed on a Bruker D2 phaser diffractometer. XRD patterns were analyzed with the use of Material Data Inc. DIFRAC.EVA software and standard reference patterns. The mineralogical characteristics of mine waste and sediments are the most important factor of AMD quality. It is therefore critical to evaluate the mineralogical characteristics of a mine waste.

The bulk chemical composition of solid mine-waste samples was determined with the use of inductively coupled plasma-mass spectrometry (ICP-MS) following acid-digestion of the sample with a mixture of HCl, HNO_3, $HClO_4$, HF (Briggs, 2002a; Briggs and Meier,2002). Acid-base account (ABA) was originally designed to estimate the inherent capacity of coal-mine waste to produce or to neutralize acid (Sobek and others, 1978). Currently, this method is used to evaluate metal-mine waste and it typically includes the determination of paste pH, which is a quick measure of relative acid generation or acid neutralization (White and others, 1999).

Synthetic Precipitation Leaching Procedure (SPLP) are important in revealing the soluble phases of a sample, predicting geochemical effects of flushing a material, helping to quantify toxic mobilization, and revealing the organic/inorganic constituents that are made available to organisms.

3.2 Water chemistry

Water samples were analyzed for cations by ICP-MS and for the anions chloride, fluoride, nitrate, and sulfate. Water temperature, pH, specific conductance, DO, ORP, dissolved metals were measured on site at the time of sample collection.

3.3 Geochemical modeling

The computer program PHREEQC was used to model the equilibrium speciation of the waters (Parkhurst and Appelo, 1999). PHREEQC was also used to investigate the mass-balance of interactions between unimpacted waters and leachate waters from mine waste dump, and downstream effects through its inverse modeling capabilities.

4.0 RESULTS

4.1 Mineralogy and geochemistry of mine wastes

Mine waste and sediment samples were dominated by marcasite and pyrite. The gangue mineralogy consisted of andesine, microcline, calcite quartz and minor feldspar.

Approximately 88- 95% of S in the mine waste samples were sulphate with the remainder as sulphide, whereas in sediment samples 25-68% were sulphide and the rest were in sulphate form (Table 2). The most abundant minor or trace elements in mine waste and sediment samples in order of decreasing abundance were Pb (2,400–25,700 mg/kg), Zn (247–12,900 mg/kg), Ba (618-5,000 mg/kg), As (218–4,600 mg/kg), Cu (39-140 mg/kg), Hg (14–32 mg/kg) and Mn (89–210 mg/kg).

Acid–base accounting diagram (Fig.2) for mine waste and sediment samples indicated that both had high acid-generating potential (PAG) and little or no acid-neutralizing potential. Paste pH values ranged between 4.4 to 6.93. Acid generating potentials (AP) calculated on the basis of sulfide sulfur ranged between 0.9 and 65.6 kg $CaCO_3$/tonne, and neutralization potentials (NP) ranged between 0 except one point with 16 kg $CaCO_3$/tonne, yielding net neutralization potentials (NNP = NP-AP) of -65.6 to 8.5 kg $CaCO_3$/tonne.

Table 2. Acid Base Accounting results

Sample ID	Category	Total-S %	Sulphide-S %	AP kg $CaCO_3$/t	NP kg $CaCO_3$/t	NP/AP	Inorg. C. %	NNP	Crushed pH
GQ-SB-09	Mine Waste	2	0.1	3.1	0	0	0.04	-3.1	5.08
GQ-SB-07/08		1.8	0.2	6.3	0	0	0.04	-6.3	4.68
SED-SB-01	Sediment	0.91	0.03	0.9	0	0	0.05	-0.9	5.47
SED-SB-02		1.7	0.9	28.1	0	0	0.04	-28.1	4.51

Sample ID	Category	Total-S %	Sulphide-S %	AP kg $CaCO_3$/t	NP kg $CaCO_3$/t	NP/AP	Inorg. C. %	NNP	Crushed pH
SED-SB-03		1.3	0.5	15.6	0	0	0.05	-15.6	4.14
SED-SB-05		0.56	0.24	7.5	16	2.13	0.22	8.5	6.93
SED-SB-06		1.2	0.3	9.4	0	0	0.06	-9.4	4.4
SED-SB-07		1.4	0.9	28.1	0	0	0.06	-28.1	4.54
SED-SB-08		3.1	2.1	65.6	0	0	0.06	-65.6	4.58
SED-SB-09		0.28	0.07	2.2	0	0	0.04	-2.2	4.72

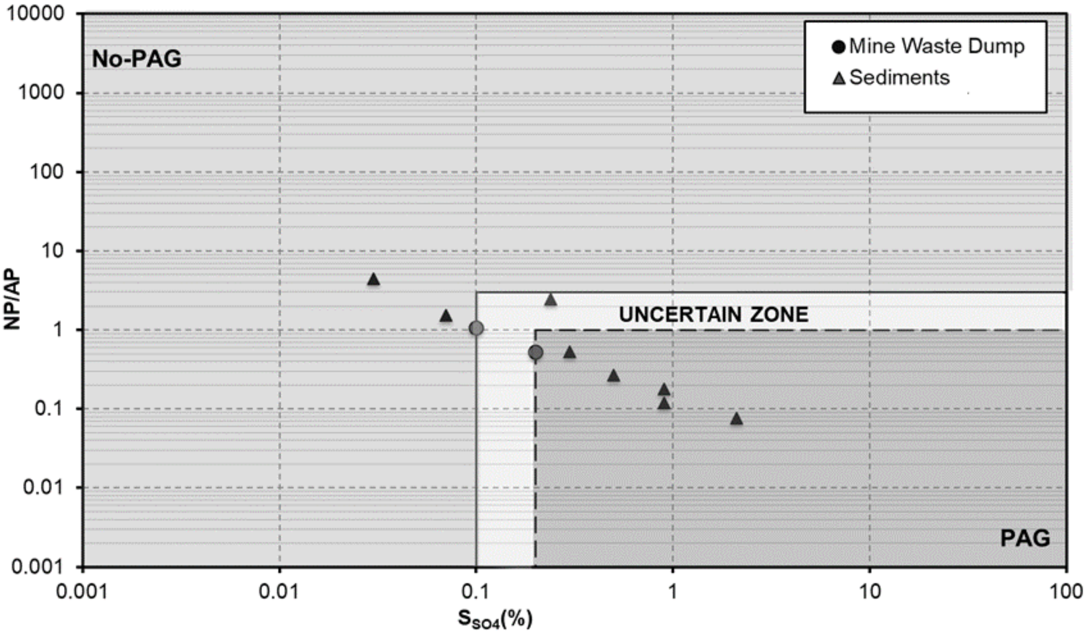

Fig. 2. **Acid Base Accounting Diagram**

4.2 Geochemistry of waters

Field parameters, including pH, specific conductance, and dissolved O_2, had similar range of values ranges (Table 3). Nevertheless, there is a difference in the lake's profile metal distribution where the highest concentrations were located in the most superficial and nearest area of the mine waste dump (Fig.3). On the other hand, the water sample located downstream of the lake presented an improvement in water quality reflected in the increasing of pH to neutral value after being in contact with the surrounding geology (limestone).

2. **Table 3.** **Physic - chemical evaluated parameters in water samples**
3.

Category samples	Sampling ID	Date	pH	T (C°)	EC (µs/cm)	TDS (mg/lL)	ORP (mV)
Lake water	LK-01-SUP	Jul-19	4.26	10.5	300	195	225
	LK-01-MED		4.81	10.02	286	186	236
	LK-01-INF		4.66	9.7	294	191	251
	LK-02-SUP		4.25	9.17	300	195	265
	LK-02-TCN		4.12	11	289	188	239
	LK-02-INF		4.36	11	287	187	225
	LK-03-SUP		4.32	10.9	288	187	253
	LK-03-INF		4.33	11.4	295	192	236
	LK-04-SUP		4.03	10.2	295	192	236
	LK-04-INF		4.02	10.3	294	191	229
Groundwater	BF-SB-06	Jul-19	4.55	9.74	298	194	204
Surface water	SW-SB-01	Jul-19	4.26	10.5	300	195	225
	SW-SB-09		6.81	8.99	178	116	119

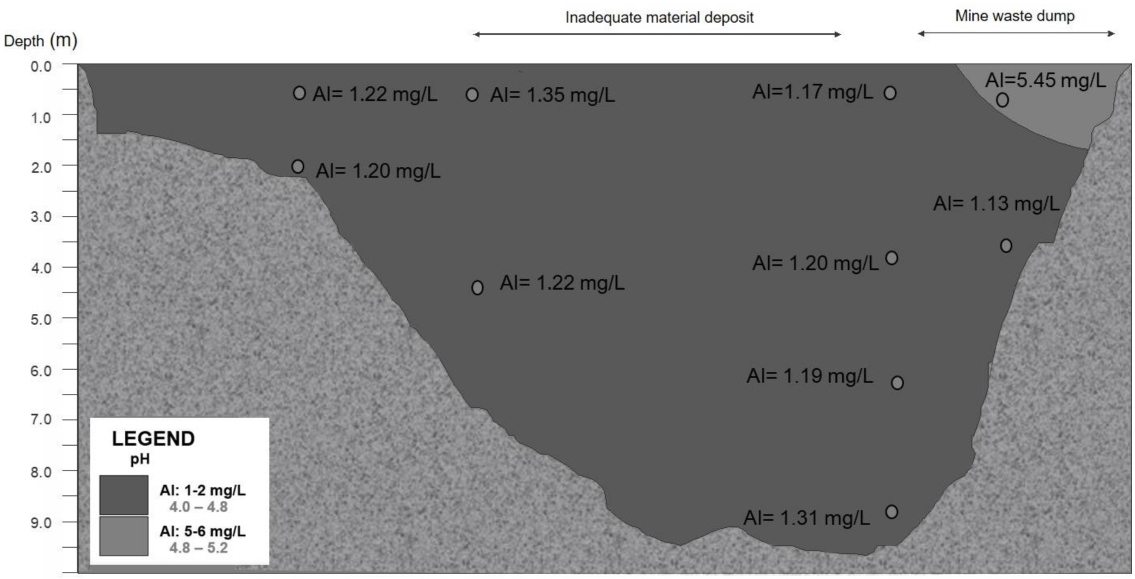

Fig. 3. **Lake´s profile and variation of aluminum concentration**

Ficklin diagram (Plumlee et al, 1999) showing the sum of dissolved base metal concentrations as a function of pH. This diagram quantifies the chemical variation of the analysed samples and allows to determine the main geological environments (Fig.4). The results showed that all lake water, groundwater, surface water and mine waste leaching test results were classified as acid and high metal concentration type. The sample located downstream of the lake has a near neutral pH and low metal concentration.

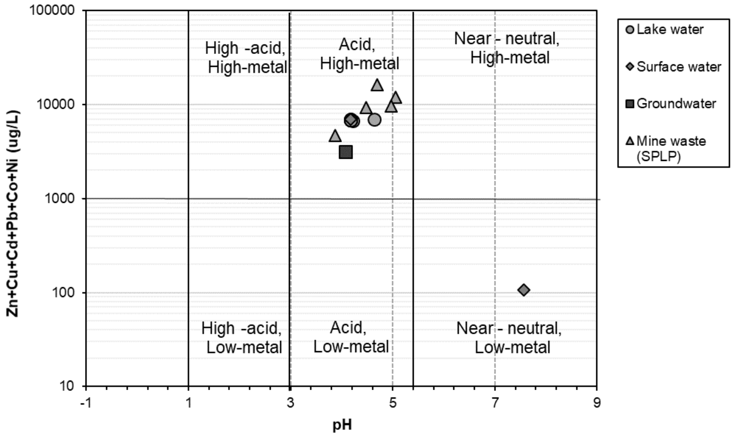

Fig. 4. **Ficklin diagram**

4.3 Conceptual Model

The conceptual model for the simulations is shown in Figure 5. This model shows the main water fluxes as well as the main geochemical zones within the mine waste dump. Main water influx is the water from rainfall. Main losses are evaporation, interstitial lock-up, seepage to groundwater and toe seepage. The main geochemical zones are: a, the oxidation zone from the mine waste surface to the oxidation front. b, the transition zone, between the oxidation and anoxic zone and; c, the anoxic zone, from the acid front to the mine waste dump base. The geochemical process identified in mine waste dump are oxidation of sulfidic minerals, acidification of water, leaching of heavy metals into groundwater and runoff to the lake, nevertheless this oxidation zone in the lake is just the superficial area down to a depth of 3 m. The fluxes into the lake are rainfall, superficial flow from mine waste and the infiltrated leaching from mine waste dump into groundwater and finally lake. After the interaction of water fluxes into the lake and the mix as a result of the wind and difference of temperature the effluent is the stream. Downstream the predominant process in the neutralization of water acidity as result of its interaction with carbonated geology.

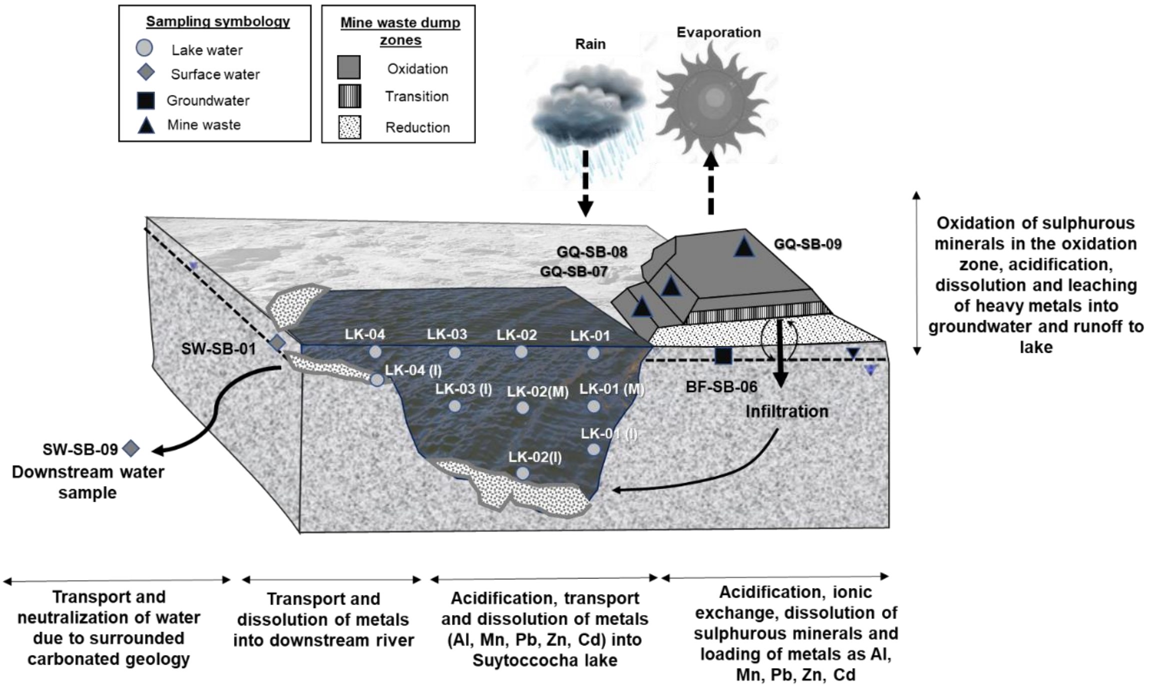

Fig. 5. **Conceptual model of geochemical process in the study lake**

4.4 Geochemical modeling

Inverse modeling, using observed mineral assemblages and minerals inferred from PHREEQC, can reveal the roles of mineral dissolution and precipitation, and dilution in establishing the drainage chemistry. The simulations are limited to the cations Al, As, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn and SO_4^{-2} as the dominant anion. Phases allowed to react included dolomite, calcite, k-feldspar, albite-low, anorthite, pyrite, chalcopyrite, sphalerite, galena, hematite, gypsum, kaolinite, arsenopyrite, pyrolusite, malachite and magnesite.

4. Table 4. Water analyses used in inverse modeling

Parameters	Unit	Precipitation	Groundwater
		Solution 1	BF-SB-06
pH	Unidad pH	7.91	4.07
pe	mV	13	14
SO4-2	mg/L	0.24	130
Ca	mg/L	1.52	22
Mg	mg/L	0.008	6.85
K	mg/L	0.02	5.3
Na	mg/L	0.11	2.3
Al	mg/L	0.01	3.65
As	µg/L	0.015	0.29
Cd	µg/L	0.005	11.0
Co	µg/L	0.005	20.45
Cu	µg/L	1.03	6.3
Fe	µg/L	7.4	3200
Mn	µg/L	0.65	1504.4
Ni	µg/L	0.1	24.4
Pb	µg/L	0.1	1370
Zn	µg/L	38	1710

The inverse models indicated that pyrite and chalcopyrite dissolution by oxidation was the most important contributor to the drainage chemistry in the vicinity of the mine, which required proportional amounts of dissolved O_2 for oxidation (Table 5). Near the mine site, sphalerite and galena were the next most important contributors, followed by muscovite of plagioclase.

Inverse modeling suggested that precipitates in both reaches were dominantly hematite, malachite, combined with kaolinite and feldspar.

5. Table 5. Results of inverse modeling showing mass fluxes needed to produce changes in water chemistry between paired samples per liter of starting solution

Parameters	Formula	Precipitation / Groundwater
Reactants		Moles
Chalcopyrite	$CuFeS_2$	1.23E-03
Pyrite	$Fe_{0.987}Ni_{0.01}Co_{0.003}S_2$	1.34E-07
Galena	PbS	6.61E-06
Sphalerite	$Zn_{0.95}Cd_{0.05}S$	2.70E-05
Albite	$NaAlSi_3O_8$	9.52E-05
Gypsum	$CaSO_4{:}2H_2O$	1.79E-04
Magnesite	$Mg(CO_3)$	2.82E-04
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	2.98E-04
Calcite	$CaCO_3$	3.33E-04
Arsenopyrite	FeAsS	3.67E-09
Pyrolusite	MnO_2	1.44E-03
Products		
Malachite	$Cu_2(CO_3)(OH)_2$	6.15E-04
Hematite	Fe_2O_3	5.86E-04
Kaolinite	$Al_2(Si_2O_5)(OH)_4$	3.46E-04
K-feldspar	$KAlSi_3O_8$	1.63E-04

5.0 CONCLUSIONS

The geochemical models developed for this study indicated that seepage from the mine waste dump are acidic and contain elevated concentrations of trace metal concentrations, specifically Al, Cd, Mn, Pb, Zn impacting the lake. In the lake, the dominant process was the dilution and conservative mix, differencing two areas of higher concentration in metals, being the oxidized zone the most superficial and the nearest to the mine waste dump. The dominant process affecting the water chemistry 1 km downstream from the site, was the neutralization, and sorption of metals on secondary precipitates.

Further research efforts should be focused on the coupling of detailed geochemical models and detailed hydrologic transport models to evaluate the influence of oxygen and heat transport on mine waste dump and to evaluate the final shallow groundwater plume characteristics into the lake.

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MANAGING AMD AND CLOSURE RISK THROUGH THE LIFE OF MINE: THE BAN HOUAYXAI GOLD-SILVER OPERATION WRD CASE STUDY

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ABSTRACT

Phu Bia Mining Limited (PBM) operates PanAust Limited's Ban Houayxai-Gold Silver Operation (BHX) in Laos. The open-pit operation is located approximately 100 kilometres northeast of Vientiane, Laos' capital. Commercial operations commenced at BHX in 2011 and the first gold-silver doré was poured in 2012.

Waste rock extracted during operations is deposited either in-pit or within the main waste rock dump (WRD). At the end of production, the BHX WRD will have a footprint of approximately 40 hectares (ha) and a vertical height of 200 metres (m). The WRD was built from the bottom up, with an oxide encapsulation layer progressively placed on the batter areas as construction progresses. This encapsulation cover system is designed for long term landform stability and to minimise advection fluxes and oxidation of potentially acid forming (PAF) materials during construction.

The cover system reduces diffusive oxygen fluxes so that acid generation rates match background silicate neutralisation rates. Geochemical modelling was used to develop the required performance criteria for diffusive oxygen flux to manage oxidation of PAF material. Oxygen and water flux modelling were used to assess the likely performance of the cover system and define construction specifications of the encapsulation layer. Geotechnical testing and visual inspections are performed to check construction specifications are met. Data collected to date from oxygen sampling tubes and piezometer temperature measurements shows good performance of the encapsulation layer with reduced oxygen concentrations within the WRD and a lack of significant oxidation reactions indicated by relatively steady ambient WRD temperatures.

1.0 INTRODUCTION

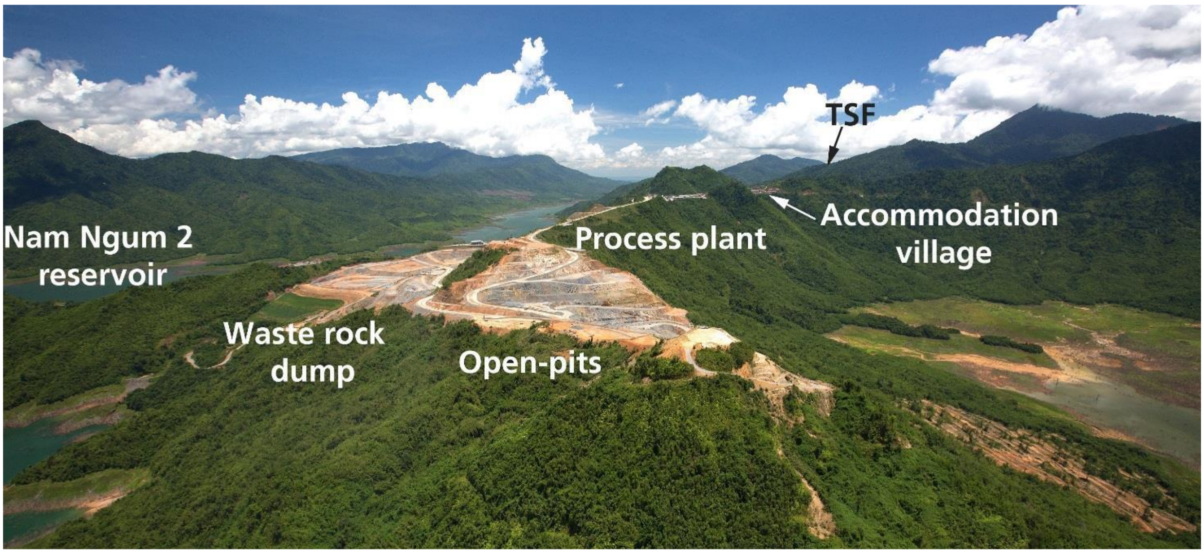
The Ban Houayxai Operation is located in the Longchaeng district of Xaysomboun Province of Lao PDR, approximately 100 kilometres (km) northeast of the capital of Laos, Vientiane.

PBM commenced mining activities at the Ban Houayxai Operation in 2011 and the first gold was poured in 2012. The Operation comprises an open-pit mine, process plant, waste rock dump (WRD), Tailings Storage Facility (TSF) and non-process infrastructure. The Operation produces a gold-silver doré for sale. Under the 2017 LOM plan, production at Ban Houayxai is scheduled to conclude in 2022.

The area where the operation is located is characterised by steep and hilly terrain which is typically covered with regenerating vegetation, forested hillsides, and abundant freshwater reserves. The topography ranges from steeply sloping hills, with elevations of between 375m and 1,400m above sea level, and narrow river valleys with limited flat areas.

The area has a tropical monsoonal climate with distinct wet and dry seasons. The wet season occurs between May and September. Annual rainfall averages approximately 3,000 millimetres (mm). Monthly rainfall can exceed 1,000mm and intense rainfall events are common. Maximum temperatures generally exceed 30 degrees Celsius (°C) throughout the year and minimum temperatures generally stay above 14ºC. Monthly evaporation rates range from 45 mm in January to 150 mm in May-June.

The Ban Houayxai Operation is located within the catchment of the Nam Ngum, a major tributary to the Mekong River. It is situated on a peninsular formed by inundation of the Nam Ngum 2 Reservoir which was constructed as part of the Nam Ngum 2 Hydroelectric Project.



2.0 WASTE ROCK STORAGE

Waste rock from the mining operation is placed either in-pit as backfill or in the main waste rock dump. The main waste rock dump is located to the southeast of the open-pit on the side of a hill above the Nam Ngum 2 reservoir. The life of mine design of the waste rock dump allows it to store up to 50Mt of waste rock. At the end of production, the dump will have a footprint of approximately 40ha and will be approximately 200m in vertical height from the toe to the final crest. The face of the waste rock dump embankment will have an overall slope angle of 20 degrees.

Waste rock mined and delivered to the waste dumps is classified as either non-acid forming (NAF) or potential acid forming (PAF). NAF oxide waste is used as an encapsulation layer for the PAF/NAF waste core of the dump.

2.1 Operation and Closure

The WRD is developed as a valley-fill with bottom-up construction. A mix of PAF and NAF material is placed within the core of the dump (away from embankments) in 5 m lifts. The outer embankment is built in 3 m lifts of oxide material, which is also compacted for the outer 8 m section. This compacted oxide material forms the encapsulation layer and is progressively placed as deposition of the NAF/PAF core progresses. This encapsulation cover system is intended for long term landform stability, and to minimise advection fluxes and oxidation of exposed PAF materials during mining operations. At the end of operations, a cover system will be placed on the remaining exposed PAF material, mainly on the top plateau area. The cover system is designed to reduce diffusive oxygen fluxes so that acid generation rates match background silicate neutralisation rates.

A basal drainage system was built under the WRD to manage potential water mounding within the waste resulting from surface infiltration during operation and prior to placement of the final cover system.

3.0 COVER SYSTEM DESIGN

3.1 Oxidation Rate Modelling and Performance Criteria

Geochemical modelling was used to develop the required performance criteria for the cover system. The cover system manages rates of diffusive oxygen flux to the underlying PAF material. An oxygen flux of 0.3 kg/m^2-yr has been established by EGi (2017) as the required performance criteria for the NAF cover profile on the BHX waste rock dump. This value is based on meeting background silicate neutralisation rates as described by Miller et al (2010) with a target of less than 10t H_2SO_4/ha/yr, which corresponds to an oxygen flux of approximately 0.6 kg/m^2/yr. The 0.3 kg/m^2-yr target is therefore considered conservative.

3.2 Cover System Modelling

Oxygen and water flux modelling were used to assess the likely performance of the cover system in meeting the performance criteria for oxygen flux. The SoilCover model was used to estimate the water balance of the proposed cover system. As elevated saturation values reduce oxygen fluxes through a given soil (Aubertin, 2005), saturation level was used as a surrogate for oxygen flux in determining relative performance of the proposed cover system profile with varying thicknesses.

Results of the oxygen flux modelling showed that a 3 m thick NAF cover at 70% saturation would result in an oxygen flux of 0.29 kg/m^2-yr, with an oxygen concentration of zero at the base of the cover, thus maximising the oxygen gradient as a conservative assumption. Water balance modelling for the cover system predict saturation levels within the cover profile to be maintained between 60 and 80% throughout the year. Results from *in situ* oxygen concentration measurements within the WRD showed a typical oxygen concentration of 10%. This value was used in a second iteration of oxygen flux calculation, reducing the oxygen gradient by 50%. This reduced oxygen gradient resulted in a modelled oxygen flux of 0.26 kg/m^2-yr, thus meeting the performance criteria for the cover system.

4.0 PERFORMANCE MONITORING

Results from the cover system modelling were used to determine construction specifications for the encapsulation layer on the WRD embankments in addition to eventual construction of the final cover system on the plateau area. The encapsulation layer is built as part of progressive closure initiative to manage oxygen diffusion and advection. Regular geotechnical testing and visual inspections are performed to check that construction specifications are met, including saturation targets for the cover layer.

Oxygen monitoring arrays were installed in the lower level of the waste rock dump through the encapsulation zone. The oxygen concentrations dropped to near zero within weeks as would be expected from reactive material within the encapsulation zone. Temperature data from piezometers installed in the dump shows that the temperature in the dump is relatively constant and near ambient, indicating a lack of significant sulphide oxidation reactions.

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THE EVOLUTION OF THE NEW SOUTH WALES LEGACY MINES PROGRAM

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ABSTRACT

The NSW Legacy Mines Program has existed in one shape or form since its inception in 1974 by the NSW Government as the Derelict Mined Lands Rehabilitation Program. Commencing with an annual budget of $125,000, the program was tasked with safety and minor environmental works at abandoned mines across NSW.

In 1976, a major environmental works project was carried out by NSW Public Works in parallel to the Derelict Mined Lands Rehabilitation Program when the Captains Flat Mine was remediated. Remediation of Captains Flat Mine involved reshaping and capping waste rock dumps and diverting surface water runoff away from the main workings. The Captains Flat works were one of the first major government-driven efforts aimed at reducing acid metalliferous drainage (AMD) in NSW.

For most of the program life, contaminated site assessments were cursory, while environmental works mirrored the strategies that were used at Captains Flat, with an emphasis on using physical structures to manage pollution, in keeping with the soil and erosion control focus of the industry at that time. The concept behind this approach was that it was a cost-effective means of interrupting the pathways linking contamination sources to receptors.

The installation of clean water diversions, construction of sediment and water retention basins, capping and erosion controls were the norm. Geochemical strategies to neutralise AMD were limited to the occasional use of anoxic or open limestone drains. As the program matured, site assessments have become more sophisticated with acid-base accounting at AMD sites.

Geochemical strategies based on engineered cover systems, oxygen exclusion, immobilisation and neutralisation are being developed and implemented, while retaining earlier remediation strategies aimed at eliminating contamination pathways. A recent addition to the program is a greater emphasis on pre-and post-works monitoring to evaluate the effectiveness of remediation efforts.

Over the past 40 years, the program budget, risk assessment, governance, assessment and remediation frameworks have improved incrementally, to the point that the government has created a stable platform for long-term strategic management of issues relating to abandoned mines. This paper outlines a brief evolution of the NSW Legacy Mines Program, with case studies provided to highlight advances in developing detailed site knowledge and greater assurance regarding the suitability and success of remediation strategies employed to manage AMD risk.

1.0 ESTABLISHING A PROGRAM TO REMEDIATE ABANDONED MINES

The Legacy Mines Program has existed in one shape or form since its inception in 1974 where it began life as the Derelict Mined Lands Rehabilitation Program (hereafter simply referred to as LMP). Administered by the then NSW Department of Mineral Resources, the LMP then had a static annual budget of $125,000 through to 1994.

The commencement of the LMP coincided with major environmental remediation works by NSW Public Works at the Captains Flat Mine, east of Queanbeyan in southern NSW. The driver for the remediation work at Captains Flat arose over concerns that damming of the Queanbeyan River (via construction of Googong Dam) and reduced flows, would see concentration of heavy metals in the river system downstream of the Molonglo River. Remediation involved reshaping and capping waste rock dumps and diverting surface water runoff away from the main workings (Dobos and Associates, 2002; GHD, 2018). The Captains Flat works was one of the first major government-driven efforts aimed at reducing acid metalliferous drainage (AMD) in NSW. Despite best efforts, heavy metal contamination as a result of AMD persists today (GHD, 2018).

Towards the latter part of the 1974 to 1994 period, the static budget meant that LMP was limited to small-scale remediation and maintenance activities such as shaft backfilling, fencing and minor water management strategies.

In 1995, the LMP received a significant funding boost ($500,000) in recognition of increased costs of remediation. The annual budget continued to increase to its current level of approximately $3 million per year. The improved financial position of the LMP resulted in a more systematic approach to risk assessing and managing abandoned mines. Improvements included:

- establishing a multi-agency steering committee with industry representation
- establishing an abandoned mine site register to catalogue sites, set priorities and track projects
- a systematic approach to works comprising site assessments, monitoring and forward planning for future remediation projects
- an increased extent of remediation at small sites, and
- staged remediation of larger, complex sites.

In doing so the government created a stable platform for long term strategic management of issues relating to abandoned mines.

2.0 COST-EFFECTIVE AMD AND ENVIRONMENTAL RISK MANAGEMENT

2.1 Early sediment and water management strategies

Despite the stable annual budget, it was necessary for the LMP to apply a cost-effective approach to addressing the risks from abandoned mines. In many ways, this manifested as risk-managed works and making incremental environmental improvements rather than detailed site remediation planning or creative environmental solutions.

For most of the program life, and with a few exceptions (e.g. Dobos and Associates, 2002; SMEC, 2010), contaminated site assessments and remediation planning were cursory, with a focus on heavy metal concentrations in soils or unfiltered water. Due to the accepted practices of the day, only minor consideration was given to the soluble fraction of heavy metals, acidity or acid-base accounting of mineral wastes to determine AMD-related impacts. For example, there are some instances where slag was used in drainage construction—presumably because it was inert, however recent LMP assessment has shown that this may not be the case (Gore and Ashelford, 2019).

Consequently, environmental works mirrored the strategies that were used at Captains Flat, with an emphasis on using physical structures to manage pollution. Clean water diversions were routinely employed at many sites, along with sediment control structures aimed at reducing the velocity of surface flows (Figure 1). This approach does little to prevent dissolved contaminants from discharging offsite, especially from underground workings with continual flow or during rainfall events that cause dams and drains to overtop.

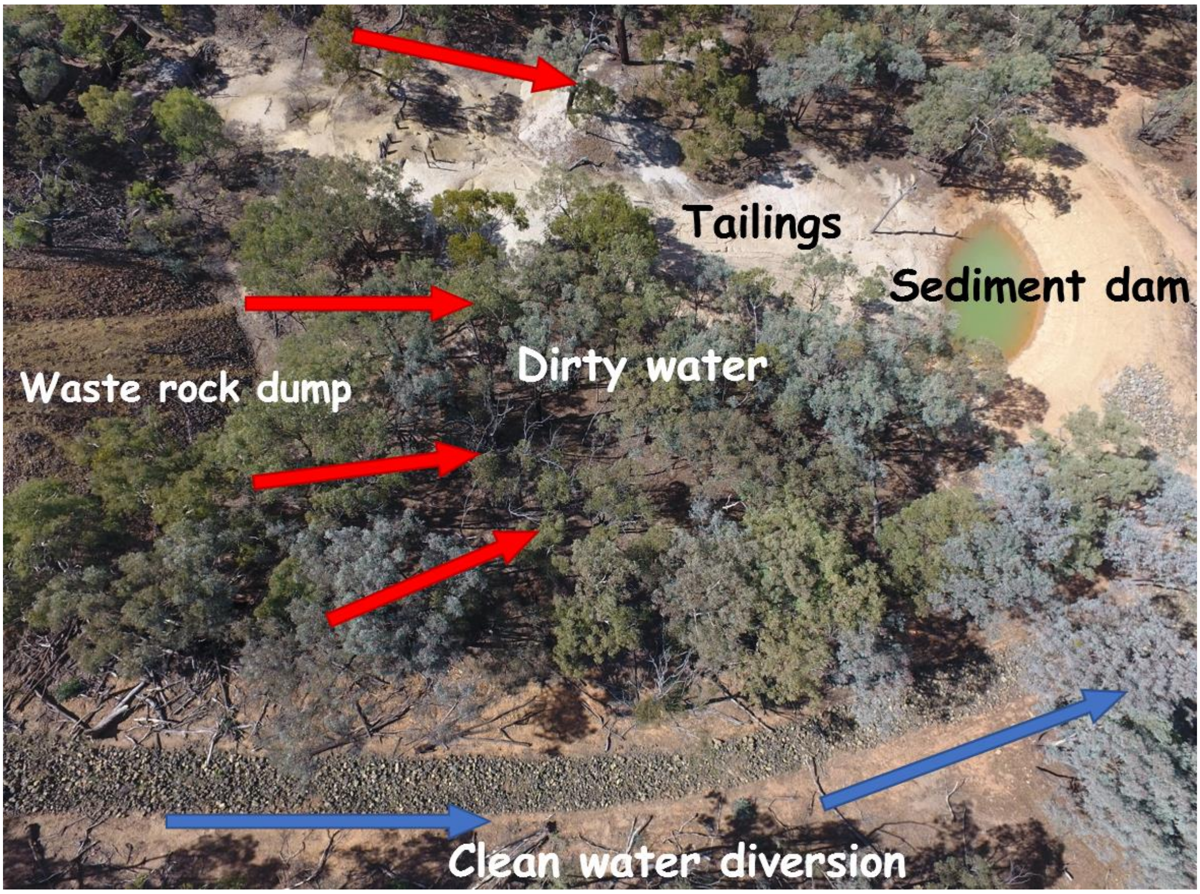

Fig. 1. **Water and sediment control measures, south west NSW.**

The concept behind this approach was that it limited the extent of contamination to mostly within the site footprint and reduced the site catchment. Combined with the dilutionary effects of high rainfall events, this strategy was considered a practical and cost-effective means of interrupting the pathways linking contamination sources to receptors. However, the overall effectiveness of the water management and sediment control strategies is largely unknown.

2.2 Early strategies for managing AMD

During the 1990s and 2000s, the LMP started implementing remediation strategies targeted at managing AMD. Most notably, this involved the construction of surface water drains using limestone and to a lesser extent anoxic limestone drains or even diverting AMD back into underground workings.

For most remediation works, there was little in the way of remediation planning in support of these strategies compared to current day practices. Rather, the existing approach to water and sediment control was applied, coupled with a neutralising agent—in most cases limestone rock drains (Figure 2). The limestone drains were typically installed as a permanent solution without any real understanding of acidity loads, discharge volumes, climatic conditions or geochemistry. With regards to diversion of surface water back into underground workings, there was no consideration of groundwater connectivity and dynamics—it was simply the lesser of two evils, with a potential geochemical benefit.

Fig. 2. Limestone drain used to neutralise AMD, central west NSW.

The suitability of the AMD control structures remains largely unknown, as their effectiveness was never measured via pre and post works monitoring. Based on the assumption that the limestone would neutralise AMD, the LMP constructed these drains at several sites across NSW. Whether such structures have made an appreciable difference to contaminant loads is unknown however recent assessments indicate that AMD risks persist.

3.0 ADVANCEMENTS IN ASSESSING AND MANAGING AMD RISK

3.1 Recent assessment and understanding of AMD risks

In the period since 2013/14, the LMP has invested greater effort and funding in the scoping and developing detailed site characterisations and remediation action plans. There has been a greater emphasis on acid-base accounting and calculating the relative contribution of point sources and domains to allow for targeted remediation. In doing so, clearer remediation and pollution reduction targets are being set. Dedicated pre and post works monitoring will determine if they are being met.

A comparison of early remediation versus planned and more recent remediation efforts is provided in the following section for three abandoned mine sites.

3.2 The Ottery Mine: creative geochemical solutions

The Ottery Mine was a tin and arsenic mine that ceased operating in 1957. Along with the nearby Glen Smelting tailings emplacement, both sites are responsible for discharging arsenic and AMD into the Beardy River catchment.

Selective surface remediation works were undertaken at the Ottery Mine in the 1990s to reduce AMD from entering the Beardy River. Works included reshaping of waste rock dumps, partial covering, and stabilisation and revegetation of a graded slope (with waste rock) below the arsenic processing plant (Figure 3). In later years, the works were considered ineffective due to ongoing pollution impacts and further assessment was carried out in 2014 (Earth Systems, 2014). The resulting conceptual remediation plan outlined an approach for reducing the existing 35 tonnes of H_2SO_4 equivalent by up to 85% (Earth Systems, 2014).

Fig. 3. Ineffective revegetation works on reshaped waste rock, Ottery Mine.

The remediation strategy is a multi-faceted geochemical stabilisation process that involves consolidating mineral wastes from both Ottery and Glen Smelting into a single encapsulation cell (detailed in GHD, 2017) (Figure 4).

The geochemical stabilisation approach includes:

- strategic limestone addition to assist with acid neutralisation and to retard sulphide oxidation,
- air entry control to the encapsulation cell using fine-grained mineral wastes,
- oxygen concentration control using non-acid forming (but oxygen consuming materials) to retard sulphide oxidation,
- adsorption of arsenic from near-neutral leachate utilising haematitic mine wastes;
- passive conversion of relatively soluble arsenical oxides to low solubility minerals using the controlled addition of calcium, and
- water infiltration management through clay capping, revegetation and water diversion drains around the encapsulation cell.

The above approach was validated by bench trials with the remediation works still in the planning phase. However, the LMP has commenced baseline water quality and sediment monitoring in preparation for remediation works.

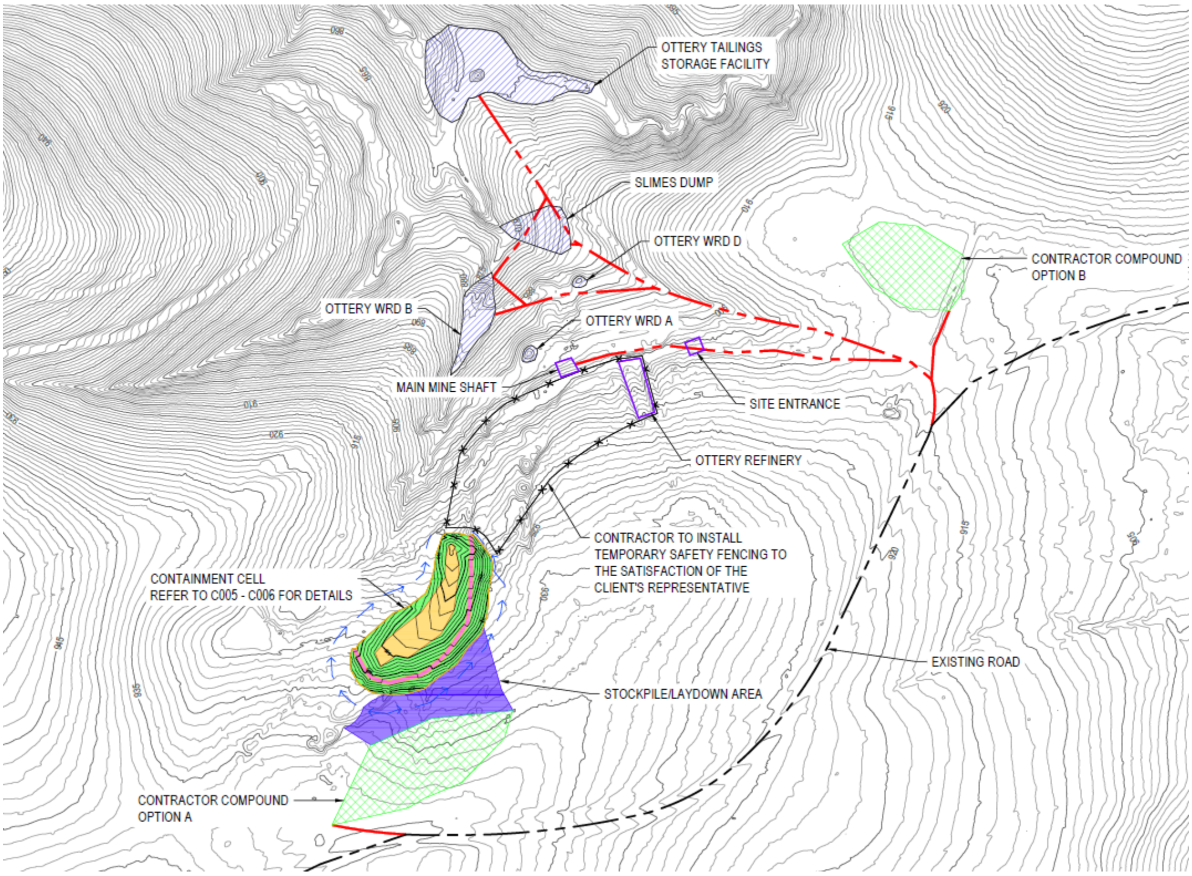

Fig. 4. **General arrangement plan, Ottery and Glen Smelting remediation action plan (from GHD, 2017).**

3.3 Conrad Mine: consolidation and capping

The Conrad Mine is a former base metal mine located near Inverell in the New England region of NSW. The site is highly disturbed and there are numerous contamination sources and domains.

In the early 2000s, the LMP made a significant investment at the site with the assistance of an NSW Environmental Trust grant of nearly $1.2 million. The works were aimed at reducing polluted surface water discharging to Borah Creek, achieving site stability and a reduction of safety hazards. Environmental works included:

- capping and containment of the upper tailings dump,
- containment of the lower tailings dump via installation of gabion basket retaining and diversion of clean water flows (Figure 5), and
- creek bank stability works around the Conrad shaft and upper Borah Creek areas to prevent erosion of heavy metal contaminated materials and leachate production.

The efficacy of these works is unknown, but a study commissioned by LMP in 2013 (URS, 2014) identified that the tailings dump and other waste rock piles were still contributing high contaminant loads. This resulted in the development of a large-scale consolidation and capping project, whereby waste rock was consolidated into the lower tailings dump, the dump footprint was expanded, and an engineered cap was designed and constructed to minimise water ingress and suppress AMD leachate from the tailings dump (Figure 6).

Fig. 5. **Remediation works at Conrad Mine in 2003 was designed to contain tailings and prevent their downstream movement.**

Fig. 6. **In 2017, the same tailings emplacement at Conrad Mine was expanded and waste rock added, before being overlaid with an engineered cover system.**

3.4 Sunny Corner and Nevada mines: air entry control works

The Sunny Corner and Nevada mines, located in central-west NSW contribute AMD for a significant distance downstream in Daylight Creek. Previous remediation works at Sunny Corner and Nevada focussed on sediment control works, burial of mineral wastes and construction of limestone drains (Figure 7). The works produced little environmental benefit, based on subsequent water quality monitoring. In addition, the strategy focussed on above-ground point sources, whereas most of the heavy metal and AMD load (65-70% at Sunny Corner) was being generated from within the underground workings.

Fig. 7. Limestone drain construction, Sunny Corner Mine.

The LMP implemented a new remediation strategy for the program, one aimed at reducing AMD from the sites through suppressing oxidation of below ground pyritic material. In 2017, all known mine workings were sealed to prevent oxygen from entering the underground mine voids (Figure 8) - a key process in preventing the generation of AMD.

Fig. 8. The level 4 adit, Sunny Corner mine post remediation, including the installed continuous monitoring equipment. Note the PVC pipe, which has an S-bend connected to allow water to freely discharge with oxygen entering the workings.

The remediation project involved substantial earthworks to block oxygen entering adits, shafts and stopes connected to the underground workings. The works were augmented by periodic monitoring of carbon dioxide from potential air points, along with continuous monitoring of local climatic conditions both outside and within the mine workings. Water quality was also monitored prior to works, and on a regular basis since earthworks were completed in 2016. The results of water quality monitoring indicate an improvement to the overall pollution load as indicated by reduced acidity (approximately 35-40%) and electrical conductivity when compared to the 2015 baseline (Bourgeot et al., 2017 and Earth Systems, 2020).

4.0 FUTURE FOCUS OF THE LMP

The LMP is continually looking at ways of improving site assessments and remediation works. Developing an understanding of groundwater interactions will become a higher priority into the future. An increased focus on preliminary contamination assessment will help to gain a better understanding of potential health and ecological risks through a bespoke risk model (in development).

Given the existing capabilities within the team, there is a trend towards undertaking preliminary site assessments with significantly more spatial resolution than past sampling efforts, due largely to the emergence and availability of portable x-ray fluorescence technology.

The LMP also has un-manned aviation vehicle and GIS capability. Consequently, mapping of contamination domains, construction of digital surface models and detailed photogrammetry can be delivered in-house. The advantage here being that these data can be packaged and provided to specialist geochemical consultants and provide a much more detailed picture of a site before they even step out into the field. In turn, the this will allow geochemical consultants to focus on data validation, remediation action planning and detailed design aspects.

Remediation works will continue to have a strong sediment and water management component, particularly on lower risk sites. However, remediation strategies on higher risk sites are expected to become more targeted, more sophisticated and with a greater focus on geochemical solutions to address AMD and contamination sources, rather than just pathways.

Finally, performance assessment and monitoring will also become a routine aspect of large-scale works. Already the LMP is moving towards incorporating laboratory validation and multi-year monitoring into remediation projects to measure the efficacy of remediation works.

5.0 CONCLUDING REMARKS

Over the past 5 to 10 years the LMP has made substantial improvement in the way in which it assesses and manages AMD risk. Assessments across the board are much more rigorous than in the past and remediation strategies are more detailed with a much greater focus on geochemical solutions rather than only managing contamination pathways. Despite the improvements, it is important to acknowledge the past efforts and strategies given that were delivered in an operating environment short on resources, and given that we can now benefit from technological advances and improved knowledge of AMD management. An increased emphasis on pre- and post-works monitoring regarding large-scale remediation works, and on laboratory validation of geochemical treatments will assist to deliver tangible environmental benefits.

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INTEGRATED PROCESSES FOR CONTAMINANT REMOVAL FROM MINE DRAINAGE AND HYDROMETALLURGICAL WATERS

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ABSTRACT

Mining and rock weathering processes generate acidic drainage, which can harbor a variety of contaminants, including metals, sulfate, selenate, nitrate and acidity, that need to be removed before safe release of water. Similarly, the composition of hydrometallurgical effluents can vary depending on the type of lixiviants used for ore or concentrate processing. The treatment of complex mine drainage and hydrometallurgical effluents may require a combination of complementary unit processes to achieve adequate contaminant removal. This paper reviews recent development of integrated treatment processes that combine various physico-chemical and biological unit operations for mine water and hydrometallurgical process water treatment. The first example is the integration of hydrotalcite precipitation through Virtual Curtain technology and biological denitrification in a fluidised bed reactor (FBR) for treating a high-strength hydrometallurgical effluent from nitric acid leaching of nickel laterites. In the second example hydrotalcite precipitation was combined with biological sulfate reduction in a FBR for AMD treatment. In the third example biological unit processes were applied to sequentially remove nitrate and selenate and then sulfate from water using two consecutive FBRs. In summary, the integrated processes allowed efficient contaminants removal from mine and process waters.

1.0 INTRODUCTION

Mining operation and natural rock weathering processes expose sulfidic minerals to oxygen and water, resulting in the generation of acid mine drainage (AMD) or acid rock drainage (ARD). The drainage can harbor various contaminants, such as metals, sulfate, selenate, nitrate and acidity. Hydrometallurgical effluents can also contain a range of contaminants originating from ore or concentrate being processed and the lixiviants used (Cheng et al. 2014). If not treated properly, hydrometallurgical effluents and mine drainage can cause serious environmental impacts (Kaksonen and Puhakka 2007). Therefore, the removal of contaminants is of paramount importance before releasing the water to the environment. However, since the composition of mine drainage and hydrometallurgical effluents is often complex, application of single treatment processes may not be effective for the removal of multiple contaminants. Therefore, it may be beneficial to use a combination of complementary unit processes to achieve contaminant removal and acceptable effluent quality.

In this study, treatment of hydrometallurgical process water and mine water was evaluated using integrated processes that utilise hydrotalcite precipitation and/or various biological reductive processes conducted in fluidised bed reactors (FBRs). Hydrotalcites are a class of magnesium (Mg) - aluminium (Al) layered double hydroxide minerals (anionic clays), which are both naturally occurring and can be synthetically produced. Hydrotalcite structure has positively-charged mixed metal hydroxide layers separated by interlayers containing water and exchangeable anions (Figure 1A). A suite of divalent and trivalent cations and anions can be substituted into hydrotalcite: $Mg_6Al_2(A)(OH)_{16}\cdot nH_2O$ (where A is an anion, such as CO_3^{2-} or SO_4^{2-}), thus enabling contaminant removal (Douglas et al. 2010, 2014).

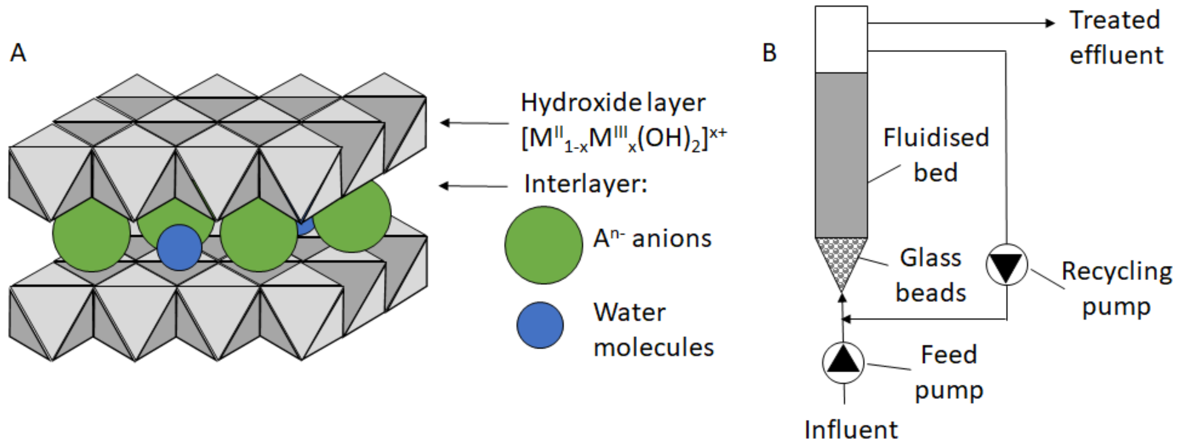

Fig. 1. **A) Structure of hydrotalcite; B) Simplified diagram of a fluidised bed reactor**

FBRs have solid biomass carrier that is suspended using high liquid flow rates that allow the carrier to be fluidised and behave as though it was a fluid (Figure 1B). FBRs have been widely used for a number of environmental engineering applications as they offer many benefits such as high mass transfer and volumetric rates, decoupling of biomass retention from hydraulic retention time, small physical footprint and the dilution of influence concentrations with high recycle rate (Özkaya et al. 2019).

This paper summarises three case studies on the development of integrated processes that are based on a combination of hydrotalcite precipitation and biological oxyanion reduction in FBRs for treating hydrometallurgical process water and mine drainage.

2.0 MATERIALS AND METHODS

2.1 Two-step process for nitrate removal

The first case study evaluated the integration of hydrotalcite precipitation and biological denitrification for treating a high-strength hydrometallurgical effluent from nitric acid leaching of nickel laterites. The effluent contained 17 g L^{-1} nitrate and had a pH of 9.1. The precipitation of hydrotalcite was achieved by adjusting the molar ratio, principally between Mg and Al in addition to other elements, as well as the elevation of the pH. Biological denitrification was conducted in two fluidised bed reactors (FBR) with granular activated carbon (GAC) as biomass carrier and acetate or methanol as electron donors for biological nitrate reduction. The reduction of nitrate with acetate and methanol is shown in reactions 1 and 2 (Cheng et al. 2014):

$$5\ CH_3COOH + 8\ NO_3^- \rightarrow 4\ N_2 + 10\ CO_2 + 8\ OH^- + 6\ H_2O \qquad [1]$$

$$5\ CH_3OH + 6\ NO_3^- \rightarrow 3\ N_2 + 5\ CO_2 + 6\ OH^- + 7\ H_2O \qquad [2]$$

The efficiency of the integrated process was evaluated by determining nitrate concentrations in the influent and after hydrotalcite precipitations and biological denitrification.

2.2 Two-step process for acid mine drainage treatment

In the second case study hydrotalcite precipitation was combined with biological sulfate reduction in a FBR for AMD treatment. The AMD had a pH of 4.3 and contained 2 g L^{-1} sulfate, and various concentrations of metals Al, Cd, Co, Cu, Fe, Mn, Ni and Zn. GAC was used as biomass carrier and ethanol as the electron donor for sulfate reduction as shown in reaction 3 (Kaksonen et al. 2004):

$2\ CH_3CH_2OH + 3\ SO_4^{2-} \rightarrow 2\ HS^- + H_2S + 4\ HCO_3^- + 2\ H_2O$ [3]

The performance of the integrated process was evaluated by determining the pH and concentrations of metals and sulfate in the AMD, hydrotalcite treated water and bioreactor effluent.

2.3 Sequential removal of nitrate, selenate and sulfate

In the third case study biological unit processes were applied to sequentially remove nitrate and selenate and then sulfate from water using two consecutive FBRs. The synthetic influent had a pH of 4.0-5.0 and contained 0.31 g L^{-1} nitrate, 0.71 g L^{-1} selenate and 2 g L^{-1} sulfate. GAC was used as biomass carrier and ethanol as electron donor for nitrate (reaction 4) (dos Santos et al. 2004), selenate (reaction 5) (Cheng et al. 2017) and sulfate reduction (reaction 3).

$5\ CH_3CH_2OH + 12\ NO_3^- \rightarrow 6\ N_2 + 10\ CO_2 + 12\ OH^- + 9\ H_2O$ [4]

$CH_3CH_2OH + 2\ SeO_4^{2-} \rightarrow 2\ Se^0 + 2\ CO_2 + 4\ OH^- + H_2O$ [5]

The performance of the integrated system was evaluated by determining selenate, selenite, nitrate, nitrite and sulfate concentrations in the influent and after each of the two bioreactors.

3.0 RESULTS

3.1 Two-step process for nitrate removal

In the first example hydrotalcite precipitation and biological denitrification in a FBR were integrated for treating a high-strength hydrometallurgical effluent from nitric acid leaching of nickel laterites. The hydrotalcite precipitation removed 41% of the influent nitrate as an interlayer anion with an approximate formula of $Mg_5Al_2(OH)_{12}(NO_3)_2{\cdot}6H_2O$. Acetate supplemented FBR performed better than the methanol supplemented one and increased the overall nitrate removal to >90% (Cheng et al. 2014).

3.2 Two-step process for acid mine drainage treatment

In the second example hydrotalcite precipitation was combined with biological sulfate reduction in a FBR for AMD treatment. The hydrotalcite precipitation readily neutralised the AMD (pH 4.3) and removed >99% of a range of metals (Al, Cd, Co, Cu, Fe, Mn, Ni, Zn) and 10% of sulfate. The sulfate-reducing FBR increased the overall sulfate removal to 73%.

3.3 Sequential removal of nitrate, selenate and sulfate

In the third example biological unit processes were applied to sequentially remove nitrate and selenate and then sulfate from water using two consecutive FBRs. The first FBR removed >99% of the influent nitrate and selenate and neutralised the influent (pH 4.0-5.0). The second FBR removed >80% of the influent sulfate.

4.0 CONCLUSIONS

This paper reviewed three case studies where various physico-chemical and/or biological unit processes were combined to treat high-strength hydrometallurgical process water and complex mine drainage. The hydrotalcite treatment enabled the removal of nitrate and various metals and neutralisation of acidity. Biological nitrate, selenate and sulfate reduction complemented the physico-chemical treatment by removing oxyanions. In summary, the integrated processes allowed efficient contaminant removal from mine and process waters.

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ELECTROCHEMICAL TREATMENT FOR TARGETED RECOVERY OF RARE EARTH ELEMENTS AND YTTRIUM FROM ACID MINE DRAINAGE

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ABSTRACT

This work demonstrates a novel approach to tackle acid mine drainage (AMD), whereby staged electrochemical neutralisation is employed to treat AMD and concomitantly recover metals as precipitates. This approach was guided by physico-chemical modelling and tested on real AMD from two different legacy mine sites in Australia, and compared against conventional chemical-dosing-based techniques using hydrated lime ($Ca(OH)_2$) and sodium hydroxide (NaOH). The electrochemical produced less voluminous and more easily settleable sludge than $Ca(OH)_2$. Moreover, the staged treatment approach demonstrated the potential to produce metal-rich powdered solids with a targeted composition, including rare earth elements and yttrium (REY). REY were recovered in concentrations up to 0.1% of the total solids composition, illustrating a new avenue for AMD remediation coupled with the recovery of critical metals. Based on these findings, future work will evaluate the integration of biological and chemical processes to improve the separation of REEs and PGMs, under the principle of circular economy.

1.0 INTRODUCTION

Acid mine drainage (AMD) is a challenge for current and legacy mining operations worldwide given its potential to severely harm ecosystems and communities if inadequately managed. Treatment costs for AMD are amongst the highest in the industrial wastewater treatment sector, with limited sustainable options available to date. Therefore, a circular economy approach to AMD where concomitant resource recovery is highly appealing to offset the high treatment costs (Fernando et al., 2018; Naidu et al., 2019). Targets for recovery from AMD include metals and metalloids, sulphur products (e.g. elemental sulphur, sulfuric acid), electrical energy, construction materials (e.g. gypsum), agricultural soil conditioners or adsorbents (Naidu et al., 2019; Nleya et al., 2016; Pozo et al., 2017; Simate & Ndlovu, 2014). A further product of special interest are higher-value rare earth elements and yttrium (REY) (Naidu et al., 2019). REY are required for clean energy generation, rechargeable batteries, photovoltaic cells, fibre optics and lasers, and their demand is expected to grow significantly in the near future (Alonso et al., 2012; Arshi et al., 2018; Baldi et al., 2014; Browne et al., 2019; Thomas & Harris, 2016). There already are anticipated issues with the accelerated growth of REY consumption due to unsustainable mining, monopolistic supply conditions and potential geopolitical conflicts (Alonso et al., 2012; Browne et al., 2019). These problems could however be alleviated by substitution, security-of-supply policies and finding alternative REY sources, such as recovery from AMD treatment (Arshi et al., 2018; Barnhart & Benson, 2013). The high volatility of metal prices and variability in metal demands are main factors restricting the development and upscaling of metal recovery technologies, particularly for wastewaters which typically contain lower metal concentrations. As a result, full scale application for metals recovery from acid mine drainage are implemented only if the process is economically feasible.

In this work an electrochemical treatment for pH neutralisation of AMD with concomitant targeted recovery of metals was evaluated. In the electrochemical system a cathodic reduction reaction drives metal hydroxide, oxide or sulphate precipitation. The concentration of hydroxide ions in the solution increases through the electrode reaction concomitantly with the migration of sulphate from the AMD through an anion exchange membrane (AEM) into a separate solution. Metals distribution and optimal conditions for selective recovery in the different steps of the proposed configuration will be assessed. This approach was guided by physico-chemical modelling, tested on real AMD from two different legacy mine sites in Australia, and compared against conventional chemical-dosing-based techniques. Additionally, alternatives to improve the separation and concentrations of metals by integrating chemical and biological process into the electrochemical system were also discussed in this work. The approaches proposed herein, following the concept of circular economy, are meant to evaluate the use of the product effluents from the electrochemical system to separate critical metals for their potential recovery and reduce sulphate concentrations in the final effluent to meet standard regulations. The evaluation of these process will give us an ideal configuration for the selective recovery of critical metals.

2.0 MATERIALS AND METHODS

2.1 Acid mine drainage

AMD was collected at two separate locations from legacy sites in Queensland, Australia, where it posed a major environmental risk. The first site was at Mt Morgan gold mine, where the AMD had remarkably high concentrations of sulphate (29 g L^{-1}), Al (2.3 g L^{-1}), Mg (4.6 g L^{-1}) and Mn (2.4 g L^{-1}), with a pH of 2.7. The second site of AMD collection has been de-identified. This site was found to have high concentrations of Al (0.4 g L^{-1}), Fe (0.3 g L^{-1}) and Mg (0.7 g L^{-1}) with a lower sulphate concentration of 9.4 g L^{-1} and similar pH of 2.7, compared to Site 1.

2.2 Modelling methods

Simulations using PHREEQC (Version 3) were performed to understand saturation and precipitation of high concentration metals during the different experiments in the cathodic reservoir of the electrochemical experiments and a single reservoir for the chemical addition experiments.

2.3 Electrochemical reactor setup

The electrochemical system followed the principle that by applying a current between the cathode and anode, the electrochemical reactions increase the pH of the cathodic solution, decrease the pH of anolyte solution and cause anions (in this case sulphate ions) to migrate from the cathode chamber to the anode chamber through an AEM. The increase in pH of the cathodic solution will concomitantly drive the precipitation of metal (oxy)hydroxides and sulphates. The electrochemical reactor consisted of two custom-made acrylic chambers separated by rubber gaskets, a 4 cm by 4 cm mesh stainless steel cathode, a 4 cm by 4 cm mesh platinum-iridium oxide coated titanium electrode anode (Magneto Special Anodes B V, Netherlands), and an AEM (Membranes International IC., USA, AEM-7001) with effective surface area of 32 cm^2. Both chambers were 8 cm high, 4 cm wide and 1.2 cm thick (38.4 cm^3). A pump (Watson Marlow Sci 323) was used to supply the electrolytes at a flow rate 85 mL min^{-1} (90 RPM) through the reactor with anolyte and catholyte individually recirculated to external reservoirs (see Fig. 1). The reservoirs were vented to maintain atmospheric pressure.

3.0 RESULTS AND DISCUSSION

Figure 1 shows that the electrochemical system removes iron, aluminium, magnesium and sulphate, while levels of sodium and calcium remain constant. The modelling results show some discrepancies with the experimental data that could be due to inaccurate chemical databases (Parkhurst et al., 2013) and the complex solutions with high ionic strength requiring a model accounting for more complex activity correlations (Parkhurst et al., 2013; Thompson Brewster et al., 2017). Lime addition displays similar removal efficacy compared to ECR treatment. However, towards the high end of the pH range Ca concentrations in the liquid phase increase.

For both Site 2 and Site 1 AMD, all 3 treatment options removed nearly all listed contaminants to meet these guidelines, except for sulphate and manganese and with lime treatment Al in Site 2 and Pb in Site 1 (Table 1). For Site 2, the lime treatment removed 23-26% more sulphate compared to electrochemical treatment. For Site 1, ECR treatment removed the most sulphate by approximately 14-25% compared to lime. In both cases, NaOH chemical treatment did not considerably diminish the sulphate concentration. Lime and electrochemical treatment were similar overall. However, lime treatment had two exceptions in meeting the discharge guidelines. Sulphate levels from all the experiments did not meet discharge guidelines. It is likely that with further work an improved electrochemical configuration (e.g. different membrane type, current density, flow rate and/or chamber size) could improve sulphate removal during electrochemical treatment.

Figure 2 AND 3 shows the variation in sludge composition at the different pH stages. These graphs clearly illustrate the possibility of producing solid products with targeted composition dependent on the pH stage. Differences in staged composition are largely dependent on the initial composition of the AMD. The variation in bar colour highlights the precipitation of Fe, Al, Zn, Mg and Mn with increasing pH stages (Fig. 2). The maximum concentrations of REYs occur between a specific pH of 5 – 7 and is consistent between the two types of AMD (Fig. 3). The highest concentration REYs are Yttrium (Y), Neodymium (Nd), Cerium (Ce), Gadolinium (Gd), Dysprosium (Dy) and Samarium (Sm). Also detected in lower concentrations were Erbium (Er), Europium (Eu), Holmium (Ho), Lutetium (Lu), Praseodymium (Pr), Terbium (Tb), Thulium (Tm) and Ytterbium (Yb). In the dried solids, metals recovered during the chemical experiments were found in lower concentrations compared to metals in the electrochemical experiments, indicating that an electricity-driven process can increase the concentration of metals. More important, in all cases, the electrochemically-generated solids had a higher REYs percentage composition compared to chemically-generated solids (data not shown).

4. FUTURE WORK

Based on the results obtained, further improvement of the proposed electrochemical treatment will focus on the selectivity and concentration of REYs to improve the economic feasibility of the process and to meet sulphate discharge standards in case this is required.
The proposed potential alternatives towards the effective recovery of REYs are:
1. Use of sulphate rich stream from the electrochemical system, to produce sulphide that can be used for the precipitation of major metals (Al, Fe, Zn, Cu etc.). Sulphide is an excellent chemical to remove metals from waste streams because it allows the formation of insoluble salts, even at low metal concentrations and low pH solutions and allows easier reprocessing. Additional advantage is that REEs and PGM can keep dissolved in the effluent due to the low affinity for sulphide. As a step forward, the use of a bioreactor for sulphide production by biological sulphate reduction can increase the economic and environmental sustainability of the metal recovery (Fig. 4). Main reasons are that it eliminates the costs associated with the

acquisition of sulphide reagents, it uses the sulphate already present in the AMD and finally, it allows the production of sulphide on-site, thus avoiding transportation of a hazardous chemical.(Villa-Gomez & Lens, 2017)

2. Use of the sulphuric acid produced by the electrochemical system for selective leaching of REYs (Fig. 4). Sulphuric acid is commonly applied as leaching agent in copper-cobalt, nickel and uranium industries. Recently, the use of sulphuric acid for leaching of REEs on minerals used in primary REE production such as bastnaesite and monazite has been evaluated [15]. However, the use of sulphuric acid on hydroxides sludge for REEs recovery has not been assessed. Nevertheless, using this acid to leach REEs and PGMs from the metal hydroxide precipitates can be feasible, since REEs and PGMs can be co-precipitated or sorbed on the surface of metal hydroxides and adding acid can help to release them. The key point to optimize the leaching process is to find a way to increase the purity of the dissolved product. By tuning the concentration of the added acid, load and leaching time, the REEs and PGMs could be dissolved completely by the diluted sulphuric acid produced int he AEM system, while the major metals such as iron could remain in the sludge.

Table 1. Treated water quality, a comparison of electrochemically treated (ECR), sodium hydroxide chemical dosing (NaOH) and lime dosing (lime). Shaded values are higher than at least one of the guidelines

	Site 1				**Site 2**				**ANZECC 2000 guidelines**	
Element (mg L^{-1})	**Original**	**ECR**	**NaOH**	**Lime**	**Original**	**ECR**	**NaOH**	**Lime**	**Stock water***	**Recreational purposes****
Al	2317	0.6	0.03	0.7	443	0.6	0.3	5.1	5	0.2
B	0	2.7***	0	0	0.7	0.8	0.6	0.6	5	1
Cd	0.1	0	0	0	0.1	0	0	0	0.01	0.005
Ca	364	234	354	442	368	367	377	489	1000	Not listed
Cr	0.02	0	0	0	0.3	0	0	0	1	0.05
Co	5.2	0	0.01	0.06	3	0.01	0.05	0.02	1	Not listed
Cu	65	0.03	0.05	0.07	9	0.2	0.5	0.4	0.4	1
Fe	66	0	0	0	324	0.3	0	0.09	Not sufficiently toxic	0.3
Pb	6.2	0.1	0.07	0.1	1.3	0.01	0.06	0.05	0.1	0.05
Mg	4564	1022	2148	1188	715	318	245	7.4	2000	Not listed
Mn	245	0.8	0.2	0.2	63.4	0.9	0.7	0.1	Not sufficiently toxic	0.1
Ni	2.1	0	0	0	4.7	0.01	0	0	1	0.1
Zn	55	0	0	0	106	0.3	0.03	0.1	20	5
SO_4-S	29 547	4962	27 938	5769	9391	4195	8597	3099	1000	400

*** Boron increase due to the experimental choice of anolyte (sodium borate) and will not be present during continuous operation

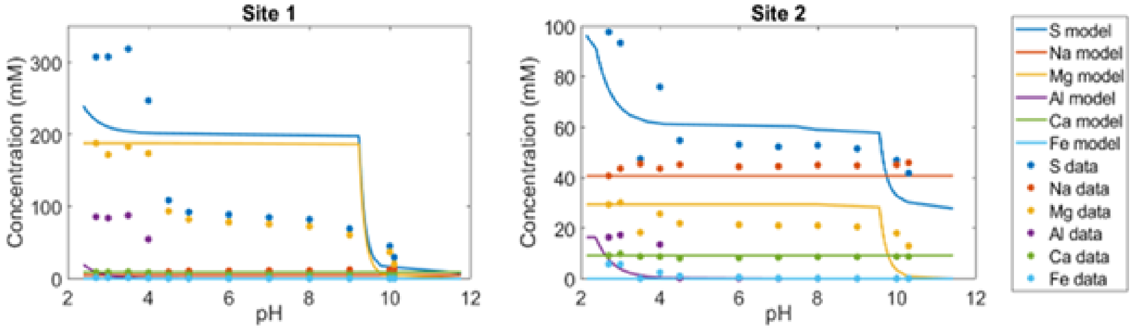


Fig. 1. Experimental (markers) and modelled (lines) contaminants in the liquid phase during electrochemical treatment of acid mine drainage.

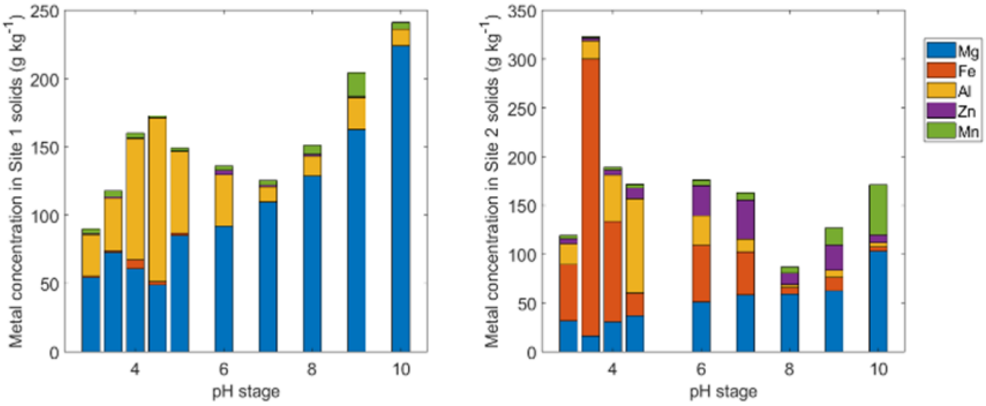


Fig. 2. Solids composition of key major metals at increasing pH stages. Left: results Site 1. Right: results Site 2.

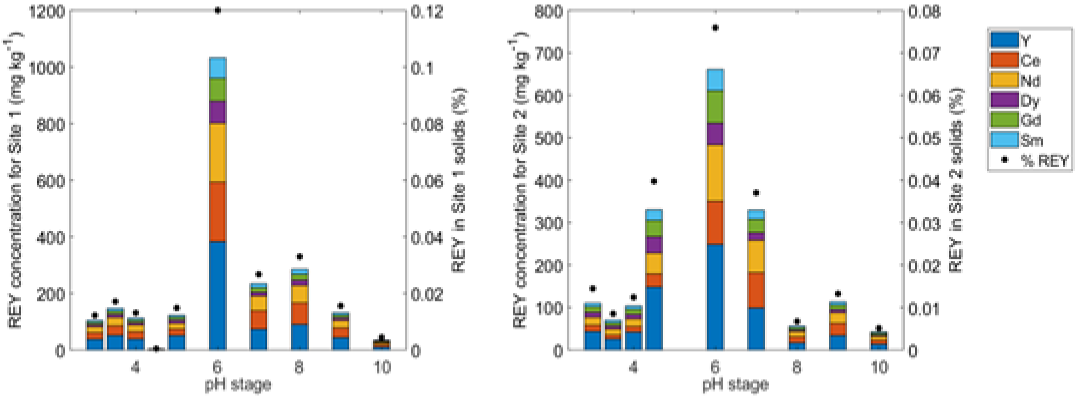
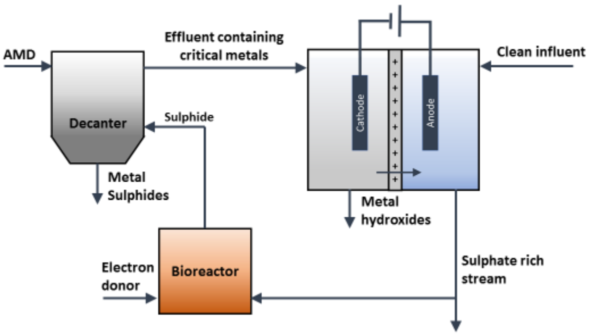


Fig. 3. Solids composition of rare earth element oxides at varying pH stages. The gap between the presented REYs and the total percentage is comprised of Er, Eu, Ho, Lu, Pr, Tb, Tm and Yb. Left: results Site 1. Right: results Site 2.



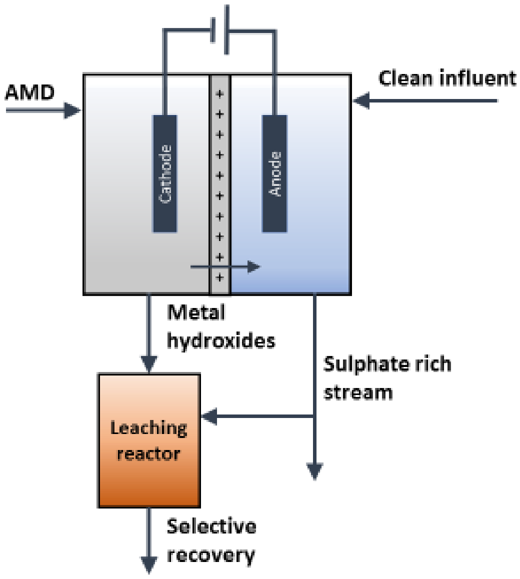


Fig. 4. Proposed potential alternatives that can be integrated to the electrochemical system: Left: bioreactor for sulphate reduction Right: leaching reactor.

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RECOVERY OF VALUABLE HEAVY METALS DURING NEUTRALISATION OF ACID AND METALLIFEROUS DRAINAGE (AMD)

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EXTENDED ABSTRACT

AMD frequently contains substantial concentrations of valuable heavy metals, particularly copper and zinc, and if these can be recovered during AMD neutralisation as usable minerals, they could be sold to offset the cost of the treatment, providing both economic and environmental benefits. For example, an AMD discharge of 50 L/sec with 100 mg/L Cu contains ~155 t Cu/yr; if this could be recovered, at the current copper price of ~US$10,000/tonne, it would be worth ~A$2 million/year (although this requires treatment of ~1500 ML/yr).

Standard AMD neutralisation with Ca(OH)2 causes precipitation of a mixture of metal hydroxides (±sulphate), mostly ferrihydrite/ schwertmannite and gibbsite/hydrobasaluminite, with adsorbed heavy metals. To recover the valuable heavy metals requires separation from the relatively valueless Fe and Al which dominate the composition of the AMD precipitate; any separation process should preferably be simple and easily added to the standard neutralisation procedure at AMD treatment sites.

Sanchez-Espana and Reyes (2019) suggested that different heavy metals are adsorbed to ferrihydrite/schwertmannite and gibbsite/hydrobasaluminite, offering the potential to separate these metals by desorption. Alternatively it may be possible to precipitate the metals separately using pH control.

This research investigated both these processes using bench-top experiments using synthetic AMD with a pH of 2 containing Fe (350 mg/L), Al (150 mg/L), Cu (50 mg/L) and Zn (20 mg/L), neutralised by progressive addition of Ca(OH)2.

Initial experiments using Fe as Fe2+ showed that all the metals precipitate over much the same pH range (Fig. 1), with individual metals precipitating at consistent pHs (Fe: 3.5-6, Al: 3.5-5, Cu: 4-5.5, Zn: 5-6). Fe and Al generally precipitated as ferrihydrite and gibbsite rather the sulphate-containing species schwertmannite and hydrobasaluminite. Experiments without Al showed that the Cu and Zn were adsorbed onto ferrihydrite, as has been previously demonstrated (e.g. McDonald et al. 2006).

The results did not confirm Sanchez-Espana and Reyes' (2019) findings that Cu and Zn were adsorbed by hydrobasaluminite during AMD neutralisation, probably because in their experiments ferrihydrite precipitated at a low pH and hydrobasaluminite precipitated rather than gibbsite, due to the more oxidising conditions and higher SO4 concentrations.

Desorption experiments were then carried out; these showed that both Cu and Zn can be desorbed from ferrihydrite by dropping the pH, as previously demonstrated by McDonald et al. (2006), but only a small percentage is released before the Fe and Al hydroxides start to dissolve. This suggests that further experiments on releasing metals adsorbed to ferrihydrite/schwertmannite and gibbsite/hydrobasaluminite are unlikely to yield useful results.

In the second set of experiments dissolved Fe was oxidised entirely to Fe3+ using H2O2 so that the Fe precipitated at relatively low pH in order to alter the precipitation sequence of Fe and Al (Seo et al. 2017). The results showed that both Fe and Al were completely removed by pH 5.3 (Fig. 2), leaving Cu and Zn in solution. Raising the pH to 7 formed a blue-green precipitate of Cu and Zn, probably as hydroxides/carbonates, along with gypsum.

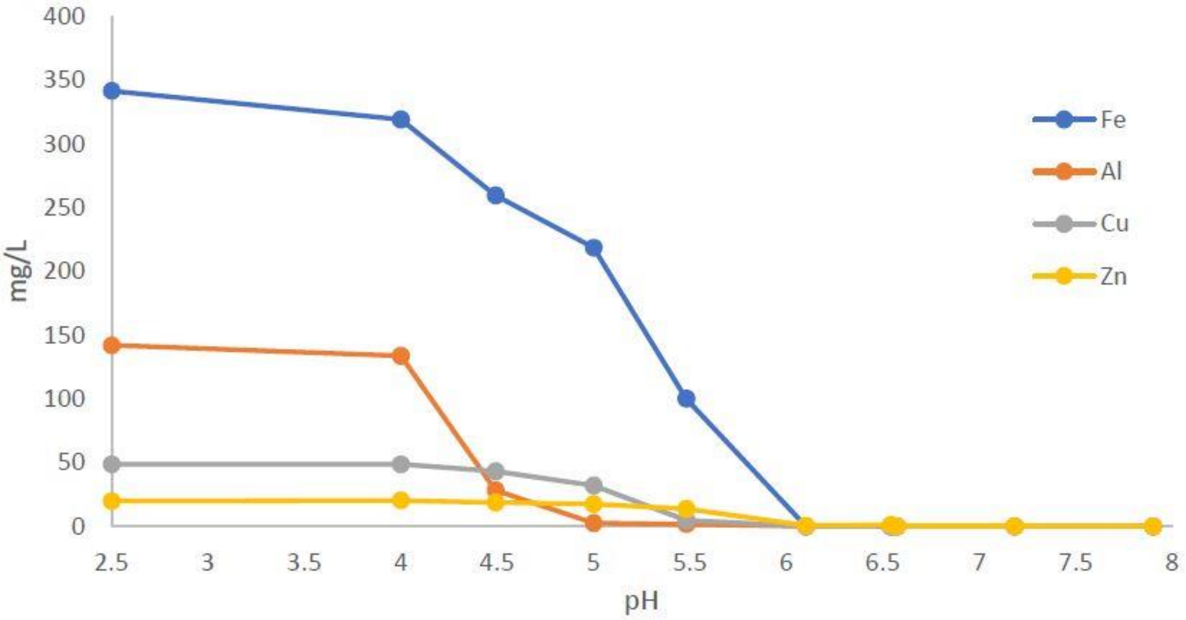

Figure 1. Neutralisation of synthetic AMD containing dissolved Fe as Fe2+.

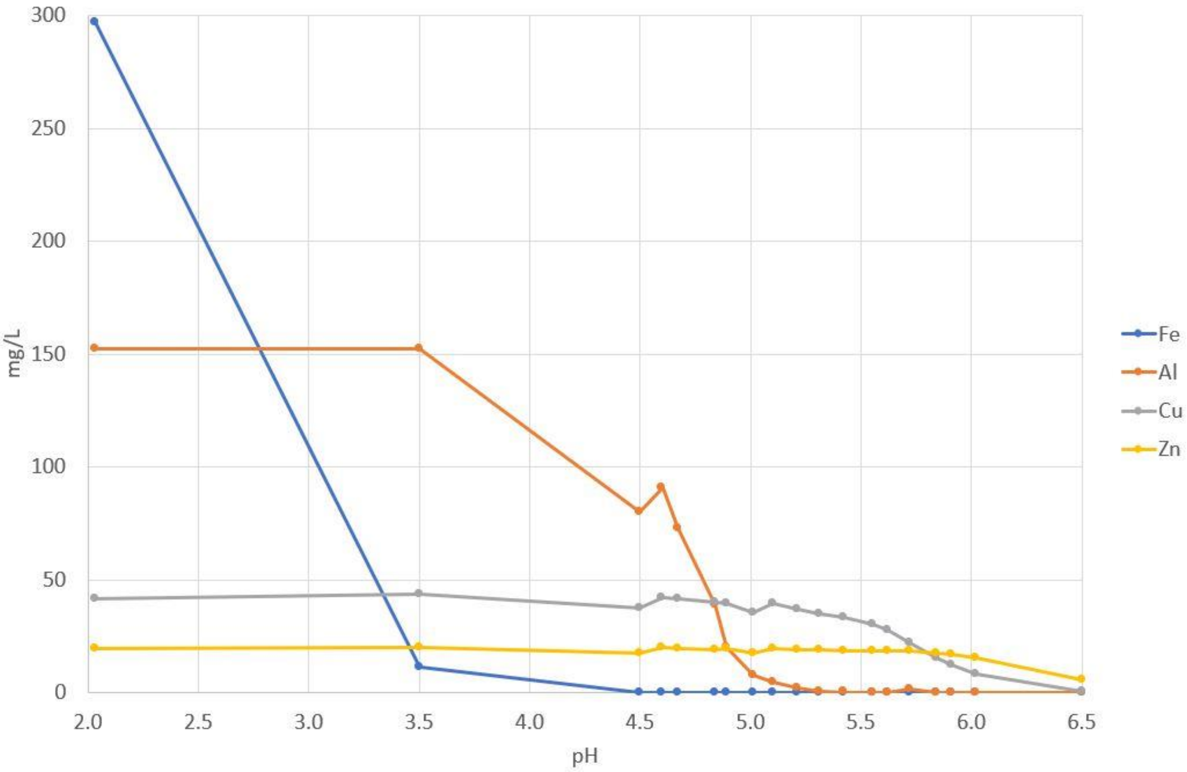

Figure 2. Neutralisation of synthetic AMD containing dissolved Fe as Fe3+.

Although the high Cu and Zn content of this precipitate means that it is potentially saleable, the mineralogy is not immediately amenable to separation of the Cu and Zn, and the gypsum could be a problem.

The next experiments will investigate the cheapest and easiest way to precipitate the Cu and Zn as sulfides. Precipitation as sulfides has many advantages: lower solubility, fast reaction rates, improved settling properties and the potential for the direct use as smelter feedstock (Lewis 2010). Some difficulties may need to be overcome: any excess sulphide is both toxic and corrosive, and the initial metal sulphide precipitates may be colloidal (Veeken et al., 2003).

Separation of the precipitated Cu and Zn sulfides could be achieved by selective precipitation using the controlled addition of S2- and accurate pH adjustment (e.g. Gharabaghi et al. 2012); however this is expensive and requires specific sources of S2- like thioacetamide. Instead we will initially investigate a simpler procedure: precipitating a mixture of Cu and Zn sulfides by direct addition of S2- as Na sulfide. This mixture has the potential to be later separated by the standard metallurgical procedure of flotation (provided the precipitate grains are single sulfides and not intergrown).

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MINE PIT LAKES: CHARACTERISATION OF WATER QUALITY AND GEOCHEMISTRY TO INFORM MINE CLOSURE

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ABSTRACT

Western Australia has more than 2000 mine voids, many of which fill with water when dewatering of the void is discontinued after mining ceases. The geochemistry and environmental impact of the pit lakes that form is not well understood, particularly in arid environments with high net evaporation. In a project funded by CRC CARE and MRIWA we have been compiling the first comprehensive database of mine pit lakes water quality in Western Australia. A systematic analysis of current mining operations in Western Australia resulted in a shortlist of mines to target for inclusion in the study. Pit lakes of a variety of ages and environmental conditions, and from a variety of representative geologies, mineralogies and hydrogeological situations have been sampled, providing a "time capsule" of how future systems are likely to behave. The water quality of each mine pit lake was measured at regular depth intervals throughout the water column, in order to identify oxic and anoxic regions within each pit lake. Analysis of water samples include field measurement of water quality parameters (e.g. pH, oxidation/reduction potential, conductivity), and laboratory anlysis of wide suite of major and trace elements, nutrients, salinity, turbidity and dissolved organic carbon. This water quality analysis has been complemented by comprehensive analysis of representative pit wall rock and sediment samples from each pit lake, as well as data mining of existing water quality databases sourced from project collaborators (CSIRO and DWER) and industry participants. Data collected to-date has highlighted the varied methods that industry is currently employing to assess pit lake quality, reinforcing the need for support tools to inform environmental impact assessment. The dataset provides validation for current practices in geochemical modelling, and enables development of new lab-based decision support tools and better guidance for mine closure.

1.0 INTRODUCTION

Mine pit lakes form in deep open pit mining voids after the end of mining and associated pit dewatering. Over time, groundwater, rainwater and surface run off accumulate in the void, leading to the formation of a permanent lake. The impact of this lake on the local environment will depend on how deep the pit lake becomes, and its water quality (McCullough, 2011). Potential risks and impacts of poorly managed pit lakes include contamination of local and regional groundwater bodies, poor vegetation health, and adverse effects on fauna that use the pit lake as a drinking water source. Alternatively, pit lakes can be managed to provide numerous benefits, including storage of process water for mining operations, storage of waste rock or tailings as a management option for waste, or providing new sites for recreation, irrigation, aquaculture, livestock drinking water or wildlife habitat.

Western Australia has more than 2000 mine voids, and more than 150 mines operating below the water table (Johnson and Wright, 2003). However, there are gaps in the current knowledge of the pit lake geochemistry, particularly in arid environments with high net evaporation, which commonly occur in the Pilbara, Kimberley and Goldfields. Mine pit lake water quality evolves for many years past mine closure, which makes regulation and management of these legacy sites challenging. Mine closure plans typically use geochemical models to make long-term predictions but greater confidence is needed in both the predictive models, and the input data used for modelling (Oldham, 2014). Both government and industry need informed policy and guidance on which data should be collected and which methodologies should be employed to better inform predictions of long term environmental impacts.

Geochemical processes that can occur in a mine pit lake are illustrated in Figure 1. Many pit lakes in WA are characterised by high salinity because evaporation rates are high compared to surface runoff flows and rainfall, and the underlying groundwater is often saline as well. However, the effect of salinity on metal leaching from rock materials is poorly understood. Acidification can also occur in pit lakes when sulphides in the pit walls oxidise, resulting in acidic and metalliferous drainage collecting in the pit lake. pH is a major determinant of solubility for many minerals, and thus will also control concentrations of dissolved metals and metalloids in the pit lake water.

ChemCentre is collaborating with CSIRO and WA government agencies to characterise mine pit lakes for *in situ* metal recovery opportunities and cost-effective environmental management. As part of this study we aim to comprehensively assess the water quality of representative mine pit lakes, resulting in the first comprehensive database of mine pit lake water quality in Australia. Pit lakes of a variety of ages and environmental conditions, and from a variety of representative geologies, mineralogies and hydrogeological situations are being studied, effectively providing a “time capsule” of how future systems are likely to behave. The dataset provides “in the field” evaluation for current practices in geochemical modelling, and enables development of new lab-based decision support tools, and enable better guidance for mine closure.

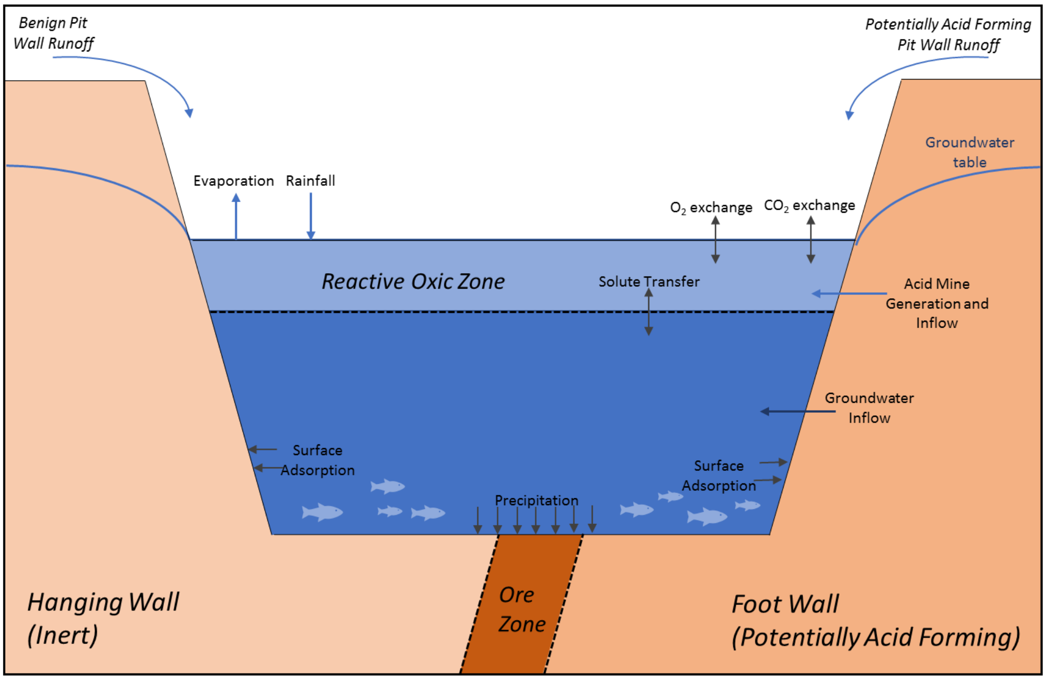

Fig. 1. **Conceptual geochemical model of a pit lake system**

2.0 METHODOLOGY

2.1 Study Sites and Classification

A systematic analysis of current mining operations in Western Australia resulted in a shortlist of mines to target for inclusion in the study. All major commodities mined in Western Australia and all major mining regions were considered. Initially mines were classified based on region and commodity (Table 1). However, while some regions and commodities were well represented, a number of commodities and regions would not achieve a sufficient number of samples for representative sampling.

Table 1. Classification of mine participation based on commodity and region. Note: mines may have more than one pit lake

Region	Gold	Nickel	Copper	Iron	Other	Overall
South West	0	0	0	0	2	Insufficient
Goldfields	6	3	0	1?	0	>5 likely
Murchison	6	2	1	0	1	> 5 likely
Pilbara		1	2	1	1	> 5 unlikely
Kimberley			1		1	Insufficient
Overall	> 5 likely	> 5 unlikely	> 5 unlikely	Insufficient	• N/A	

An alternative set of criteria was therefore proposed, considering underlying geology and groundwater salinity, as described in Table 2. The salinity criteria were based on a classification of water quality according to total salt concentration, devised by Hillel (2000), and previously applied to stream salinity in Western Australia (Mayer et al., 2005).

Table 2. Proposed criteria for grouping pit lakes, based on underlying geology and groundwater salinity

Geology Criteria	Groundwater Criteria
1. Sedimentary sequences – sandstone shale, banded iron formations, typically with low buffering capacity 2. Igneous mafic and ultramafic rocks (e.g. dolerite, basalt, gabbro) , typically weathered to 50 m 3. Other, including volcanic massive sulphide (VMS) deposits, dominated by volcanic or volcanic-derived rocks, associated with felsic volcanic rocks	1. Fresh/Brackish/Moderately Saline <500-5000 mg L^{-1} 2. Saline to Highly Saline 5000-35000 mg L^{-1} 3. Hypersaline/Brine >35000 mg L^{-1}

Table 3 shows that, using this classification system, overall comparisons should be possible for salinity, as well as sedimentary and igneous geologies. However, not all sub-categories have sufficient numbers of samples for appropriate statistical comparison. Therefore it was decided to focus on sampling for the following five sub-categories, which were considered most representative for Western Australia: Sedimentary: Fresh and Saline, and Igneous: Fresh, Saline and Hypersaline.

Table 3: Classification of mine participation based on geology and groundwater salinity. Note: mines may have more than one pit lake

Region	Fresh/Brackish	Saline/Highly Saline	Brine	Overall
Sedimentary	4	2		6
Igneous	7	7	6	20
VMS and Other	3			3
Overall	14	9	6	29

2.2 Sampling and Analysis

A detailed sampling plan was developed for each pit lake, utilising existing historical data, to determine the best sampling location for each pit lake. Historical data was also used to identify rock lithologies that were the most representative of the floor and walls of the pit lake, and nearby water bodies (e.g. ground water or natural lakes) that could also be sampled.

Typically, there were no water inputs to each pit lake, other than groundwater flow and run-off. For most pit lakes studied so far, it was assumed that there would be low horizontal spatial variability in chemical concentrations, but some variations with depth, and that surface water samples may not represent the whole water column (Zhao et al., 2010). Therefore, for most pit lakes, water samples were collected at a single location, typically using a Niskin or Van Dorn bottle sampler, at the deepest point in the lake to ensure deep stratification layers (e.g. the monimolimnion) were sampled. Generally, between 5 and 7 samples for each pit lake were collected every 5 or 10 m through the water column, depending on the water depth. For quality control, a duplicate sample was taken at one of the middle depths for most pit lakes. Samples were collected using appropriate sampling containers, and kept cool (in an ice box) during transport back to the ChemCentre. Field measurements were recorded for each sample using portable meters for pH, conductivity, temperature and oxidation-reduction potential (ORP). Samples for dissolved metals and organic carbon were also filtered through 0.45 µm membrane filters in the field. In addition to water samples, rock samples and sediment samples were also collected and analysed for each site. These samples will be discussed in a later publication.

Water samples were analysed for a consistent suite of chemicals (Table 4) that was informed by previous recommendations for mine pit lake sampling (Zhao et al., 2010) and requirements for geochemical modelling (Salmon et al., 2008; Salmon et al., 2017). Additional speciation analyses was also undertaken for some samples, where historic data indicated that Cr, Se or As would be greater than a relevant default guideline value for moderately disturbed freshwater systems (95% species protection) from the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018). Gravimetric total dissolved solids (TDS) was also measured when conductivity was greater than 8000 mS/m (approx. TDS 56 000 mg L^{-1}), as correlating TDS to conductivity is difficult for hypersaline samples. Finally, a rare earth element (REE) suite (Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) was included for sites with expected enrichment of REE, based on historic data or mineralogy.

Analysis at ChemCentre was performed in accordance with accepted international analytical methods, Australian standards, or specialised in-house methods, under a Quality Management System certified to ISO 17025 2017. Routine quality controls include replicate analysis of at least every 10th sample, an ongoing external QC control every 20th sample, the use of matrix matched certified reference materials with every analytical batch (where possible), fortified sample matrix spikes with every analytical batch, and method blanks.

Table 4: Chemical analysis and field measurements for each pit lake

Standard analytical suite for all samples
pH, conductivity, turbidity
fluoride, chloride, dissolved organic carbon, total dissolved nitrogen, alkalinity
Dissolved metals and metalloids by ICP-AES or ICP-MS (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pt, Pd, Rb, S, Sb, Sc, Se, Si, Sn, Sr, Th, Ti, Tl, U, V and Zn)
Speciation analysis for select samples
Chromium (VI) when total Cr >1 µg L^{-1}, the default guideline for Cr(VI)
As (III) and As (V) when total As >13 µg L^{-1}, the default guideline value for As(V)
Se (IV) and Se (VI) when total Se > 11 µg L^{-1}, the default guideline value for total Se

3.0 RESULTS AND DISCUSSION

3.1 Summary of Mine Pit Lakes Sampled To-Date

Thirteen mine pit lakes were sampled during 2019. A similar number of pit lakes is anticipated for sampling in 2020, with an aim to sample approximately 25 mine pit lakes during the project. Table 5 classifies the pit lakes sampled to date by geology and groundwater salinity. The focus for 2020 will be to target additional pit lakes that will allow sufficient sampling in each target sub-category.

Table 5: Pit lakes sampled in 2019 classified by geology and groundwater salinity

Region	Fresh/Brackish	Saline/Highly Saline	Brine	Overall
Sedimentary	4			4
Igneous	3	1	5,	9
VMS				
Overall	7	1	5	13

3.1 Overview of Mine Pit Lake Water Quality

To-date, full water quality characterisation has been completed for 10 of the 13 pit lakes sampled, with data for the other pit lakes expected in early 2020. The 10 pit lakes ranged in water depth from 8 to 60 m, with a median depth of 22.5 m. The pit lake age, defined as the time since mining ceased, ranged from 1.5 to 47 years, with a median age of 17.5 years.

3.1.1 Changes in water quality indicated by depth profile field measurements

Figure 2 shows depth profiles of conductivity, temperature, pH and ORP for the 10 pit lakes. Typically, profiles of pH, conductivity and ORP were constant through the water column, which would suggest that most pit lakes were homogenous with depth at the sampling point. Temperature (Fig. 2b) generally decreased with depth, with more dramatic decreases for PL 1 and PL 3 suggesting that density stratification due to temperature changes could be in effect in these pit lakes. Only one pit lake (PL 6, classified as igneous and hypersaline) showed variations in conductivity, with much lower conductivity (~2500 mS m^{-1}) measured in the top 5 m of the pit lake, compared to the bottom 20 m, which had a conductivity of 20500 mS m^{-1}. Groundwater in this area is known to be around 200000 ppm TDS (~12500 mS m^{-1}), which suggest a lens of fresh water, presumably from rain runoff, sits upon the hypersaline groundwater. The stratification in PL 6 also affected pH (~6.5 in the lower layer compared ~ pH 8.5 in the top 5 m) and temperature, with the lower layer (~38 °C) much warmer than the surface waters (~26 °C), but ORP only decreased slightly with depth in the water column. PL 6 is directly next to PL 5, sharing common groundwater and geology, but PL 5 had constant conductivity (20425 mS m^{-1}) and pH (~6.5) with depth, suggesting the local geomorphology does not concentrate run off in the same manner in this pit lake. However, ORP increased with depth in P L6, with higher values (26-34 mV) at depth than in the surface water (-77 mV). Typically ORP, would be considered to be highest at the surface, where oxygen can readily dissolve in the water, before becoming depleted at depth (Stumm and Morgan, 1996). The ‘reverse’ pattern in PL 5 would suggest another species is controlling redox in this system, or than redox reactions are not in equilibrium (Stumm and Morgan, 1996). A similar pattern of higher ORP at depth compared to the surface was seen for PL 1 (classified sedimentary fresh). While PL 1 had relatively constant conductivity and pH with depth, the temperature profile suggests density stratification may exist.

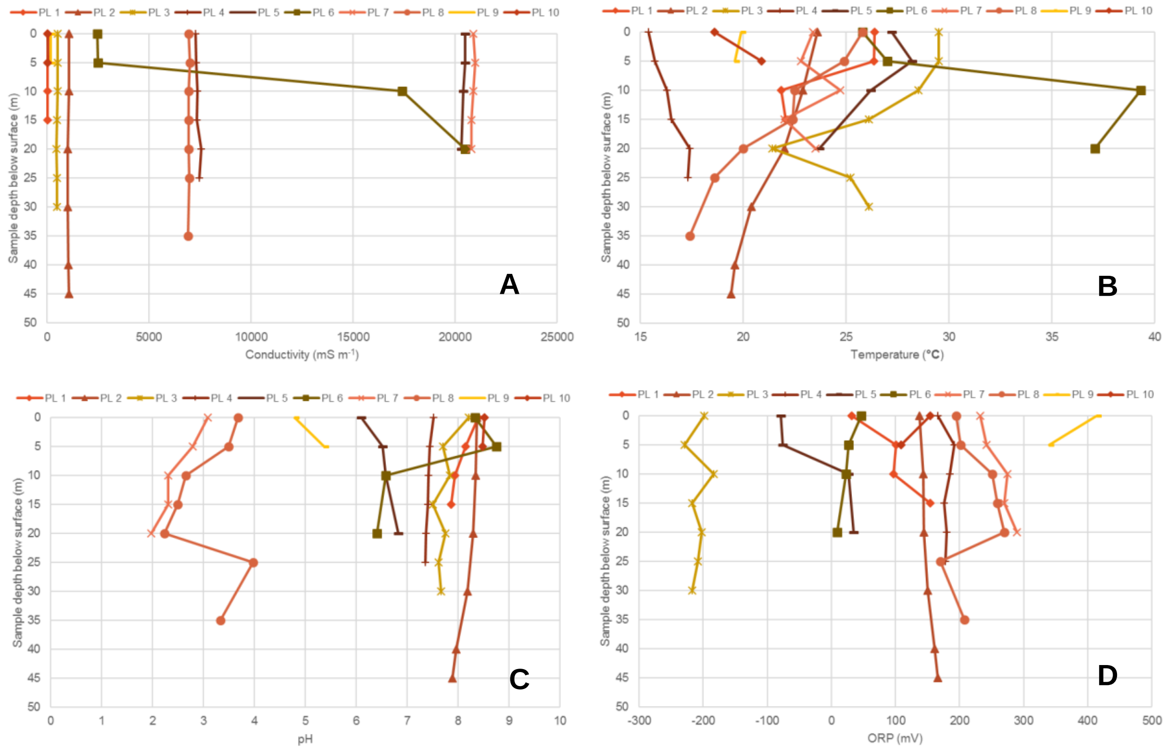

Fig. 2. **Depth profiles of a) conductivity; b) temperature; c) pH; d) ORP in sampled pit lakes**

PL 8 (classified as igneous and hypersaline) also did not show stratification with respect to conductivity, however changes in temperature, pH and ORP in the bottom 10 m suggested there was a denser unmixed layer at the bottom of this pit lake. PL 3 (igneous and fresh) was the deepest pit lake sampled in this study to-date (60 m), however only the top 30 m were sampled. There was consistent pH, ORP and conductivity with depth for this pit lake, while temperature decreased slightly.

3.1.2 Comparison of water quality in surface and bottom waters

The range of values for surface and bottoms waters over all pit lakes is reported in Table 6. Generally, there was little difference in the range of values reported over all 10 pit lakes, with typically minor variation within individual pit lakes. Values for some analytes varied widely between pit lakes, with further analysis of individual pit lakes required.

3.1.3 Screening assessment of health and environmental risk of mine pit lakes

Table 6 compares aggregate data for surface and bottom waters for the pit lakes to several water quality guidelines:

- Australian Drinking Water Guideline (ADWG) human health limits, with aesthetic quality limits presented in parentheses.(NHMRC and NRMMC, 2011)
- Livestock drinking water quality limits related to cattle (ANZECC and ARMCANZ, 2000).
- Long term trigger values (up to 100 years) for irrigation of crops and pastures (ANZECC and ARMCANZ, 2000).
- Generic assessment criteria developed by WA Department of Health (DoH, 2014) to evaluate and manage chemicals in ground or surface water in suspected or known contaminated sites This value is generally 10 times the corresponding ADWG health value, or equal to the ADWG aesthetic value.
- Trigger values for protection of 95% freshwater aquatic ecosystems for slightly to moderately disturbed systems, such as that in existing rural land use (ANZG, 2018). For those parameters that are not considered toxicants, the default value guideline for physical and chemical stressors is presented instead.

Typically, the lowest guideline values were for 95% environmental protection, with 79% of guideline values (15 of 17 reported guidelines) exceeded in at least one or more pit lakes. In contrast less than 30% of guideline values were exceeded for the livestock (5 of 17 reported guidelines) and non-potable groundwater guidelines (6 of 21 reported guidelines).

Arsenic and nickel were present in at least one pit lake at concentrations that are higher than all five water quality guidelines, while uranium, boron, selenium, manganese, chloride and sulphate) exceeded three or more guidelines in at least one pit lake. This suggests these analytes are more likely to exceed guidelines for mine pit lake water quality, however further analysis of individual pit lakes is required to confirm these analytes as potential indictors.

Table 6: Comparison of surface and bottom waters to relevant health and environmental water quality indicators. All values reported are mg L^{-1}. Values based on aesthetic quality, rather than health or environmental effect, are presented in parentheses. Values in bold indicate water from one or more pit lakes exceeded this guideline.

Parameter	Surface water Range	Bottom sample Range	ADWG	Livestock	Irrigation	Non-potable groundwater	95% Aquatic Ecosystem Protection
Aluminium	<0.0005-0.08	<0.0005-0.08	(0.2)	5	5	(0.2)	**0.055 (pH > 6.5)**
Arsenic	<0.001-0.61	<0.001-0.64	**0.01**	**0.5**	**0.1**	**0.1**	**0.013 as As(III)**
Barium	<0.02-0.26	<0.02-0.21	2			**20**	
Beryllium	<0.0001-0.0003	<0.0001-0.0003	0.06	[e]	0.1	0.6	
Boron	0.08-15	0.06-15	**4**	**5**	**0.5**	40	**0.37**
Cadmium	<0.0001-0.006	<0.0001-0.0058	**0.002**	0.01	0.01	0.02	**0.0002**
Calcium	4.3-720	4.4-706	**(80)[a]**	1000			
Chromium	<0.0005-0.0069	<0.0005-0.0066	0.05	1	0.1	0.5	**0.001**
Cobalt	<0.0001-0.044	<0.0001-0.048		1	0.05		0.0014[c]
Copper	<0.0001-0.034	<0.002-0.031	2 (1)	1	0.2	20	**0.0014**
Gold	<0.0001-0.014	<0.0001-0.013					
Iron	<0.05	<0.05	(0.3)	[d]	0.2	(0.3)	
Lead	<0.0001-0.0007	<0.0001-0.0006	0.01	0.1	2	0.1	0.0034
Magnesium	6.8-15100	6.9-14600	[a]	[d]			
Manganese	<0.0001-2.7	<0.0001-2.7	**0.5 (0.1)**		**0.2**	5	**1.9**
Molybdenum	<0.001-0.016	<0.001-0.016	0.05	0.15	**0.01**	0.5	0.034[c]
Nickel	<0.001-19	<0.001-19	**0.02**	**1**	**0.2**	**0.2**	**0.011**
Selenium	<0.001-0.02	<0.001-0.018	**0.01**	**0.02**	**0.02**	0.1	**0.011**
pH	3.0-8.5	2.0-7.9	**6.5-8.5**				**6-9[f]**
Sodium	38.9-104000	36.5-103000	**(180)**		**115-460**	**(180)**	
Uranium	<0.0001-0.022	<0.0001-0.022	**0.017**	0.2	**0.01**	0.17	**0.0005[c]**
Vanadium	<0.002-0.055	<0.002-0.048		[e]	**0.1**		**0.006[c]**
Zinc	<0.001-2.3	<0.002-2.4	(3)	20	**2**	(3)	**0.008**
Nitrate as NO$_3$	4.9-94	4.2-88	**50**	400		500	**0.044[f]**
Dissolved Total N	0.24-31	0.35-28			**5**		**0.35[f]**
Fluoride	0.1-1.5	0.1-1.5	1.5	2	**1**	15	
Dissolved TP	<1	<1			0.05		0.01[f]
Sulphate as SO$_4$	19.2-17600	19.1-17300	**500 (250)**	**1,000**		**5,000**	
Cl	51-180000	47-180000	**(250)**		**175-700**	**(250)**	

Notes: [a]Ca and Mg ions are regulated as Hardness in the ADWG, expressed as mg/L CaCO$_3$; [b]All guidelines reported for Cr(VI); [c]The level of protection for this guideline is unknown; [d]Not sufficiently toxic; [e]Insufficient data. [f]Parameter is not considered a toxicant, so a conservative default guideline value for physical and chemical stressors is provided instead.

4.0 CONCLUSIONS

Field data indicates that some pit lakes likely have some temperature-induced density stratification, but this typically had minimal effect on the depth profile of other field parameters (e.g. pH, conductivity, ORP). Only one pit lake showed conductivity-induced density stratification, which had much more significant influence on changes with depth of the other field parameters. Overall the temperature-induced stratification did not cause changes in overall water quality in the bottom waters compared to surface waters, with aggregate ranges over all pit lakes very similar for both top and bottom. Further analysis is required to investigate the effect for individual pit lakes.

A screening risk assessment using a range of health and environmental guidelines indicated that water quality was more likely to impact environmental quality, rather than limit use for livestock or non-potable reuse. Eight analytes (arsenic, boron, chloride, nickel, selenium, manganese, uranium and sulphate) were identified as most likely to be over range in a number of guidelines. Individual screening analysis for each pit lake at depth would be required to determine the potential for individual pit lakes to be used as a water source.

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CLIMATE CHANGE AND THE ASSESSMENT OF ACID AND METALLIFEROUS ROCK DRAINAGE: WHAT ARE THE CONSIDERATIONS FOR OUR TECHNICAL DISCIPLINE?

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ABSTRACT

Pressure to recognise and deal with the implications of climate change is "heating up" in Australia. Loss of property and habitat, water and food security, air quality and health concerns are just some ways climate change influences our everyday lives. But how, or even does, climate change affect the way we undertake acid and metalliferous drainage (AMD) assessments and use the information to complete mine water quality predictions? What are the practical implications of the common statement that climate change will result in higher temperatures and more variable rainfall?

This paper explores the implications of climate change to mine waste management and water quality prediction. A review of guidance documents found Australian-based literature that specifically addresses climate change and the assessment of AMD is lacking. To fill this gap and encourage conversation between mining professionals, this paper presents a summary of potential climate change impacts and their implication to mine waste and water management.

Implications from direct climate change impacts in AMD assessments are largely associated with water quality prediction as an input to mine waste and water management plans. Such impacts reinforce the importance of quantifying "first-flush" concentrations, estimating fluctuations in precipitation, and understanding the hydrological response in mine waste catchments following high rainfall events. Other direct impacts relate to the design of pits, pit lakes, waste rock dumps, tailings storage facilities, covers, water management structures, and water treatment to which AMD assessments are critical inputs. Indirect impacts are mainly financial or social in nature and may influence a mine's capacity to effectively manage AMD risks. Suggestions are provided to direct efforts to address the need for climate change adaptation in AMD assessments as part of best practice.

1.0 INTRODUCTION

Climate change in Australia is predicted to bring more hot days and shifting rainfall patterns, including more intense rainfall events and longer dry periods (CSIRO 2019). Notable impacts on the mining industry, its value chains, and the regional communities that support them are evidenced in recent bushfire and flood events. For example, the 2010/11 floods in Queensland closed or restricted production of 40 out of Queensland's 50 coal mines costing more than $2 billion in lost production (Mason and Giurco 2013). The economic cost of lost infrastructure, temporary closure, and disruption to supply chains by the 2019/20 bushfires is yet to be quantified.

This paper explores the implications of climate change to mine waste management and water quality prediction. It examines guidance documents available in Australia and benchmarks these against similar international publications. A summary of the potential impacts of extreme weather events and longer-term changes in climate on mine waste and water management is provided. The intent is to stimulate dialogue among mining professionals by asking whether we are doing enough to address the challenges of climate change in our assessments and management of AMD and where efforts should be directed to address the need for climate change adaptation in AMD assessments as part of best practice.

2.0 LITERATURE REVIEW

Reviewed guidance documents are broadly divided into two categories:

- AMD guidance documents that mention impacts associated with extreme weather events and longer-term changes in climate; and
- Climate change adaptation documents that mention impacts associated with AMD or more broadly, mine waste and water management considerations.

The documents are discussed below in these terms.

2.1 AMD Guidance

Guidance documents commonly referenced within Australian AMD assessments include the handbook, *Preventing Acid and Metalliferous Drainage*: *Leading Practice Sustainable Development Program for the Mining Industry* (DFAT 2016) and the *Global Acid Rock Drainage (GARD) Guide* (INAP 2009).

DFAT (2016) gives specific recommendations to address potential climate change impacts within the context of:

- Modelling the water balance of pit lakes with recommendation to incorporate "...projected climate change effects out to several hundred years".
- Cover design with recommendation to "...address the potential effect of climate change on input parameters ...given performance needs to be maintained over the long term".

Impacts from extreme weather events were mentioned in case studies but no specific recommendations were made to address these impacts in AMD assessments or mine water quality predictions.

The GARD Guide recognises the general importance of climate in determining mine drainage chemistry. While it does not explicitly address the potential impacts of climate change, the potential effects of extreme weather events are mentioned in relation to water quality prediction (Section 5.3.3), engineered barriers (Section 6.6.6), water covers (Section 6.6.7), and water treatment (Section 8.4.3).

2.2 Climate Change Adaptation

Adaptation of the Australian mining industry to the impacts of extreme weather events and longer-term changes in climate has received greater explicit focus in recent years by mining companies, industry research bodies, and government organisations. Undoubtedly, this surge in effort was stimulated by extreme weather events with measurable economic costs, such as the previously mentioned 2010/11 floods in Queensland.

2.2.1 The Role of Government

The *National Climate Resilience and Adaptation Strategy* (DEE 2015) identifies principles for effective adaptation practice and resilience-building across key sectors, including agriculture, forestry and fisheries, water resources, and natural ecosystems. Impacts on the mining industry are not specifically addressed by the strategy, and by default, fall under the roles and responsibilities of state and territory governments and private industry.

Various state and territory governments have adaptation plans that outline the role of government, including the provision of climate change projections and vulnerability assessments, emergency response to extreme weather events, and coordination with local governments and business. Typically, the plans address impacts on other primary industries such as fisheries, farming and forestry but do not explicitly address impacts on the mining industry. Arguably, the mining industry is vulnerable to the impacts of climate change owing to its reliance on water and energy, and given the typically remote, geographically fixed locations of mining operations. A possible exception may be the forthcoming Sector Adaptation Plan for industry and resources (in development) under the *Queensland Climate Adaptation Strategy 2017 to 2030* (Qld DEHP 2017).

Local governments are important in facilitating effective climate change adaptation in mining communities. In particular, given their functions related to planning and development, transport, water supply, waste treatment, flood mitigation, environmental controls, and emergency management in regional and remote communities (Loechel et al. 2013a).

2.2.2 Industry-based Research

In Australia, the CSIRO and National Climate Change Adaptation Research Facility (NCCARF) reviewed climate change adaptation risks in the Australian mining industry (Hodgkinson et al. 2010; Loechel et al 2013b; Mason and Giurco 2013; Hodgkinson et al. 2014). Looking overseas, the Mine Environment Neutral Drainage (MEND) Program released a high-level risk analysis of climate change and acid rock drainage (ARD) to the Canadian mining industry (MEND 2011). Most recently, the International Council on Mining and Metals (ICMM) released the report, *Adapting to a Changing Climate: Building Resilience in the Mining and Metals Industry* (ICMM 2019). Each of these reports are discussed briefly below.

The CSIRO have produced several mining-related publications under their Climate Adaptation Flagship Program. In 2010, the CSIRO undertook a workshop with mining experts and completed a preliminary review of (then) available literature (Hodgkinson et al. 2010). They concluded that, although most stages of mining are influenced by climate and extremes, the production stage was most at risk from climate change largely owing to concerns of water and energy availability, and health and safety in and around mine workings for mine equipment and personnel. AMD was not specifically addressed but was mentioned as a consideration for potential impacts following mine closure, such as the potential for over-spill from tailings dams during high rainfall events.

The CSIRO also undertook workshops focusing on climate adaptation in the Goldfields-Esperance region of Western Australia and various mining regions in South Australia (Loechel et al., 2013b; Hodgkinson et al. 2014). They identified likely seasonal impacts on the mining value chain from restraints on water and electricity supply, disruptions to road, rail, and port transportation, and changes to the liveability of the region. Again, AMD was not specifically addressed but associated impacts identified by workshop participants included the potential for discharge of tailings and other mine waste following intense rainfall events.

In 2013, researchers from NCCARF assessed the level of readiness of the Australian mining and minerals industry to address climate change adaptation risks, and developed a guide for climate change adaptation and planning for industry professionals (Mason and Giurco 2013; Mason et al. 2013). Their assessment included a desktop literature review, a stakeholder consultation workshop with AusIMM members, and an online survey of end-users and selected interviews. They concluded that:

- There is a strong business case for using adaptive management with a focus on a changing climate within broader risk planning processes.
- The risk assessment and management processes of mining operations are a key concern of local, state, and federal authorities, as well as insurers.

- Mining professionals have key roles to play in meeting the changing expectations of stakeholders by ensuring that operational responses to a changing climate are well grounded in leading practice and current information.

The resulting guide addressed impacts, adaptation measures, and case studies for mines during flooding and storms (including flooding of abandoned mines), drought, and higher temperatures (Mason et al. 2013). In the guide, AMD was mentioned within the context of uncontrolled drainage from abandoned mines and as a consideration when examining options to reduce the footprint of tailings dams, for example, by dry stacking.

MEND (2011) specifically addressed climate change and ARD risks. They concluded that incremental changes in climate will not be sufficient to increase ARD or lead to significant changes in the strategies to prevent ARD during mine operation. Greater concern was expressed for mine closure and post-closure infrastructure required for the perpetual storage of mine waste, noting it “adds” to the existing policy and technical challenges of ensuring the long-term integrity of mine sites post-closure. Many of the conclusions from this report are presented in the following section which discusses the practical implications to mine waste and water management in Australia.

ICMM (2019) undertook a survey of its members and identified the key concerns in relation to climate change adaptation were water management, the performance of facilities with long lifespans where the design criteria may include certain climate-related assumptions (e.g. rainfall), and how climate change may impact closure and post-closure where adaptive management is difficult and/or costly. Similar to Mason and Giurco (2013), the ICMM report encouraged companies to integrate climate change considerations within existing risk management and planning procedures, and to not “…reinvent the wheel”. AMD was not specifically addressed but the report did identify several related factors that would influence AMD assessments, including more stringent water quality regulations and increased public scrutiny as potential consequences of water scarcity.

3.0 GOING BEYOND HIGHER TEMPERATURES AND MORE VARIABLE RAINFALL: PRACTICAL IMPLICATIONS TO MINE WASTE AND WATER MANAGEMENT

Table 1 lists a summary of potential impacts from extreme weather events and longer-term changes in climate to Australian mines and their implication to mine waste and water management. The summary has been compiled based on literature (Section 2.0) and from the author’s own personal observations and discussion with colleagues from the last 12 years working within the Canadian and Australian mining industries.

In summary, direct impacts on AMD assessments are associated with water quality prediction as an input to mine waste and water management plans. Temperature increases up to 3.5°C are insufficient to cause a measurable impact from increased sulphide oxidation rates (MEND 2011). However, longer dry periods and droughts will lead to greater accumulation of secondary oxidation products in mine wastes emphasising the importance of quantifying “first-flush” concentrations, in addition to average or “stable” element release rates determined by kinetic testing (Nordstom 2009; Maest and Nordstrom 2017).

Water quality predictions, particularly those evaluating post-closure scenarios where the potential for offsite discharge cannot be managed actively, may be improved by estimating fluctuations in precipitation (for example, by using non-stationary geostatistical methods presented by Tallon et al. 2015) and moving away from reliance on mean annual precipitation values. Evaluating the downstream impact of first-flush concentrations requires consideration of a waste facility’s hydrological response to high rainfall events (i.e. seepage flows and duration) and the interaction between surface discharges and shallow groundwater environments common to many arid and semi-arid areas of Australia which is not necessarily captured in siloed assessments of surface versus groundwaters.

Other direct impacts relate to the design of pits, pit lakes, waste rock dumps, tailings storage facilities, covers, water management structures, and water treatment to which AMD assessments are critical inputs.

Indirect impacts are mainly financial or social in nature and may influence a mine's capacity to effectively manage AMD risks. Such potential impacts should be considered within existing risk management and planning procedures, and include:

- Increased periods of care and maintenance in response to unforeseen capital expenditure following extreme weather events or changing market conditions.
- Greater likelihood of more frequent geohazards exacerbated by prolonged dry periods followed by intense wet periods contributing to the failure of tailings and rock storage facilities.
- Water scarcity and competing demands for water with other industries and townships during times of drought.
- Operational constraints when pumping water (energy) or hauling waste (CO_2 emissions) reinforcing the importance to make informed decisions about mine design and resource allocation.
- Increased need for post-closure infrastructure, monitoring, and management plans for the perpetual storage of mine waste, including water treatment.

4.0 SUGGESTIONS FOR THE PURSUIT OF BEST PRACTICE

Best practice for AMD assessment in response to potential climate change impacts requires:

- Quantification of first-flush concentrations in mine water quality assessment and prediction.
- Estimating fluctuations in precipitation, including extreme lows and highs, and moving away from reliance on mean annual precipitation values.
- Understanding the hydrological response from waste facilities following high rainfall events, i.e. seepage flows and their assimilation into receiving environments.
- Effectively communicating residual uncertainty and potential implications to mine waste and water management to stakeholders, including sample representation, scaling laboratory results to field-scale waste facilities, and acid-onset timeframes.
- Utilisation of new technologies, such as automated samplers, drones, and telemetry, to eliminate the need for personnel to access waste facility or discharge sites in times of extreme heat or flood.
- Making the link between business risk and climate change adaptation by encouraging stakeholders to invest in upfront mine waste characterisation and water quality prediction to allow informed waste management decisions prior to closure.

5.0 SUMMARY

Australian-based literature that specifically addresses climate change impacts on AMD is lacking; although, the higher-level impacts on mine waste and water management are generally recognised in existing adaptation guidelines developed for the mining industry. The potential impacts of extreme weather events and longer-term changes in climate reinforce the importance of accurate and thorough AMD characterisation and mine water quality prediction at the different stages of mine planning and design. In short, our role as AMD practitioners and getting the "job done right" is more important now than ever to allow informed decision-making in a carbon constrained, competitive global economy.

Table 1. **Summary of potential impacts from extreme weather events and longer-term changes in climate to Australian mines and their implication to mine waste and water management**

Mine Phase	Potential Impact	Implication to Mine Waste and Water Management
Planning and Operation	• Increased periods of care and maintenance in response to unforeseen capital expenditure or changing market conditions.	• Unintended exposure of PAF, NMD and/or spontaneously combustible rock in pit walls and incompletely constructed waste rock dumps. • Insufficient personnel to maintain drainage and water treatment infrastructure. • Loss of personnel and associated knowledge of site-specific waste management practices and placement history.
Planning and Operation	• Greater likelihood of more frequent geohazards exacerbated by prolonged dry periods followed by intense wet periods contributing to the failure of tailings and rock exposed by mining.	• Reinforces importance of maintaining an inventory of waste placement and AMD potential characteristics to make timely and informed decisions in the event of facility failure, in addition to aiding mine closure or assessing remining potential.
Planning and Operation	• Water scarcity and competing demands for water with other industries and townships during times of drought.	• Efficient water management requires a strong understanding of site-wide water quality and flows. For example, when deciding to utilise reclaim water from open pits and tailings impoundments for make-up process water or dust suppression.
Planning and Operation	• Operational constraints when pumping water (energy) or hauling waste (CO_2 emissions) reinforcing the importance to make informed decisions about mine design and resource allocation.	• Reinforces importance of accurate and thorough characterisation of mine waste for AMD potential and mine water quality prediction relevant to the different stages of mine planning and design.
Operation and Closure	• Greater accumulation of secondary oxidation products in mine wastes during longer dry periods and droughts. • Variable rainfall changing design of water management structures and how AMD is assimilated by the environment.	• Quantification of “first flush” concentrations and associated downstream impacts. • Understanding the hydrological response from waste facilities following high rainfall events, i.e. seepage flows and their assimilation into receiving environments. • Understanding the interaction of surface discharges and shallow groundwater environments common to many arid to semi-arid areas of Australia. • Increase capacity of water diversion and storage structures.
Closure	• Prolonged dry periods followed by intense wet periods contributing to cover failure. • Exposure of sulphidic waste in facilities designed for perpetual water cover during drought. • Discharge of water from facilities designed for perpetual water cover during flood.	• Increased need for cover and pit lake simulations to estimate fluctuations in precipitation (for example, by using non-stationary geostatistical methods presented by Tallon et al. 2015) and move away from reliance on mean annual precipitation values. • Plan for increased pumping and treatment or enhance other water storage options.
Closure	• Failure of vegetated cover systems due to increased evapotranspiration and impacts from extreme events, such as bushfires and extended droughts. • Loss of topsoil following extreme rainfall events.	• Planning for longer periods of support (water and fertiliser addition) to aid plant establishment before mine lease relinquishment. • Consideration of geosynthetic covers as a lower risk approach to closure. • Increase erosion resistance of mine waste landforms by using flatter slopes, earlier vegetation, and armoured runoff channels.
Closure	• Increased need for post-closure infrastructure required for the perpetual storage of mine waste, including water treatment.	• Minimising the need for perpetual water treatment by investing in upfront mine waste characterisation and water quality prediction to allow informed waste management decisions prior to closure.

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BIOGEOCHEMICAL CYCLING, POTENTIAL LINKAGES BETWEEN AMD AND ASS AND CONSIDERATIONS FOR LONG TERM WATER QUALITY MANAGEMENT – A CASE STUDY FROM RANGER URANIUM MINE

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ABSTRACT

Acid and metalliferous drainage (AMD) presents one of the most significant potential environmental impacts associated with mining. Where climatic conditions and contaminant loads allow, wetlands can present effective water quality treatment systems at sites affected by AMD. The biogeochemical cycling that leads to immobilisation of sulfur and metals in wetland sediments can however create potential acid sulfate soils (ASS). If these sediments were exposed to oxidising conditions through changes in the hydrodynamics at a site, the sediments may present a secondary source of acidity, metals and sulfate to the environment. In this manner, AMD and ASS can be intrinsically linked through biogeochemical cycling at mine sites, and an understanding of these linkages and associated hydrodynamic controls is key for the management of potential longer-term water quality impacts.

The Ranger Uranium Mine, located in the Northern Territory of Australia, is in the process of undertaking studies in preparation for mine closure by 2026. While ASS are expected to occur naturally in the region, activities at the mine and neutral drainage with elevated sulfate concentrations may have influenced the formation of ASS by affecting sulfate and water balance dynamics. These dynamics may change following mine closure and the potential significance of ASS is being further assessed to inform management under current and future conditions. This includes development of a site-wide ASS conceptual model to inform the understanding of ASS source dynamics (potentially naturally occurring and potentially mine influenced ASS), potential pathways from ASS sources to surface water and groundwater receptors, and potentially complete source-pathway-receptor linkages. This extended abstract provides an outline of the methodology of the assessment works. The presentation associated with this extended abstract will present the findings of the ASS conceptual model development, the role of biogeochemical cycling in source dynamics and important water quality management considerations.

1.0 INTRODUCTION

Acid and metalliferous drainage (AMD) (which includes acid rock drainage, neutral mine drainage and saline drainage [DITR, 2007]) presents one of the most significant potential environmental impacts associated with mining (DITR, 2007; DIIS, 2016). Where climatic conditions and contaminant loads allow, wetlands can present effective water quality treatment systems at sites affected by AMD. The biogeochemical cycling that leads to immobilisation of sulfur and metals in wetland sediments can however create potential acid sulfate soils (ASS). If these sediments were exposed to oxidising conditions through changes in the hydrodynamics at a site, the sediments may present a secondary source of acidity, metals and sulfate to the environment. In this manner, AMD and ASS can be intrinsically linked through biogeochemical cycling, and an understanding of these linkages is key for the management of potential longer-term water quality impacts.

2.0 CONSIDERATION OF ASS AT THE RANGER URANIUM MINE

ERA operates the Ranger Uranium Mine located in the Northern Territory (NT) of Australia. The mine site is progressing towards closure and ERA is in the process of undertaking studies and activities in preparation for mine closure and rehabilitation of the mine by 2026.

Observed acidification events in Coonjimba Billabong - a wetland located on the mine site (see Figure 1) during the early wet seasons in recent years indicate that on-site sediments may present a source of acidic water, metals and sulfate.

Fig. 1. Site Features at the Ranger Uranium Mine

While ASS are expected to occur naturally in the Magela Creek catchment (Hart et al., 1987; CSIRO, 2011) within which the Ranger mine is located, activities at the mine may have influenced the formation of ASS (both potential and actual ASS) in areas such as the Coonjimba Billabong by affecting sulfide, sulfate and water balance dynamics.

These dynamics may change post-decommissioning (for instance previously water-logged sediments may dry, becoming oxidised more frequently, if there is less water discharge from mine features). In recognition of the aforementioned, the potential significance of ASS is being further assessed to inform management under current conditions and during closure.

The assessment works are being undertaken in several phases, with the assessment works planned and carried out in consultation with the Supervising Scientist Branch (SSB). The current phase (Stage 1) entails the development of a preliminary site wide ASS conceptual model, focused on desktop data review and assessment of existing data. Following completion of this stage, it is anticipated that Stage 2 will include targeted fieldworks to address data gaps (as informed by the preliminary site wide ASS conceptual model), development of location-specific ASS conceptual models and consideration of closure planning decisions for these location-specific conceptual models.

This extended abstract provides an outline of the methodology of the assessment works. The presentation associated with this extended abstract will present the findings of the ASS conceptual model development, the role of biogeochemical cycling in source dynamics and important water quality management considerations.

3.0 METHODOLOGY

A preliminary site wide ASS conceptual model was developed based on existing data. The tasks included source definition, pathway evaluation, receptor identification and an assessment of potentially complete SPR linkages as described below:

3.1 Source Definition

The source definition was based on the identification of the key constituents that contribute to the formation of potential ASS, these being:

- The presence of elevated sulfate;
- Water logged conditions; and
- An electron donor/sulfate reducing agent (typically organic matter).

The approach involved review of the spatial extent of these constituents to identify potential ASS areas for the Ranger Uranium Mine site, which included collation and review of groundwater and surface water chemistry and elevation data. Due to the large volume of data available, and in order to account for temporal, climatic and seasonal effects, a review was undertaken of changes in water management and historical rainfall variations since 2010 (the largest and most reliable surface water and groundwater data set is available for the site from 2010 onwards). Based on this review, six key timeframes were selected for further assessment which included three wet seasons and three dry seasons.

Geographical information system (GIS) tasks including the interpolation of groundwater elevations within catchments, overlay of groundwater elevation and topography data within these catchments to evaluate depth to water table and where the water table may intersect the ground surface, overlay of sulfate groundwater and surface water concentration data. A digital elevation model (DEM) based on available LIDAR data for the site was used for the topography elevation component.

3.2 Receptor Identification

Receptor Identification included a review of potential groundwater and surface water receptors. This included review of aerial imagery, relevant databases, surface water and groundwater related monitoring reports.

3.3 Pathway Evaluation

Pathway evaluation included consideration of potential migration pathways from potential ASS areas to identified receptors such as creeks (e.g. from Coonjimba Billabong to Magela Creek) as well as pathways to potential groundwater receptors. The pathway evaluation included consideration of groundwater-surface water interactions which vary across the site, depending on the local hydrogeologic and seasonal conditions. Discharge of groundwater to surface water is inferred for many surface water features. Discharge of groundwater to surface water also varies seasonally, reflecting variations in the groundwater levels with seasonal rainfall.

3.4 Assessment of Potentially Complete SPR Linkages

SPR linkages that are considered to be potentially complete were evaluated to assess the potential risk associated with identified areas of ASS or areas of potential ASS. This included an assessment of the temporal variability of sources, pathways and receptors in terms of wet vs dry season conditions. This assessment included the identification of material data gaps where uncertainty remains regarding source terms or receptors, with these data gaps to be addressed during the follow up Stage 2 works.

4.0 OUTCOMES

The presentation associated with this extended abstract will present the findings of the ASS conceptual model development, the role of biogeochemical cycling in source dynamics and important water quality management considerations. This will include a series of figures showing potential ASS source areas for the six key timeframes selected, a description of groundwater and surface water receptors identified, groundwater and surface water pathway evaluation as well as an assessment of potentially complete SPR linkages. The role of biogeochemical cycling and hydraulic controls in long term water quality management will further be discussed.

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PEAK HILL GOLD MINE - CASE STUDY ON FINAL LANDFORM DEALING WITH AMD

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ABSTRACT

Alkane Resources Ltd (Alkane) is a metal explorer and gold producer with a focus on the Lachlan Fold Belt of Central West NSW. Alkane was founded in 1969 and is an ASX listed public company. Alkane owned and operated the Peak Hill Gold Mine (PHGM) from 1996-2005. The Peak Hill ore body is a high sulphidation epithermal deposit with potential to produce acid mine drainage from non-processed waste rock. Alkane's drill and blast/heap leach operation moved five million tonnes of waste rock (including sulphide material) and five million tonnes of oxide ore.

The 815,000t of sulphidic waste rock (containing >1.0g/t Au) at PHGM is encapsulated in a 27Ha waste rock emplacement (WRE) constructed from oxide waste rock. The sulphides sit on a compacted oxide base and have a compacted oxide cap. The entire three-tiered WRE has been covered with 200mm of topsoil and sown to grasses and forbs. The cap and batters are designed to shed rainwater to a single concrete-line downslope flume constructed in 2002.

The rehabilitated spent heap leach material has been shaped and contoured by a bulldozer top-soiled by scraper, pastured by super spreader to direct rainfall to a single rock-lined downslope drain.

The five final voids contain exposed sulphides and AMD concentrates on the floor of the voids. The largest open cut floor is below the groundwater table and contains a lake with a pH of 2.3. The Proprietary pit is the premier feature of the tourist mine which occupies the areas around the voids. There is no environmental harm posed by the open cut voids as there are no local groundwater aquifers which support extraction of water.

The Peak Hill Gold Mine provides a good example of innovation in final land use (exploration base, biodiversity, solid waste transfer station and tourist mine) while keeping the option open for future gold extraction.

1.0 INTRODUCTION

The initial phase of gold mining in Peak Hill from 1889 to 1916 is the reason the township of Peak Hill was established. In the intervening years Peak Hill became a service centre for a mixed farming district but one which was a pioneering area for wheat growing in the Central West. Peak Hill boast the first concrete bulk silos constructed in NSW in 1918 (Chappel 1989).

Gold Exploration was carried out at Peak Hill by several companies from 1964 until the early 1990s. Explorers included CRA Exploration Pty Limited (1978), Alkane Resources (1980 -> present), Goldfields Exploration (1982-1986). Peko-Wallsend Ltd (Geopeko) (1987) and Ashton Mining (1990). Geopeko and Ashton in partnership with Alkane, undertook a wide variety geological, metallurgical, geotechnical and environmental investigations (RW Corkery & Co (1993)).

Peko-Wallsend and Ashton declared commercial and/or geological and metallurgical reasons were given for the failure to proceed with the development of the Peak Hill Gold Project at that time.

Alkane saw the potential to recover the gold resource using heap leach technology (relatively novel in NSW at the time) that could reduce the environmental impact of the project footprint by acquiring adjoining farm land on which to locate the project infrastructure.

In 1993 Alkane joint ventured with Associated Gold Fields NL. However, delays caused by an Aboriginal Land Claim resulted in the JV partner withdrawing from the project.

RW Corkery & Co coordinated the environmental investigations and produced the Environmental Impact Statement for the project (RW Corkery & Co (1993)).

2.0 PEAK HILL GOLD PROJECT

2.1 Project Description

The EIS proposed a drill and blast operation to extract approximately 1.8 million tonnes of ore and 3.0 million tonnes of waste rock over a 4-5 year mine life.

The crushing plant consisted of a primary jaw crusher and a secondary cone crusher to take the ore down to <7 mm size prior to agglomeration with cement and stacking to 10 metres high on an HDPE lined heap leach pad.

The heap leach was to be irrigated with a low concentration of sodium cyanide with gold to be recovered from solution through carbon adsorption, elution and electrowinning to produce 2 400 kg of gold bullion.

Mining ore in the open cut was to the base of oxidation only because the fresh rock contained sulphides gold and copper which are moderately refractory by standard metallurgical processes.

2.2 High sulphidation deposit

Gold mineralization at Peak Hill is hosted by Late Ordovician Mingelo Volcanics which consist mainly of andesitic lavas and andesitic pyroclastic rocks with minor interbedded sedimentary rock types. The rock sequence has been tightly folded so that the sequence dips steeply to the east.

Hydrothermal alteration of the original silicate minerals has seen them replaced by secondary minerals, especially quartz, sericite mica, pyrophyllite and paragonite.

The Peak Hill ore body has one of the highest sulphide concentrations in deposits in Australia with some of the fresh ore containing 50% pyrite.

The gold resource for the heap leach operation was largely contained within the zone of oxidation which extended from the surface to an irregular base of moderate oxidation (BOMO fig 3.2) 10 to 100m below surface (averaged 40m).

It was the irregular boundary of oxidation that has led to some contamination of the heap leach and waste rock emplacements with pyritic material. The bulk of the sulphide waste was separated out from oxide waste by the 110 tonne excavator used on site and separately stockpiled and ultimately encapsulated.

The acid mine drainage potential of the Peak Hill waste rock is on clear display in the lake of the Proprietary pit. Pods of grey sulphides can be seen in the open cut batters and the indigo-coloured pit lake (ground water table supplemented by rainfall). In October 2004 the pit lake had a pH of 2.3, 15 300 mg/L TDS, 10,800mg/L SO_4, 163mg/L Cu and 2.59mg/L As.

The water table in the proprietary pit is around 245m RL and the monitoring bores to the north and northeast have SWL between 210-222m RL.

2.3 Sulphide management at PHGM

The EIS predicted sulphides to make up 10% of total movement at the Peak Hill Gold Mine. However, the project ultimately got extended through the addition of satellite resources (Parkers Pit, Parkers Cutback, Great Eastern, Bobby Burns pits). The cut off grade at PHGM was 0.5g Au/t and the initial strip ration was 1.6:1 (waste rock:ore).

Because of good recoveries from the heap leach processing, dump leaching was trialed and successfully employed on the low grade ore 0.5-0.75g Au/t. This ore was blasted and trucked direct to the heap leach pad and dumped for leaching. Ore that was potentially destined for the waste rock emplacement ended up being treated for gold recovery. The final strip ratio was closer to 1:1 (waste:ore).

Of the 4.9Mt of waste rock movement,16.4% was sulphide material and that was stockpiled within the waste rock emplacement in two areas according to grade. Greater than 1g Au/t has been segregated.

The Waste Rock Emplacement (WRE) at PHGM was designed as per the EIS in 2 x 10m lifts plus a 1.5m lift. Waste rock was paddock dumped by 50tonne dump trunks and compacted by dozer and truck traffic. The sulphides at PHGM sit on a 2m deep compacted oxide waste rock floor and were covered by a 1.5m deep oxide cap. This was compacted by truck traffic during construction to the point where a permeability rate of $<10^{-8}$ m/s was achieved before a vibrating roller was introduced. The top of the WRE was shaped with a 1:200 fall to a concrete flume. The flume was designed and constructed by Soil Works (NSW Soil Conservation Service) and the berms that run around the 23Ha WRE intersect at the flume.

The batters and cap of the WRE were progressively top-soiled (1996-2001) by the PHGM mining fleet and seeded by hand or super spreader towed behind a tractor.

The pasture mix used for the final seeding in November 2002 contained a mixture of introduced and native perennial and annual species in addition to fertilizer and lime.

The theory of the “shotgun mix” of species was that given the variable seasons in the Central West a least some species would be able to respond when rain fell at any given time. The pasture establishment at PHGM has been very successful in a achieving a long term stable land form.

The only maintenance required since 2002 has been volunteer tree removal above the sulphides and on batters where they grow so thickly as to limit grass cover. Macropods are also controlled under licence.

Some of the pasture species used successfully at PHGM have been rejected by the Resources Regulator for use at Tomingley Gold Operations.

2.4 Innovation in mine closure

A consent condition placed on the PHGM development by Parkes Shire Council (PSC) was that Alkane provide 4Ha of land for a new waste transfer station when the facility operating at the time ran out of land-fill space.

For several decades, PSC had a land-fill waste management facility on Crown Land that was ultimately partially enclosed within the mining lease. It was convenient for both parties to extend the WRE over the old landfill areas as it buried any legacy issues that site may contain.

Alkane subdivided 4Ha from the freehold portion of the mining lease and transferred that land at no cost to PSC. That 4 Ha had the benefit of being located behind the hill from town and there was mine infrastructure that could be recycled to form the new waste transfer facility. The contractors steel and concrete workshop, wash-down bay, bunded area, water and power supply were repurposed rather than demolished and removed.

The mining history of Peak Hill has always been important to many of the local residents and for that reasons several conditions were imposed to interpret and preserve that mining history. To meet those expectations Alkane developed a mining museum display in the Main Street of Peak Hill and established a tourist mine. The tourist mine consists of 22 interpretive signs, walking trails, picnic areas, a viewing platform, interpretive shelter/entry and public toilets.

The tourist mine was a finalist in the 2003 NSW Tourism Awards and continues to generate economic activity for the local town.

Parkes Shire Council and the NSW Government have contributed infrastructure and resources to the operating tourist mine.

The tourist mine is a rare opportunity for visitors to get close to a modern gold mine just 200m off the Newell Highway.

3.0 CONCLUSIONS

While Acid Mine Drainage was identified in the EIS as a potential environmental issue, the design and operation of the mine has seen the risk of AMD well managed and mitigated.

51 Ha of final landforms (WRE, spent heap leach and ROM) are long term stable and wait sign off from the Resources Regulator. Those final landforms have been shown through landscape function analysis to be close to the quality of the pre-mining agricultural landscape (Graminus 2014). Fifty five percent of the environmental security over the leases held by the regulator was released to Alkane in 2006.

Through mining activity on the leases, biodiversity across the whole 198Ha site has increased dramatically. The number of bird and macropod species has doubled on site between 1993-2014.

Mine legacies of historic voids, mine tailings and AMD contaminated soils have been properly contained.

The mined landscape continues to generate economic activity through tourism and commercial photography in the local area despite a hiatus in mining.

Mine infrastructure has been re-purposed as a Council asset.

With improvement in metallurgical processes and increased gold price, the sulphide resources remaining at Peak Hill are currently being reviewed with a view to an underground development. This possible development would introduce additional sulphide waste managemen challenges.

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Peak Hill Gold Mine was a drill and blast/heap leach operation from 1996-2005. At a capital cost of just $5M and located 200m from the residential edge of town, the mine employed fifty people and produced 153,000 ounces of gold from 10Mt of movement.

ADAPTIVE MANAGEMENT: AN ESSENTIAL PROCESS FOR AMD SITES

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ABSTRACT

Acid and metalliferous drainage (AMD) is a common issue across the global mining industry. The worldwide cost for the remediation of current and future AMD has been estimated at one hundred billion dollars (Lottermoser, 2015). This liability does not present an image of sustainability and negatively affects the mining industry's social licence to operate (SLTO).

Mining operations need to demonstrate that they have taken all practicable efforts to reduce the quantity of AMD and that they also have contingency plans in place for event-based risks and uncertainty in AMD predictions. Such uncertainty can be addressed through adaptive management processes, which provides internal and external stakeholders confidence that the future risks associated with AMD can be managed.

The process of adaptive management is often incorporated into AMD management plans and supporting procedures to manage uncertainty. Contemporary mine operators now utilise trigger action response plans (TARPS) to manage this uncertainty. TARPS should be developed from risk assessment workshops that are based on data and scientific analysis.

1.0 INTRODUCTION

Acid and metalliferous drainage (AMD) is a common issue across the global mining industry. Internationally, there are many examples of legacy sites where AMD risks have not been understood or managed correctly, resulting in on-going and significantly adverse impacts to the environment. The worldwide cost for the remediation of current and future AMD has been estimated at one hundred billion dollars (Lottermoser, 2015). This liability does not present an image of sustainability and negatively affects the mining industry's social licence to operate (SLTO).

Sustainability of mining is also brought into question by the fact that many mine owners have adopted treatment in perpetuity as a solution for AMD without addressing source control. For instance, nearly half the mining companies surveyed by the Mine Environmental Neutral Drainage (MEND) programme (Zinck and Griffith, 2013) plan to treat AMD impacted waters in perpetuity. Treatment in perpetuity introduces additional risks, which can lead to future legacy liabilities, where funds may not be available to address these issues should they arise. This paper looks at two key aspects of AMD management:

- AMD risk management; and
- Adaptive management of AMD risks.

Identification of AMD risks and developing adaptive management processes to address these risks can support SLTO. Such an approach provides internal and external stakeholders with more confidence that the future risks (and costs) associated with AMD can be managed.

2.0 AMD RISK MANAGEMENT

SLTO has been identified as the number one business risk for the mining industry three years in a row, (e.g., Ernst & Young, 2019, 2020). The way AMD is managed, and importantly community acceptance of the management process affects SLTO and is both a current and future risk for the mining industry.

There are many risks associated with the management of AMD. For instance, the long-term treatment of AMD often has financial appeal to mining companies as costs occur a long way into the future, yet often the costs of some key longer-term risks have not been considered. Examples include:

- Event risk as long-term treatment of AMD will have greater exposure to infrequent high-risk events;
- Current datasets may not be appropriate for the effects of climate change; and
- Changing community expectations with time leading to more stringent water quality standards.

Such AMD risks can add to unforeseen costs later in the mine life and erode final project value if they were not considered during project planning and financial analysis. Inclusion of costs for such risks provides a fairer assessment of source control costs versus long term treatment costs. For instance, the upfront cost of source control (e.g., AMD prevention and minimisation) is often less favoured when compared to long term treatment options that occur a long way into the future. The mining industry needs to focus on minimising AMD as the best practicable approach to the management of AMD and have AMD treatment as a lesser, although often necessary management option.

Generally, the risks associated with AMD can be assessed by a Source-Pathway-Receptor (SPR) model platform, which shows that a risk is only present when there is:

- A source of AMD;
- A pathway from the AMD source to the receptor; and
- A receptor that could be affected by the AMD.

The SPR platform should be based on the site conceptual model that identifies all key mine domains (potential AMD source hazards), physical pathways, and receptors of concern. Such models, supported by detailed scientific and engineering studies, can facilitate risk assessments and determine potential options and costs for AMD management.

Research demonstrates that in general, the AMD source hazard represents close to 70- 80% of the potential risk for any site affected by AMD with pathway and receptors contributing to the remainder (Richards et al., 2006). Hence, definition of the AMD source hazards helps with clarifying understanding of the potential AMD risks for any mine domain that contains hazardous materials.

Risk assessments are an essential planning step for the management of AMD at sites that have potential issues and/or have potential uncertainty about the effects of AMD. Many mining companies use an AMD risk assessment process as a key management step following source hazard characterisation studies (e.g., Pearce et al., 2019).

Source hazard characterisation is a significant and essential step in understanding AMD risk.

The risk assessment is a fundamental step in prediction of potential AMD effects and will be revisited many times over the mine life.

The determination of potential effects provides the opportunity to consider additional management options that may be required. This could include AMD management techniques such as prevention and minimisation, and if necessary, the treatment of AMD.

The six steps of AMD management (Figure 1) and the risk assessment (represented by a star) are the backbone of any AMD Management Plan.

For operational functionality, management plans are supported by standard operating procedures (SOP).

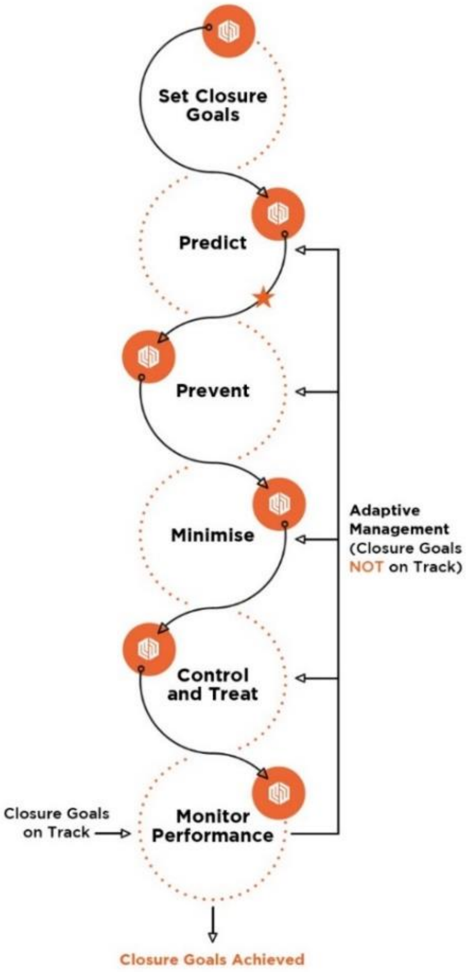

Fig. 1. AMD Management Steps

3.0 ADAPTIVE MANAGEMENT

3.1 Introduction

All mining projects have some degree of uncertainty in regards to outcome and effects. This uncertainty can be managed by a process of adaptive management. Adaptive management is a learning-orientated approach to environmental management where uncertainty exists, which may change over time to reflect new information as it becomes available. Adaptive management is an industry recognised management option. However, it requires clear environmental objectives against which management options can be measured.

Effective adaptive management is supported by understanding the nature and duration of possible events that could occur, monitoring these events, and then having options in place should there be variance from the expected condition. This requires:

- Understanding the risks (source hazards);
- Monitoring (as early warning, i.e., performance monitoring);
- Variance planning; and
- Trigger Action Response Plans.

3.2 Understanding Risk

Identification of the key AMD risks that could affect closure of the site should be identified in the AMD risk assessment. This AMD risk assessment therefore helps refine what effects could occur, what monitoring is required, and hence what key adaptive management strategies should be developed. For instance, project risks relating to AMD management could include:

- The amount of rock that will be ore or low-grade ore, and the amounts of rock that will be potentially acid forming (PAF) and/or non-acid forming (NAF).
- The materials schedule (timings) for PAF and NAF and its availability for key construction activities such as NAF covers or infrastructure areas.
- Waste rock placement (correct domain and correct placement style).
- The quality and quantity of water flow from mine domains that have the potential for AMD, e.g., toe seepage from a tailings storage facility.
- Contaminant load predictions such as the amount of acidity or other contaminants produced over time.
- Climate change, storm events, and higher flow rates / contaminant loads.

Each potential risk should have a range of potential actions developed in case there is variance from the expected case and appropriate monitoring in place, together with assigned responsibilities. Responsibilities are often managed by a RACI matrix (Responsibility, Accountability, Consulted, Informed).

3.3 Monitoring of Key Risks

Monitoring of performance is critical to help identify early departure from the expected case. Performance monitoring is an early warning system to enable a timely response to develop and implement other management options to manage the change. Monitoring should be specific to the risk and the duration of the risk. For instance, construction of a waste rock dump (WRD) to reduce impacts on the receiving environment may include monitoring of the WRD to ensure oxygen concentrations are in accordance with design specifications.

3.4 Variance Planning

Variance from the expected case is likely, and there needs to be supporting management options to show how significant variance will be managed. Therefore, for key AMD risks, it is necessary that the following processes relating to AMD uncertainty are considered:

- A range is determined such that there is confidence in the conservative and optimistic model bounds;
- The expected case, the most reasonable estimate, sits within these model bounds; and
- Management options are available for the proposed range to achieve agreed operational and closure criteria.

This range of management options can be referred to as the ‘adaptive management regime’ and needs to be acceptable to both internal and external stakeholders. Fig. 2 provides an illustrative example of the adaptive management regime for AMD impacted waters. It provides a clear graphic for explaining to stakeholders how variance will be managed as part of a learning-orientated approach (with time) to environmental management where uncertainty exists.

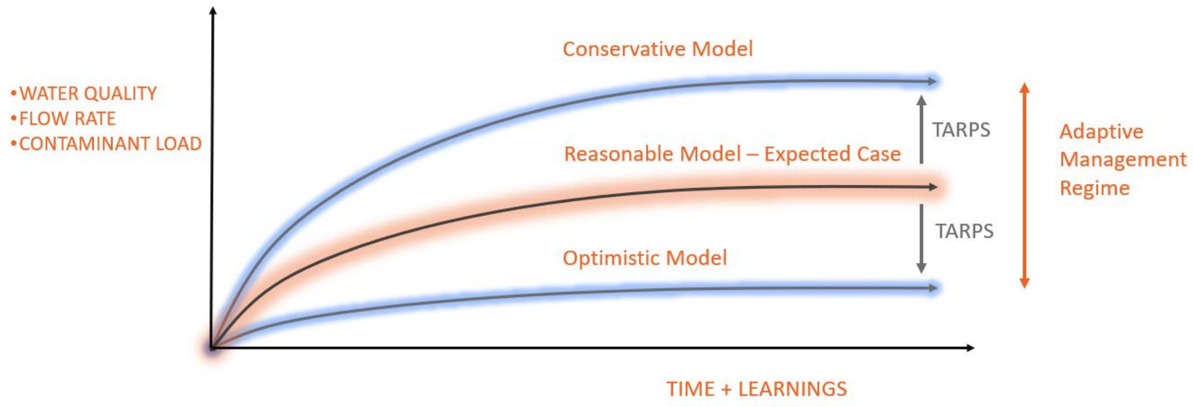

Fig. 2. Adaptive Management Regime. (Modified from Weber et al., 2018).

3.5 Trigger Action Response Plans (TARPS)

Variance from the expected case can be managed by Trigger Action Response Plans (TARPs) where appropriate. The number of TARPs is based on the desktop AMD risk assessment process to ensure potential higher risk effects have management options in place. Generally, a TARP has set trigger limits to define what a significant change is, and then describes the actions to respond to the variance. TARPs need to be developed to cover the adaptive management regime to foster stakeholder confidence. Examples of this include:

- Reconciliation of waste rock block model material volumes versus mined material quantities.
- Waste rock placement verification to ensure design methodologies are achieved.
- Performance monitoring of WRDs for oxygen content and net percolation rates.
- Monitoring of AMD discharge (rates and quality).
- Performance monitoring of treatment system effluent against design expectations.

The use of TARPS provides the framework to manage uncertainty in a manner that makes (most) stakeholders more comfortable that solutions are available and are ready to be implemented if there is variance from the expected case. Done effectively, consistently, and by adapting to new learnings about the impact of uncertainties, this approach will fundamentally support SLTO and social value for mining. The benefits of this approach should be demonstrated through rigorous environmental performance monitoring that demonstrates the agreed closure goals will be achieved.

Fig. 3 provides an example TARP for the placement of waste rock on a NAF WRD and explains monitoring requirements, event trigger levels, and responsibilities as per the RACI matrix.

State	*Normal State*	*Event Trigger 1*	*Event Trigger 2*
Monitoring Programme	Mine Environment to complete: • Visual Inspections • Acid Base Accounting QA/QC • Vehicle Fleet management • Consult and Inform as per SOP	Mine Environment to complete: • Visual Inspections • Acid Base Accounting QA/QC • Vehicle Fleet management • Consult and Inform as per SOP	Mine Environment to complete: • Visual Inspections • Acid Base Accounting QA/QC • Vehicle Fleet management • Consult and Inform and per SOP
Trigger	No PAF or materials with visible sulfides are placed on the NAF WRD each month.	PAF materials and materials with visible sulfides are being placed on the NAF WRD on a weekly basis.	PAF materials and materials with visible sulfides are being placed on the NAF WRD on a daily basis.
RACI	**Action / Response**	**Action / Response**	**Action / Response**
Mine Environment	Continue operations as per the procedure.	Undertake weekly inspections of the WRD to ensure that the issue is resolved. Ensure the quantity of materials rehandled from the NAF WRD to the PAF WRD are tracked for audit purposes	ICAM investigation to be completed. Undertake daily inspections of the NAF WRD to ensure that the issue is resolved. Ensure the quantity of materials rehandled from the NAF WRD to the PAF WRD are tracked for audit purposes
Mine Geology	Continue operations as per the procedure.	Review waste rock block model and Vehicle Fleet Management Log to understand discrepancy. Review the materials mark-up process Identify and resolve any issues.	Immediately review waste rock block model and Vehicle Fleet Management Log to understand discrepancy. Immediately review the materials Mark-up process Identify and resolve any issues.
Mine Planning	Continue operations as per the procedure.	Remove any PAF materials or materials with sulfides from the NAF WRD and place on the PAF WRD. Record incident and materials quantities.	Remove any PAF materials or materials with sulfides from the NAF WRD and place on the PAF WRD. Record incident and materials quantities.
Mine Manager	Continue operations as per the procedure.	Continue operations as per the procedure.	Review / endorse as necessary any ICAM outcomes. Continue operations as per the procedure.

Fig. 3. Example TARP: Materials Placement – Non-acid forming (NAF) WRD.

4.0 CONCLUSION

The mining industry plays a key role in enabling a sustainable future for society by providing the minerals needed for society to function. However, the process of mining also needs to be sustainable and undertaken in a best practicable manner.

Social licence to operate is now a fundamental risk to the business of mining and social value for mining must be earned by the actions of mining companies. For AMD management, the mining industry needs to demonstrate that uncertainty can be managed. The use of adaptive management processes can help with knowledge transfer, community engagement, and stakeholder acceptance of most AMD risks. Adaptive management enables a project to proceed where uncertainty exists, provided the variance can be managed, and enables time orientated learning processes as further data becomes available to ensure operational and closure criteria are achieved.

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A CALIBRATED MODEL TO PREDICT THE PERFORMANCE OF A STORE AND RELEASE COVER FOR THE TSF AT CENTURY MINE

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ABSTRACT

Century mine, owned by Century Mining Limited (CML), is an open-cut zinc (Zn) and lead (Pb) mine located in north-west Queensland. The Mine, under the ownership of MMG, ceased operations in the open-cut pit (the pit) in mid-2015 and processing and shipping of ore by early 2016. With the finalisation of processing of ore from the pit, CML has refocused the mine on the economic rehabilitation of the tailings storage facility (TSF). Economic rehabilitation is being achieved by hydraulically mining the majority of the tailings from the TSF and reprocessing them to extract the entrained Zn prior to discharge to the pit. Tailings in the pit will be rehabilitated by a permanent water cover as they will be below the permanent pit water level. Tailings remaining in the TSF will be rehabilitated by constructing a store and release cover, informed by a cover trial that has been running at the mine for the past six years. The cover trial tests three potential reduced permeability layers (RPLs) and has been instrumented with a weather station, lysimeters, and volumetric water content (VWC) and matric suction sensors throughout the cover thickness. This paper presents a brief review of the cover design process that was followed to arrive at the preferred cover option. This is followed by a description of a calibrated SVFlux model that was built using the observed results from the instrumentation. Finally, the paper presents predicted future performance of the preferred cover option using the SVFlux model.

1.0 INTRODUCTION

1.1 Background

Century mine produced Zn and Pb concentrate via an open-cut operation located in north-west Queensland. Century mine ceased operations in the pit in mid-2015 and the processing and shipping of ore by early 2016.

The focus of the previous owner MMG turned to closure and progressive rehabilitation with the finalisation of ore processing from the pit. Significant rehabilitation has already been completed by MMG, with over $70 million spent so far.

CML acquired Century mine with the opportunity to mine the remaining resources including:

- 2,200,000 t Joint Ore Reserves Committee (JORC) compliant Zn in the TSF;
- 1,000,000 t of JORC compliant Zn and Pb resources in the Silver King deposit; and
- Substantial phosphate deposits.

The hydraulic mining of the tailings has created new cash flow allowing CML to complete rehabilitation not undertaken by MMG.

1.2 TSF

The TSF was operated as a single point (outfall) down valley discharge with the main embankment 3 km south of the discharge point. Two decants were located on the main embankment, which directed supernatant into the downstream evaporation dam. At the end of the mine operational life, the TSF covered approximately 360 ha.

1.3 Cover

The preferred cover for the remaining tailings has been developed and tested over the past six years, as described by Defferrard et al. 2016 and Defferrard and Rohde 2019.

2.0 DETAILS OF COVER TRIALS

2.1 Cover Design Process

The cover design process included preliminary cover design, site material characterisation, stakeholder workshop / risk assessment, identification of preferred covers and cover trials. Preliminary covers were designed by ATC Williams (2012) and were progressed by field sampling and laboratory testing of potential cover materials (ATC Williams 2013). The outcome of the stakeholder workshop and risk assessment was the identification of three preferred covers, which were progressed to cover trials.

2.2 Preferred Covers

The three preferred covers comprised an infiltration storage layer (ISL, 1.5 m thick), covering a RPL (0.6 m thick), in turn overlying a running layer (0.3 m thick) and a capillary break layer (CB, 0.3 m thick), with three different engineered RPLs. The three engineered RPLs included: (i) minus 10 mm crusher dust conditioned with bentonite (RPL 1), (ii) a geosynthetic clay liner placed between an upper and lower layer of minus 10 mm crusher dust (RPL 2), and (iii) minus 10 mm crusher dust conditioned with an extra 15 to 30% fines (passing 0.075 mm, RPL 3).

2.3 Cover Trials

In 2014, cover trials for the three preferred covers (RPL 1, RPL 2, and RPL 3) were constructed, and instrumented to test their performance.

2.4 Instrumentation

The cover trials were instrumented with VWC and matric suction sensors, a weather station capable of estimating evapotranspiration, and lysimeters to measure seepage through the base of the covers.

3.0 NUMERICAL MODELLING OF RPL 1 PERFORMANCE

SVFlux, developed by SoilVision Systems Limited, uses the finite element method to simulate water movement for both saturated and unsaturated conditions, and was used to numerically model the performance of the preferred cover trial option (RPL 1).

The numerical model was developed in one-dimension to calculate rainfall infiltration and seepage in RPL 1. It was assumed that no surface runoff or run on occurred, and allowed ponding on the surface of the ISL. Transpiration from vegetation was conservatively excluded (i.e., the numerical model only considers evaporation).

3.1 Model Dimensions and Mesh Geometry

The numerical model was developed to replicate RPL 1. The automatic mesh generation, and automatic mesh refinement algorithms were used to generate the finite element mesh.

3.2 Initial Conditions

3.2.1 Evaporation

Potential evaporation in the numerical model was set at a constant rate at 0.0039 m/day, which is 50% of the average measured rainfall.

3.2.2 Soil water characteristic curves

The numerical model requires soil water characteristic curves (SWCCs). A SWCC is the relationship between VWC and matric suction, and was developed for each depth at which the sensors are located in RPL 1 (the in situ results). The SWCCs were fitted to the in situ results using the van Genuchten (1980) method. The average trendline for each material was used in the numerical model.

3.2.3 Analysis method

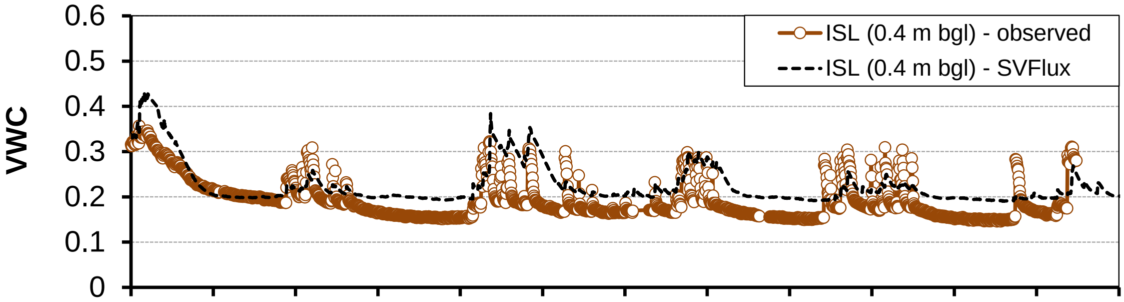
A series of transient analyses was completed for the numerical modelling including:

- the six years of measured rainfall on the cover trials; and
- the average year, the wettest year, and the driest year on record, using the 128-year data set available from Longpaddock for Century mine.

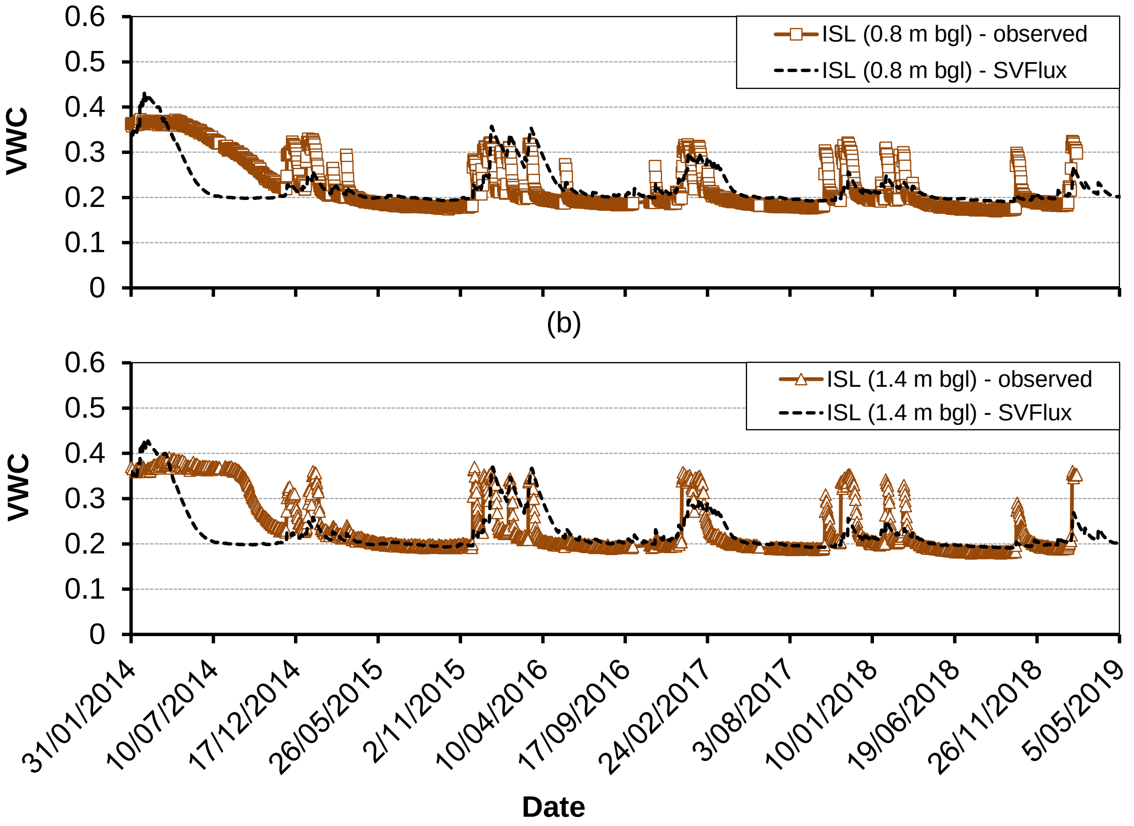
4.0 RESULTS

4.1 Calibration

The numerical model was calibrated using the six years of measured rainfall data (Figure 1 to Figure 4).



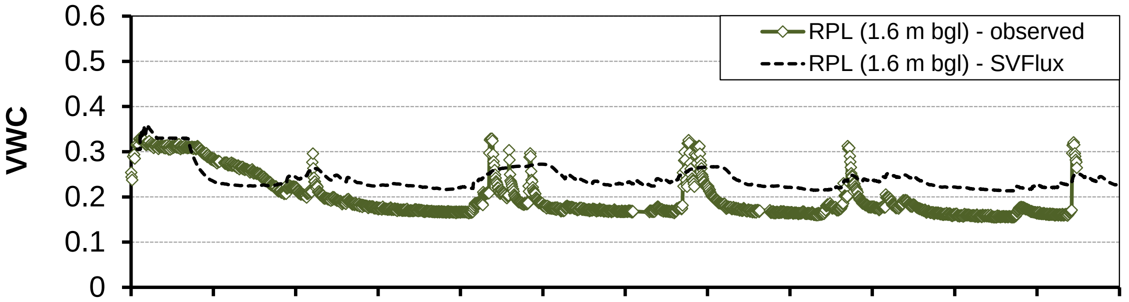
(a)



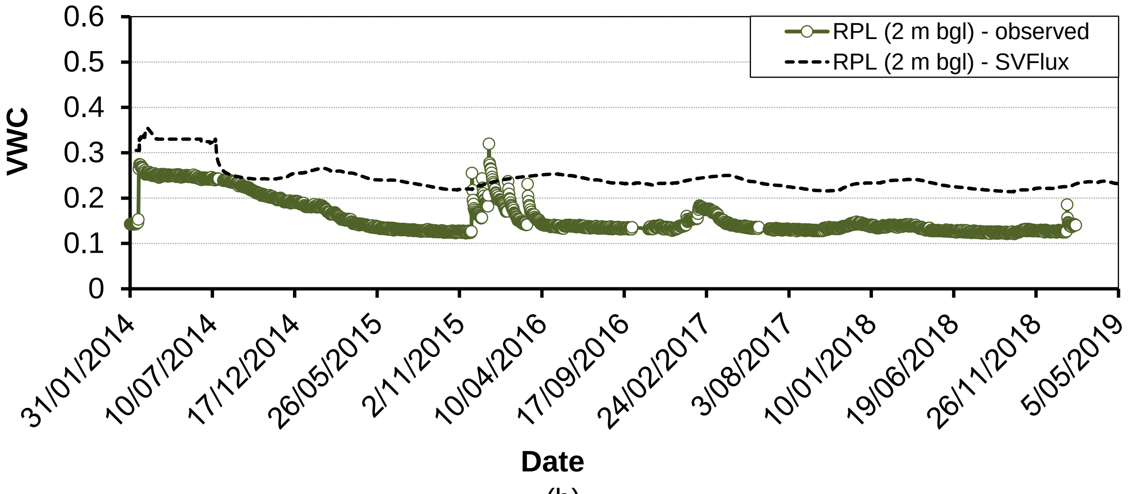
(b)

(c)

Fig. 1. ISL numerical model result compared to in situ monitoring (a) 0.4 m below ground level (bgl) (b) 0.8 m bgl (c) 1.4 m bgl



(a)



(b)

Fig. 2. **RPL numerical model result compared to in situ monitoring (a) 1.6 m bgl (b) 2 m bgl**

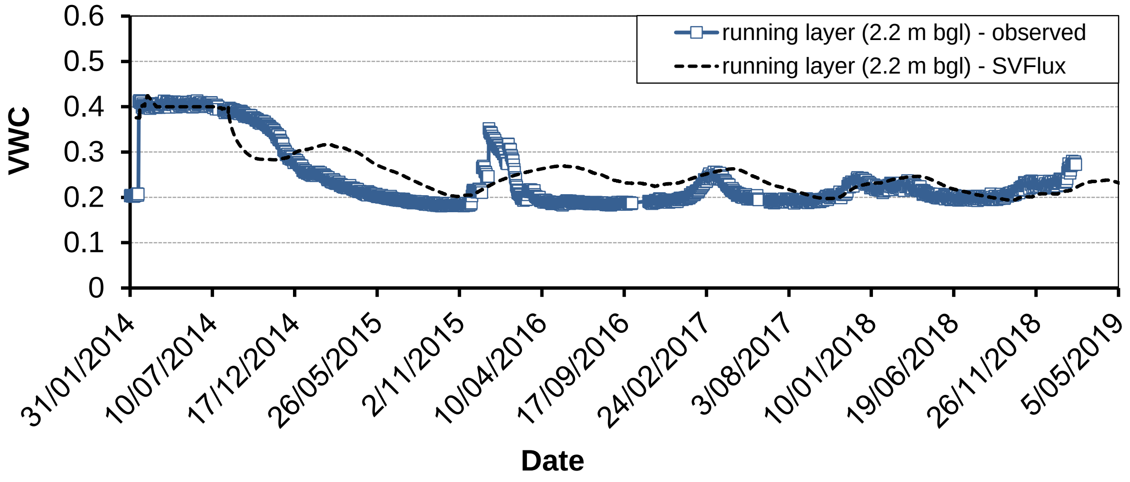


Fig. 3. **Running layer numerical model result compared to in situ monitoring**

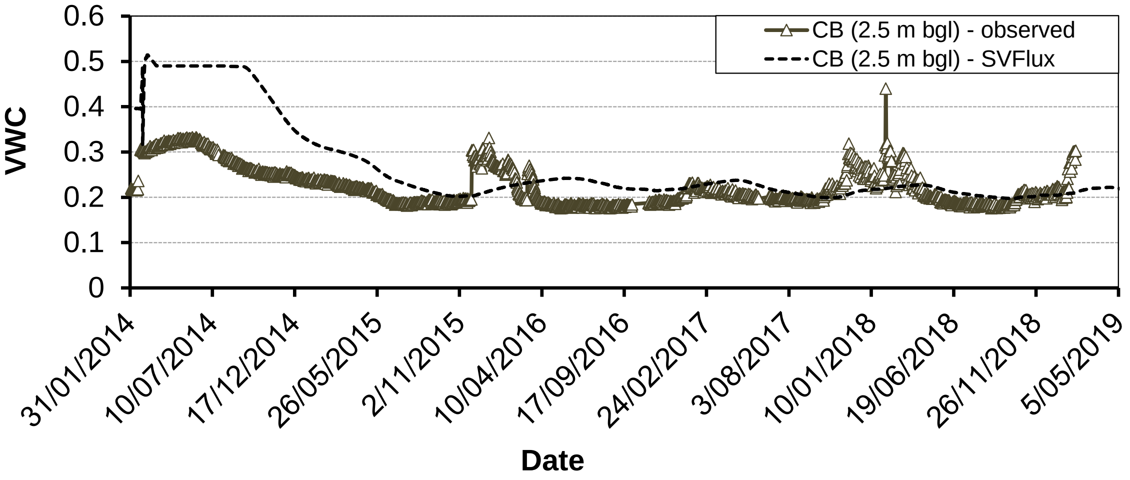


Fig. 4. CB numerical model result compared to in situ monitoring

4.2 Water Balance

The numerical model water balance output is given in Table 1.

Table 1. Numerical model water balance results

	Monitoring period	Dry year	Average year	Wet year
Rainfall (mm)	2,545	178.7	517.3	1,298.8
Stored infiltration (%)	15.4	11.5	11.6	4.5
Seepage (%)	2.4	0.0	0.0	2.3
Actual evaporation (%)	82.2	88.5	88.4	93.2

5.0 DISCUSSION

5.1 Calibration

It is notable that the numerical model closely replicates the magnitude of wetting and drying in the ISL, RPL and running layer (Figure 1 to Figure 3). The CB model result shows a prolonged period of near-saturated conditions at the beginning of the modelled period, before more closely matching the observed data (Figure 4). Overall, it is considered that the numerical model is adequately calibrated and likely to be provide a more conservative result (more seepage) then is measured in situ.

5.2 Future Performance

The calibrated numerical model indicates that RPL 1 is performing as designed and producing well below the maximum acceptable seepage rate. It is expected that seepage through the cover will not exceed 2.4% of cumulative rainfall per year and that seepage as a percentage of cumulative rainfall will approach 2.4% in the long-term.

The model predicts 2.4% seepage compared to the measured 0.005 to 4.7% seepage for the monitoring period. The calculated / inferred seepages were expected to be higher than the measured lysimeter seepage, as there is a storage component within the tailings, and seepage data are derived from the VWC sensor in the CB (Defferrard et al. 2016). The seepage results, both calculated and measured, are below the target infiltration / recharge rate for Australia – nominally 10% of rainfall (Cook et al. 2004).

6.0 CONCLUSION

CML is the owner of Century mine and is currently mining the TSF to recover Zn, resulting in a reduction in the area of tailings requiring rehabilitation. Century mine is a unique example of economic rehabilitation in Australia.

Several preliminary cover designs were narrowed to three preferred covers. The three preferred covers were constructed and instrumented as a trial on a section of the TSF in 2014, and have been monitored for the past six years. The duration of the cover trial monitoring program means it is one of the oldest of its kind in Australia, and makes it a leading and world class example of store and release cover performance.

RPL 1 was selected as the preferred cover option from the cover trial monitoring program, based on both performance and constructability.

This paper presented the calibrated numerical model that was used to accurately predict the long-term performance of RPL 1. The calibration was iterative, and found to closely match the observed results. The calibrated numerical model was run for a dry, average and wet year to predict how RPL 1 will perform in the future. Based on the prediction of future performance of RPL 1 from the numerical model, it is expected that seepage will be below the Australian target infiltration rate, and is not expected to exceed 2.4% of cumulative rainfall per year.

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MODELLING VERIFICATION OF A REGIONAL COVER DESIGN FOR THE COBAR REGION

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ABSTRACT

Cobar is located approximately 700 km west of Sydney in central western New South Wales. The region has a semi-arid climate with low humidity, low rainfall and high evaporation. Annual rainfall is approximately 400 mm, while potential evaporation averages 2,000 mm. The Cobar basin is one of the most significant metalliferous regions in Australia, containing extensive base and precious metal deposits. The typical large, high-grade deposits of the region are hosted by marine sediments and consist of multiple lenses in steeply plunging, pipe-like clusters. There are currently five operational mines in the area targeting metals including copper, lead, zinc, silver and gold.

During ore processing, potentially acid forming (PAF) tailings are generated and normally discharged to a tailings storage facility (TSF). The PAF tailings require careful rehabilitation to minimise the risk of harm to the receiving environment.

There is a significant body of work available in the public domain for the Cobar region, which suggests that a store and release cover is a potential rehabilitation strategy for minimising the risk of harm to the receiving environment. Further, the literature suggests that unlike more temperate climates, the store and release cover should be less than 1 m thick, representing a departure from other store and release cover examples in Australia, which typically range up to 4 m in thickness, although a 1.5 m thickness is typical.

This paper presents a review of cover trial work that has been done over the past two decades in the region, including two recent cover trials by the authors. The paper is largely concerned with a calibrated numerical model that has been built using SVFlux and the long-term predicted performance of various cover configurations that may be appropriate for the region. Finally, the paper describes a preferred regional cover design based on the cover trials and SVFlux model.

1.0 INTRODUCTION

The Cobar region extends from approximately 30 km north-west of Cobar to 100 km south-east of Cobar. The topography of the region is typically flat or gently undulating, dotted with stony ridges and ranges. A large portion of the region is rangeland, in which vegetation consists of poplar box woodlands, mulga communities and cypress pine. The region has been a significant source of mineral wealth for 140 years since the discovery of the Great Cobar copper deposit in 1870.

During ore processing, PAF tailings are generated and discharged underground or to a surface TSF. PAF tailings contain sulfides which, when exposed to oxygen and water, form acid and metalliferous drainage (AMD), and hence require careful management to minimise the risk of harm to the receiving environment. A cover is usually required to limit the potential for net percolation of rainfall into the tailings and for AMD to be transported. Limiting net percolation will decrease the potential for seepage and the potential impact on the receiving environment. In semi-arid environments, such as the region, there are many Australian examples of covers that have been constructed to limit interactions of tailings with oxygen and water.

2.0 SETTING

2.1 Regional geology

The regional geology is characterised by siliciclastic sediments locally intruded with felsic volcanics. The region has large, high-grade deposits which are hosted by marine sediments and consist of multiple lenses in steeply plunging, pipe-like clusters.

2.2 Regional soils

Soils in the region are relatively uniform and relate closely to the topographic position and local geology. The steeper slopes, ridges and crests tend to have sandy to earthy Tenosols. The Tenosols gradually grade down into Red Dermosols, Kandosols and Calcarosols on the lower slopes, lowlands and flats with several variants existing. Deep alluvial and sandy soils commonly occur in the channels and creeks.

2.3 Land use

The predominant land uses in the region are agriculture and mining. Agriculture in the region is mainly sheep grazing and some cattle grazing. There are currently five operational mines in the region that mine a range of metals including copper (Cu), lead (Pb), zinc (Zn), silver (Ag) and gold (Au).

2.4 Climate and cover type

Among other factors, climate is an important element in determining the type of cover most suited to TSFs in the region. The climate of the region is semi-arid with low humidity, low rainfall and high evaporation. The combined effect of evaporation and transpiration (evapotranspiration) is five times greater than rainfall. The GARD guide (GARD 2009) suggests that a store and release cover is appropriate, in combination with other safe guards (i.e., a capillary break or a reduced permeability layer (RPL)) to reduce the potential for environmental harm from TSFs after mine closure (Figure 1).

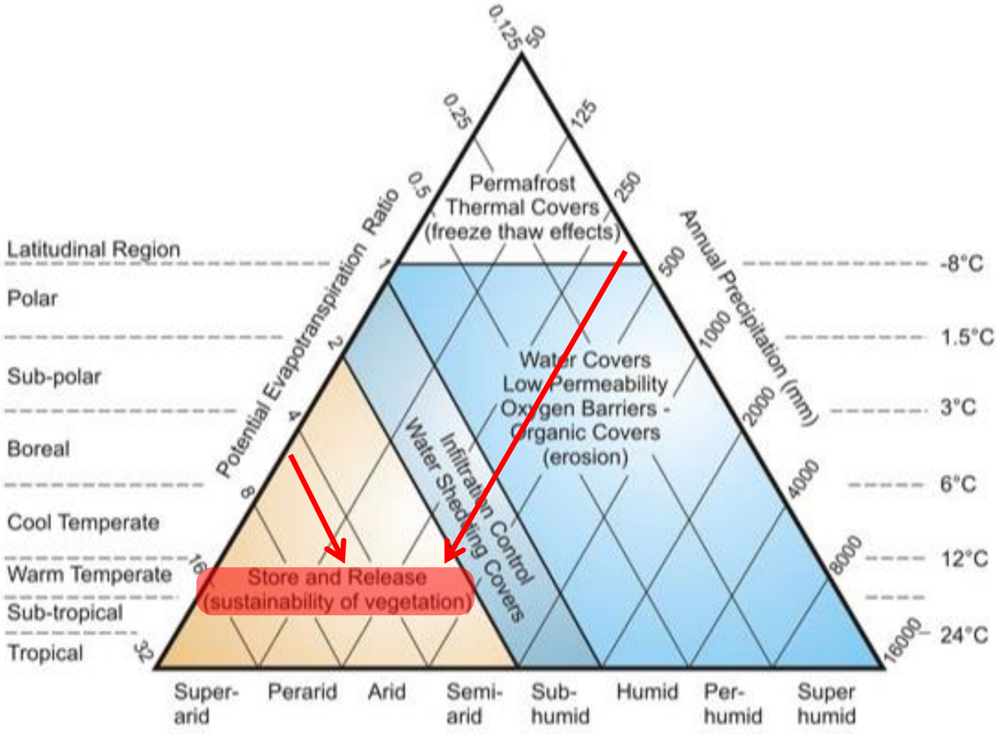

Fig. 1. **Covers and climate types (GARD 2009)**

3.0 COVER TRIALS IN THE REGION

Cover trials are a crucial step in the cover design process. It is SGME's experience that generic soil water characteristic curves (SWCCs) derived from pedotransfer functions can differ noticeably to those measured in situ, which will impact modelling outcomes significantly.

There are two options when conducting a TSF cover trial. The traditional option has been to section off an area of a TSF and construct a cover trial (ideally at least 1 ha, field trial). The low rainfall environment of the region can be a limiting factor to achieving a timely response from such a field trial. Regional experience indicates that several years of data may be required to capture a representative window of how the cover responds to seasonal and annual changes. In order to achieve interim data of cover performance, SGME has worked with two mines in the area to trial covers in large columns. Column trials are also a cost-effective way to trial multiple cover configurations.

3.1 Field Trials

Peak Gold Mine (PGM) ran field-scale cover trials from 2002 to 2009, which were reported by Schneider (2012) and The University of Queensland Centre for Mined Land Rehabilitation. The trials consisted of two simple infiltration storage layer (ISL) covers comprising either 1.5 m or 2.0 m of uncompacted waste rock. The purpose of an ISL is to store water during rainfall events, and subsequently release it back into the atmosphere through evapotranspiration.

The following overarching trends were noticeable from these field trials:

- The tailings remained near-saturated throughout the monitoring period for both the 1.5 m and the 2 m covers, with an average degree of saturation (S) ranging from 0.67 to 1. It should be noted that other cover trials in Australia have shown that a S greater than

0.6 is sufficient to result in desaturation of the layer by seepage; or in the case of the tailings, seepage to the receiving environment (Rohde 2011);

- The part of the ISL 1 m below ground level (bgl) is typically wetter, with a S ranging from 0.5 to 0.6.It is likely that the S at depth is sufficient to result in seepage to the underlying tailings resulting in the high S in the tailings; and
- Transpiration from vegetation is effective to a depth of 1 m bgl; i.e., the top 1 m of the cover oscillates between partially wet (S ~0.33) and dry (S ≤0.11). That is, infiltration below 1 m bgl cannot be effectively removed by evapotranspiration and resulted in an increase in S with depth in the cover and a high S in the underlying tailings. This suggests that a cover ≤1 m thick may be appropriate for the region.

TSF cover trials at CSA Mine reported in the Annual Environmental Management Report (AEMR, CSA Mine 2016) indicated that a 0.4 m cover will hold sufficient water and nutrients to support vegetation growth, noting that the CSA Mine trials do not appear to have addressed capillarity or the ongoing AMD potential. It is also important to note that CSA Mine intend to use the near-surface tailings as part of the ISL for the cover.

3.2 Column Trials

Endeavor Mine ran cover column trials from 2014 to 2016 that were reported by Rohde et al (2017) and Jamson & Rohde (2019). Hera Mine are currently running cover column trials that began in 2017. Three cover configurations were trialed at each mine. These were reported by Rohde et al. (2017) and Jamson & Rohde (2019).

The following trends were noticeable in the cover column trials:

- The evaporation rate for the covers varied from 70 to 97%, noting that the Endeavor Mine cover column trials ran over a longer period of time and incorporated times of the year with a lower evaporation rate (i.e., winter).
- If the cover is too thin, there is insufficient infiltration storage capacity, resulting in more rapid development of near-saturated conditions, correlating to an increase in seepage potential.
- If the cover is too thick, rainfall may infiltrate deep enough that the effect of evaporation decreases. This can result in the development of near-saturated conditions at the base of the ISL, correlating to an increase in seepage potential.
- The preferred cover options provide the best balance between infiltration storage and evaporation, resulting in the lowest recorded seepage:
    - the preferred cover at Endeavor Mine was the 0.6 m cover comprising a 0.3 m reduced permeable layer (RPL) or sealing layer, overlain by a 0.3 m ISL of soil; and
    - the preferred cover at Hera Mine was a 0.6 m cover simply comprising an ISL of soil.

4.0 CALIBRATED NUMERICAL MODEL

SVFlux, developed by SoilVision (2009), and using the finite element method to simulate water movement for both saturated and unsaturated conditions, was applied to all trialled cover configurations at Hera and Endeavor mines. The numerical modelling process for the preferred cover at Hera Mine is detailed below. A comparison of modelling outputs to the preferred cover at Endeavor Mine is given in Section 5.2.

The numerical model was developed in one-dimension to calculate rainfall infiltration and seepage. It was assumed that no surface runoff or run-on occurred and allowed ponding on the surface. Transpiration from vegetation was conservatively excluded, since no data are available (i.e., the numerical model only considers evaporation).

4.1 Model Dimensions and Mesh Geometry

The model was developed to replicate the cover column trial; that is, 1 m thick, comprising 0.4 m of tailings overlain by 0.6 m of soil.
The model automatic mesh generation and automatic mesh refinement algorithms were used to generate the finite element mesh.

4.2 Initial Conditions

4.2.1 Evaporation

Potential evaporation in the model was set at 95% of rainfall, as this was observed in the column trial.

4.2.2 Soil Water Characteristic Curves

The model requires SWCCs. A SWCC is the relationship between volumetric water content and matric suction, and was developed for each depth at which sensors are placed in the covers (the in situ results). The in situ SWCCs for each material were fitted to the in-situ results using the Fredlund & Xing (1994) method. The average trend lines for each material was used in the model.

5.0 RESULTS

5.1 Model Calibration

Figure 2 shows the results of the model volumetric water content prediction compared to the in situ results for the preferred Hera Mine cover. It is noticeable that the model prediction closely matches the response measured in the cover column trial. The model validated the initial conditions described in Section 4.2.

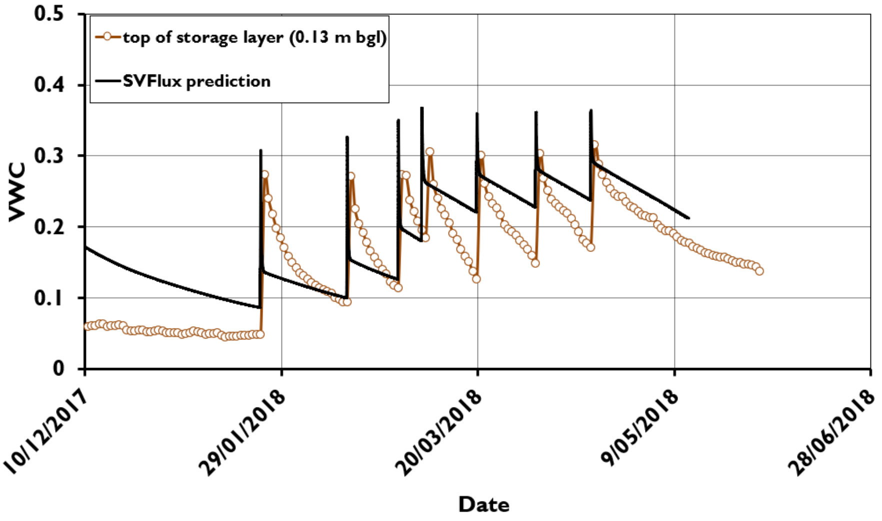

Fig. 2. **Model results compared to the 0.6 m (Hera Mine) cover column trial**

5.2 Water Balance

The numerical model provided actual evaporation results using the Modified Wilson Empirical Equation (Wilson et al. 1997). A comparison between the modelled and measured water balances is given in Table 1, which shows a reasonable correlation between the predicted and observed evaporation and seepage, but poorer correlation with predicted stored infiltration.

Table 1. Water balance comparison for 0.6 m cover (Hera Mine)

	Column	Model
Rainfall (mm)	480.0	480.0
Stored infiltration (%)	3.8	8.5
Seepage (%)	1.0	0.5
Actual evaporation (%)	95.3	90

The inconsistency of the results is likely to do with the SWCCs. That is, the model accuracy would likely improve by further segregation of the SWCCs. Further, the model cannot account for macro-pore infiltration flow in response to short duration, high intensity rainfall, which may result in bypass flow through the cover.

5.3 Future Cover Performance

The modelled performance of the preferred covers is shown for an average, wet and dry year in Table 2.

Table 2. Summary of modelled performance of preferred covers

Cover thickness	Water balance element	Dry year	Average year	Wet year
0.6 m (Endeavor Mine)	Rainfall (mm)	101.6	358.2	806.5
	Seepage (%)	0.1	0.7	1.0
0.6 m (Hera Mine)	Rainfall (mm)	101.6	358.2	806.5
	Seepage (%)	0.16	0.3	0.44

6.0 PREFERRED REGIONAL COVER

Based on the column trials and calibrated models, a suitable TSF cover for the Cobar region is a 0.6 m thick infiltration storage layer of soil, or 0.3 m infiltration storage layer of soil underlain by a 0.3 m RPL. These covers provide a suitable balance between infiltration storage and evaporation, resulting in low seepage. The results presented represent a worst-case scenario, and it is expected that these cover options will perform better at a field-scale, since the covers will be vegetated and the region is in a semi-arid environment, resulting in a highly unsaturated cover for most of the year.

7.0 CONCLUSIONS

This paper examined cover trial work for TSFs containing PAF tailings carried out over the past two decades in the Cobar region, including two cover column trials by the authors. The mines in the region share similar geology, soils, land uses and climate. Therefore, the cover system required for closure is likely to be similar.

The paper presented calibrated numerical models that were used to accurately predict the long-term performance of the two preferred covers for Endeavor and Hera mines. The predicted volumetric water content closely matched the in situ results. It was therefore accepted that the model could be used to predict the long-term performance of the covers. The model was then run for a wet, dry and average rainfall year to predict future cover performance. Seepage was predicted to be under 1% of annual rainfall in the long-term, indicating limited potential for the transport of AMD.

A suitable TSF cover for the Cobar region is a 0.6 m thick infiltration storage layer of soil, or a 0.3 m infiltration storage layer of soil underlain by a 0.3 m RPL. These covers provide a suitable balance between infiltration storage and evaporation, resulting in low seepage. The results presented represent a worst-case scenario, and it is expected that these cover options will perform better at a field-scale, since the covers will be vegetated and the region is in a semi-arid environment, resulting in a highly unsaturated cover for most of the year.

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COAL MINE SALINE DRAINAGE: A STUDY ON ALKALINITY

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ABSTRACT

Coal mining in Queensland only rarely encounters sulfides with concentration or volume to produce acidic response in worked water (ACARP 2006). In contrast, saline-alkaline worked water is common, and managing worked water in a sustainable manner is an ongoing challenge. Here, we simulate acidification of saline, alkaline water to shed light on how distribution of hydroxide species can affect reagent use (via pH adjustment).

The source of saline-alkaline water is not usually a point source, but occurs through multiple processes: evaporation, blasting residue deposition resulting in algal blooms, detergent use, groundwater seepage and salt leaching may all play roles in driving up salinity. Alkaline water results from detergent use, mineralogical or biological reactions, and at higher pH, evapoconcentration can exacerbate the effect.

We show why hydroxide distribution at elevated pH and ionic strength results in alkaline water that does not respond as readily to either dilution (as a method to reduce pH) or acid dosing due to latent alkalinity (hydroxide stored as complexed species).

Speciation modelling (and specifically hydroxide species distribution) performed by the author for the purpose of calibration of a water quality model for a simple salt solution provides valuable insights in understanding how hydroxide distribution into latent species may complicate efforts to lower pH prior in saline-alkaline worked water.

An equilibration model simulates dynamic speciation over the course of a titration (pH 10.5 to 4.4) developed by the author at University of Queensland. The equilibrium model employs a unique solve methodology built by the author, the solving mechanics are based on the fundamental assumption that equilibrium between any two oppositely charged ions can be represented by the interaction between those two ions and their bonded counterpart.

1.0 INTRODUCTION

When the word alkalinity is used, we often think of common inorganic carbon species known to occur in water, such as bicarbonate (HCO_3^-) or carbonate (CO_3^{-2}). For many naturally occurring waters, alkalinity is sufficiently represented by these species that the assumption that alkalinity *is* inorganic carbon is not far off. Alkalinity, in fact, is a measure of the *acid neutralizing capacity* (Appelo and Postma 2005). As we will see in this discussion, inorganic carbonate, at much of the pH range tested, is a considerable contributor to alkalinity, but at elevated pH, we will see a shift towards metal and cation bound hydroxide – termed latent alkalinity contributing species.

Since inorganic carbon is an effective proton acceptor, it follows that aqueous inorganic carbon is so frequently thought of as alkalinity. Worked water is an industry specific term which can broadly be defined as alkaline, saline water with a range of impurities ranging from colloidal coal particulate matter to a range of organics (Rao and Finch 1989).

Here, we explore the terms acidity and alkalinity from a speciation standpoint in context of 'worked water': Alkalinity is not *just* inorganic carbon. Worked water tends to have elevated pH and higher salinity, and based on speciation work completed to date, we find a selection of latent hydroxide and (bi)carbonate species contributing to alkalinity.

2.0 APPROACH

Historically, geochemical simulations have been performed in software utilizing the Newton Raphson method to calculate a solution to a polynomial given a starting point where the derivative of the function is not zero. The Newton Raphson method (Ypma 1995) iteratively revises an initial set of values for the unknowns and convergence (success) is when the residuals is less than some predefined tolerance:

$$r_i = -\sum_{j}^{J} \frac{df_i}{dx_j} dx_j$$

The Newton Raphson method was discarded in favour of a semi-explicit ion-specific calculation which finds an exact numerical solution for any positively charged ion (M_i) in solution acting against any other negatively charged ion (X_j) in solution, with $[M_i] = \alpha_i M_i$, where $\alpha_i M_i$ is the activity of cation i, and $[X_j] = \alpha_j X_j$.

Activity coefficients are solved explicitly for each iteration using WATEQ (Truesdell and Jones 1974) but activity coefficients for neutral (no charge) complexes is assumed to be unity. Note: concurrent studies are investigating the efficacy of various activity models (Strand and Batstone, 2019).

Any two oppositely charged, interacting ions are assumed to tend towards an equilibration state involving the (at least) three species: $[M_i]$, $[X_j]$ and $[M_iX_j]$ where $[M_iX_j]$ is calculated using the equilibrium constant $K_{M_iX_j}$. The difference between the $[M_i]_{t=n}$ and $[M_i]_{t=n+1}$ is calculated using the quadratic equation which solves for the change required to return to equilibrium over that iteration:

$$\partial[M_i] = \frac{-([M_i] + [X_j]) + \sqrt{([M_i] + [X_j])^2 - 4\{([M_i]*[X_j]) - K_{M_iX_j}[M_i][X_j]\}}}{2}$$

Note that $\partial[M_i]$ is stoichiometrically equated with $\partial[X_j]$ and $-\partial[X_j][X_j]$ or $-\partial X_j M_i$ in the case of a precipitate, and $K_{M_iX_j}$ is the equilibrium constant for $[M_i][X_j]$ (Strand et al 2017, Tian et al. 2017).

A variant of this equation is used to calculate precipitation. Change in activity is not calculated because activity is not a conservative parameter

Iterations are needed when there is more than one influence on a single ion for example, Na^+ interacts with both OH^- and HCO_3^-; iterations repeat until there are no further influences on the ion, the delta terms are zero, and Gibbs free energy is minimised.

The simulation platform used for the modelling is GoldSim, and the thermodynamic database employed is Thermo.dat; the model also has capability to model temperature effects on solubility and speciation between 0°C and 100°C, (Tian et al. 2017). Because ionic activity is calculated, no adjustment to constants from the database were used.

3.0 METHODOLOGY

Ten titrations were performed at the Landfill laboratory at University of Queensland (Hawkins Engineering Building). A model of the titration procedure was built in GoldSim. The model simulates the following processes:

- preparation of the solutions (including addition of weight of salt, addition of water weight and mixing),
- dosing with 0.1 ml 1 molar NaOH
- titrant addition (0.1 molar HCl) at regular intervals until target pH was reached

Numerical records of the titration in terms of volume of titrant added and timestamp were transcribed into GoldSim as the driver to induce stepwise change of the solution.

Since the pH of the titration was recorded, for each stepwise addition of HCl into the titration vessel there is a corresponding pH for the total mixture of salt, water, NaOH and HCl, resulting in a large number of calibration points for the simulation.

Results of the titration simulations were assessed in terms of simulated changes to speciation in the solution as well as interrogation into latent alkalinity species contributing to buffering.

4.0 MATERIALS

Ten solutions were mixed based on two mother liquors. The first mother liquor solution contained 4.1045g pure NaCl salt flakes dissolved in 500 ml millipure deionized water. The second mother liquor solution contained 9.1085 g red sea salt (RSS) flakes dissolved in 250 ml millipure deionized water. Five solutions of decreasing concentration were mixed directly from the mother liquors (serial dilution was not used, to avoid unnecessary error magnification). Mother liquor and dilution quantities for each of the 10 solutions are shown in Table 1.

Table 1. Titration solution composition

Solution #	Mother liquor type (NaCl or RSS)	Mother Liquor (g)	Final Solution (g)	Millipure DI water (by difference) (g)
1	NaCl	50.0073	50.0073	0
2	NaCl	25.0763	50.0126	24.9363
3	NaCl	12.5760	49.9756	37.3996
4	NaCl	5.0170	49.9515	44.9345
5	NaCl	2.5135	50.0197	47.5062
6	RSS	49.9999	49.9999	0
7	RSS	25.0685	49.9942	24.9257
8	RSS	12.5142	50.0133	37.4991
9	RSS	5.0172	50.0027	44.9855
10	RSS	2.5028	49.9757	47.4729

The ten final solutions (calculated) are shown in Table 2.

Table 2. Ten titration solutions with various composition

Solution #	Na (mol/L)	K (mol/L)	Mg (mol/L)	Ca (mol/L)	NH_4 (mol/L)	Cl (mol/L)	SO_4 (mol/L)	NO_3 (mol/L)
1	0.14	0	0	0	0	0.14	0	0
2	0.070	0	0	0	0	0.070	0	0
3	0.035	0	0	0	0	0.035	0	0
4	0.014	0	0	0	0	0.014	0	0
5	0.0070	0	0	0	0	0.0070	0	0
6	0.47	0.010	0.053	0.011	5.5E-07	0.55	0.027	3.5E-07
7	0.24	0.0051	0.026	0.0053	2.8E-07	0.27	0.014	1.7E-07
8	0.12	0.0025	0.013	0.0026	1.4E-07	0.14	0.007	8.7E-08
9	0.047	0.0010	0.0053	0.0011	5.5E-08	0.055	0.00	3.5E-08
10	0.024	0.00051	0.0026	0.00053	2.8E-08	0.027	0.00	1.7E-08

0.1 ml of premixed 1.0 molar NaOH standard was added to each solution to raise the pH prior to the titration. The titrant was 0.1 molar premixed HCl standard. The titration sequence was preset, which was not known until after the experiment. The pre-set titration sequence followed roughly a repeated 24 s delay of addition of titrant in 0.075 ml increments, in most cases, the final (target) pH of 4.4 was achieved after 330 seconds and the addition of ~1.05 ml of titrant.

5.0 TITRATION RESULTS

Titrations for all ten solutions were carried out, recorded, transcribed and interrogated. For the purposes of this discussion paper, only the results of the most concentrated solution are shown, titration #6..

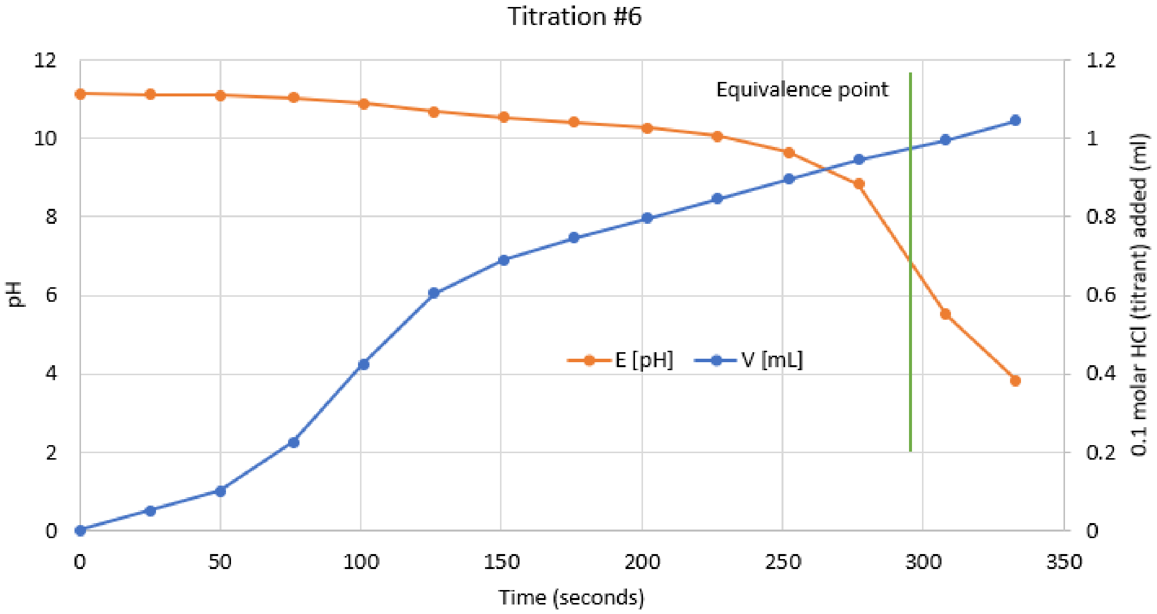

Figure 1. Titration #6 progression and equivalence point

6.0 SIMULATION DETAILS

Summary of details of the simulation are shown here for reproducibility:

- Container sizing
    - Surface area: 12 cm^2
    - Depth: 7 cm
- Volume: ~50 ml
- Head space: 0 mL (Closed system)
- Temperature: 298K
- Air pressure: 0.9943 atm at ~50m above sea level
- Water density: (calculated) 1.03 kg/L
- Runtime: Simulation 1: 200s, Simulation 2: 10000s
- Standardisation of timing: intervals of 50s used for both simulations, allowing maximum of 49 iterations per titration step
- Closed system with respect to $CO_{2(g)}$ exchange

Note: simulation details as listed were unchanged from simulation 1 to simulation 2.

7.0 INTERROGATION OF TITRATION

Speciation modelling was performed for each step of the titration, and the equilibrium species distribution are plotted for each step of the titration. As the titration progresses, various species become energetically favourable (Figure 2). Particularly those species containing hydroxide, carbonate or bicarbonate become less favourable as the pH decreases.

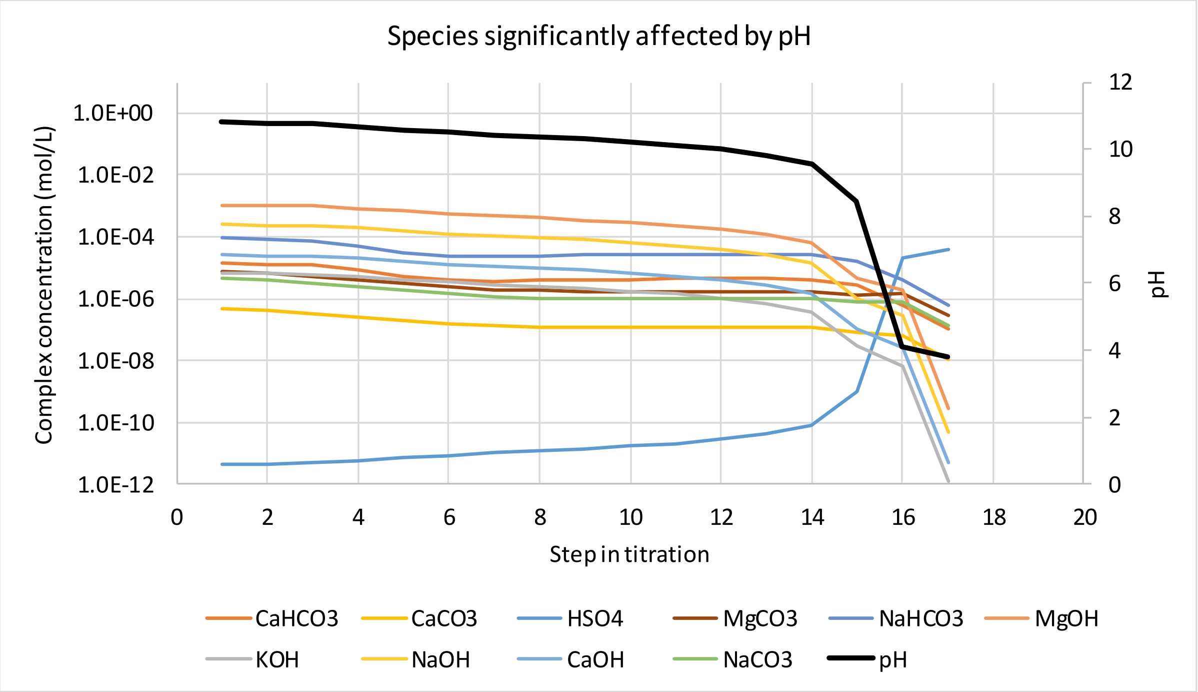

Figure 2. **Energetic favorability affecting species distribution (Titration #6)**

To assess the distribution and contribution of latent alkalinity species, only those species containing bound carbonate, bicarbonate or hydroxide are plotted after accounting for stoichiometry to assess the most significant species contributing to alkalinity. As can be seen in Figure 3, MgOH is the largest contributor of latent alkalinity in the prepared solutions. Prior to seeing a significant drop in pH, the alkalinity contributing species are depleted.

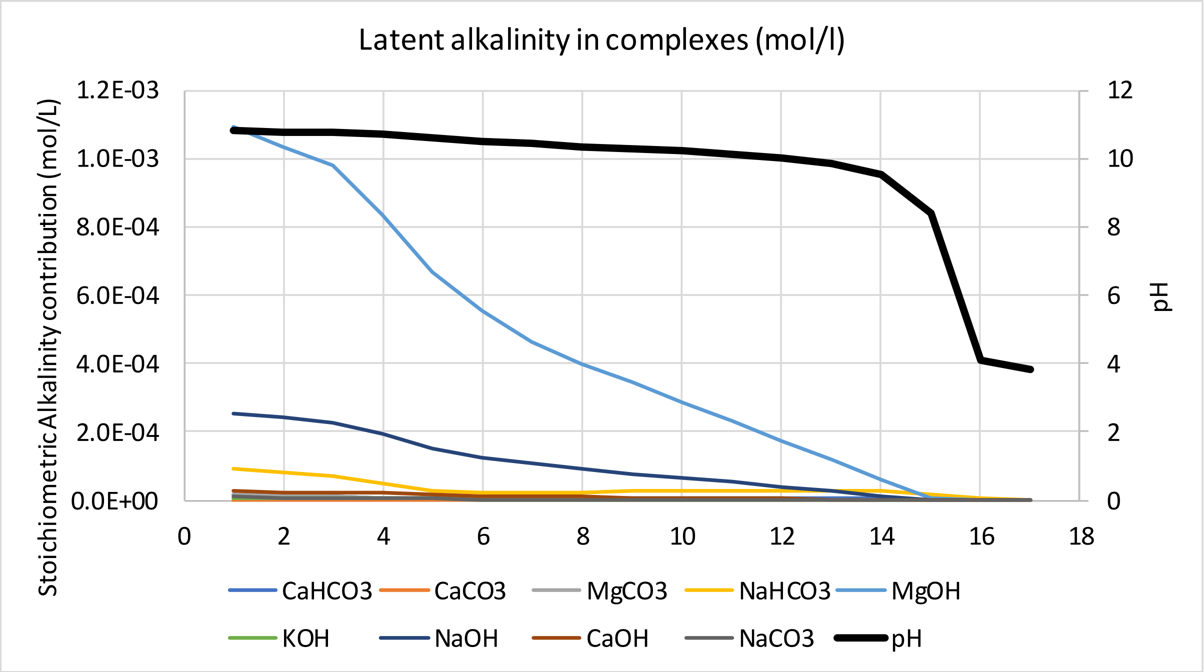

Figure 3. **Latent alkalinity contributions (Simulation 1; Titration run 6)**

The materials used in the titration did not explicitly include inorganic carbonate which may explain the somewhat depressed inorganic carbonate species present in the above figures. Since the prepared solutions did not contain appreciable inorganic carbon, a second test (simulation 2) was made to examine the effects of carbonate alkalinity.

8.0 SIMULATION 2

A second test (simulation) was programmed based on a groundwater sample from near a worked water storage facility. The analytical assessment provided sufficient information to develop a significantly different simulated response based on a similar titration sequence. The sample of water had chemical parameters as indicated in Table 3.

Table 3. **Chemical composition from worked water sample in Central Queensland Coal Mine**

pH	Na	Cl	Ca	Mg	SO_4	K	HCO_3	CO_3	Ionic error
7.33	3680	5850	246	184	0.5	16	950	0.5	23%

The simulation with the actual sample was run, and some differences were immediately observed:

- The pre-titration dose of NaOH results in a less pronounced pH shift (and is rapidly affected by preliminary doses of acid)
- There is a delayed response where buffering is based on the prevalence of HCO_3
- The titration does not have the same end point
- Bicarbonate containing complexes have a different trend compared to hydroxide containing species as the titration progresses

The results from simulation 2 are shown in Figure 4 and Figure 5. General trends are similar between simulation 1 and 2 with all alkalinity contributing species being depleted prior to the pH shift, however, some residual HCO_3 containing complexes ($NaHCO_3$ and $CaHCO_3$) persist even after the titration endpoint is achieved, albeit at significantly lower concentration.

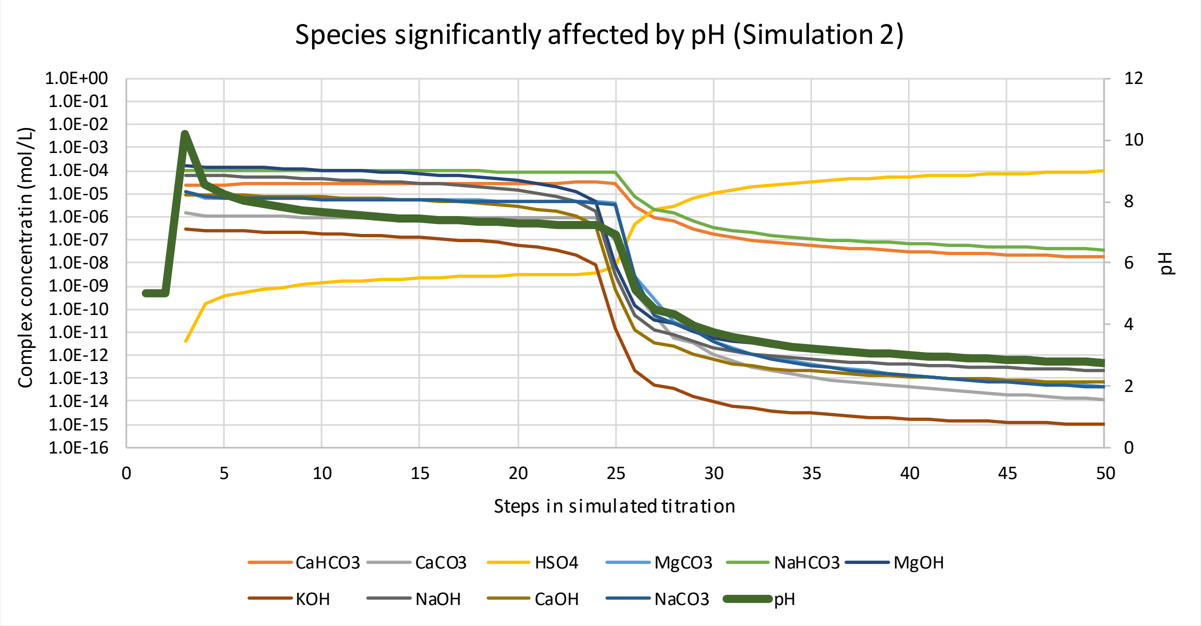

Figure 4. **Energetic favorability affecting species distribution (Simulation 2)**

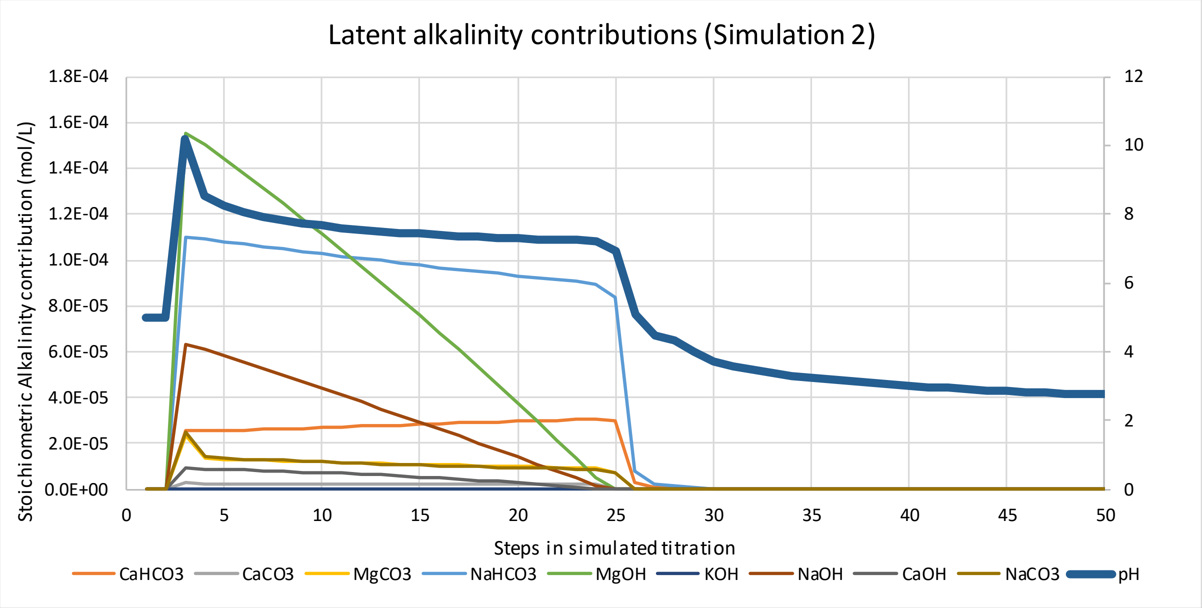

Figure 5. **Latent alkalinity contributions (Simulation 2)**

One result that is counterintuitive is the relatively slow increase in the $CaHCO_3$ complex as the titration progresses. This is unusual because we would expect HCO_3 containing complexes to decrease as the alkalinity source is consumed in the titration. This result can be explained by considering first that the solution has very high bicarbonate and moderately elevated calcium to start with, then the pre-dose of NaOH forces a rapid shift in equilibrium to favor carbonate, which immediately causes calcite to precipitate. The titration, then is not only consuming bicarbonate but slowly consuming calcite, which maintains the pH while also protonating liberated carbonate, effectively replacing *two* bicarbonates for each mole of calcite consumed. Hence, while calcite is being depleted, bicarbonate is continually being replaced. The titration endpoint is achieved not when all bicarbonate is consumed (protonated), but when the distribution of inorganic carbon no longer retains significant buffering potential – when H_2CO_3 ~ HCO_3 which occurs near pH 6.3. Indeed, this can be observed in both Figure 4 and Figure 5.

To check this interpretation directly, plots of inorganic carbon distributions were assessed against pH directly using model outputs. As can be seen in Figure 6 there is a close match. The author notes there is a minor lag in the pH, this is likely due to a numerical artifact where the software doesn't update the reported value until immediately before the next step, resulting in a visual observation not lining up exactly, overall, however, the observation holds true.

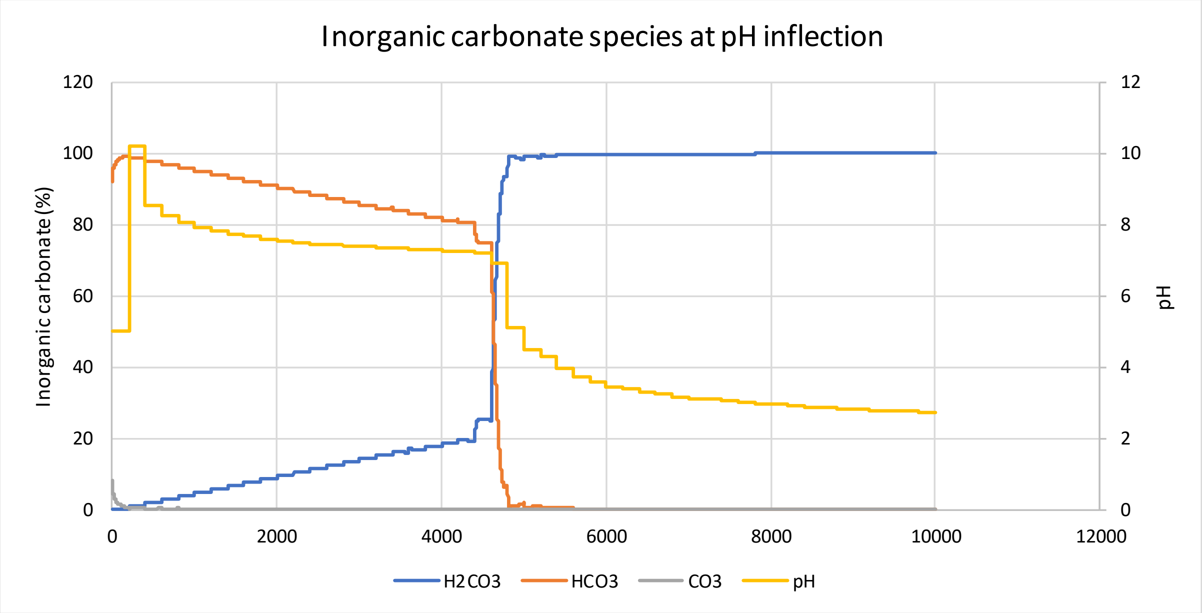

Figure 6. **Inorganic carbon distribution and pH**

9.0 CONCLUSIONS

Alkalinity distributions in solution, and in solutions undergoing acidification are fundamentally related to the starting concentrations and the quantity of inorganic carbon present. When bicarbonate is present as the most prevalent species of inorganic carbon, there is a strong tendency for the solution to buffer between pH 6.3 and pH 8.3. If other inorganic carbon species such as carbonate are present, then the pH will shift upwards towards pH 10.3, and downwards if carbonic acid is present. Above 10.3 pH, hydroxide species may start to contribute significantly more alkalinity than inorganic carbonate, and broadly, the influence of complexed species will mirror the free positive charged ions.

Some bicarbonate species tend to persist even near the pH inflection point, which suggests that the stability of bicarbonate complexes may not readily protonate until there is an abundance of protons in competition for the protonation site.

Takeaway messages: pH changes in response to acid dosing of worked water may be significantly altered by the type of alkalinity present. Changes to pH when the worked water has pH in the 8.3-10.3 range may be complicated by multiple forms of inorganic carbon (carbonate and bicarbonate), and latent alkalinity tied up in charged and uncharged complexes may aggravate efforts to neutralize the water. Measurement of pH (or pOH) is fundamentally flawed if solely used to determine the quantity of acid needed to neutralize the water. The presence of precipitated materials in contact with the solution may add considerable buffering potential as well.

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SULFUR-RELATED GEOCHEMICAL PROCESSES AND WATER CHEMISTRY AT A SOUTH AFRICAN COLLIERY

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ABSTRACT

Coal mining operations produce large amounts of waste materials that have a potential to release contamination into the environment. This case study is focused on a coal mine in eMalahleni, South Africa. The colliery produces steam and metallurgical grade coal for the export and domestic markets using the continuous mining method followed by coal washing and flotation. The coal discard dump at the mining area acts as an integrated storage facility, where both discard and slurry are stored. Only one of the pollution control dams is plastic-lined that raises the risk of the contamination of groundwater resources. Surface and groundwater qualities in the operation area highlight the impact of coal mining. As the sulfate sulfur can originate from the highly saline pore water of the underlying sediments, the first aim of the project is to assess the source of sulfur based on the sulfur isotope composition of dissolved sulfate in the mine water. Secondly to track sulfur conversions and the changes of pyrite oxidation mechanisms across the mine by measuring sulfur and oxygen isotope composition of dissolved sulfate. The expected findings of the project can ultimately be used to inform the improvement of geotechnical designs of processing and storage facilities, water management plan or water quality monitoring program.

1.0 INTRODUCTION

South Africa is one of the top countries in terms of its heavy dependence on coal mining that provides both foreign income and an energy source for the country (Reddick et al., 2008). Being the primary energy source, coal contributes to 93% of the country's electricity production (Ndlovu and Inglesi-Lotz, 2019). South Africa has the fifth largest coal deposits in the world with an estimated 33 Gt reserve base (SACRM, 2011). The majority of operating mines are currently in the Mpumalanga, Limpopo and Free State Provinces with the main resources located in the Limpopo Province. According to Pooe and Mathu (2011) out of the 73 collieries of the country, 61 were located in Mpumalanga in 2007. The major coal mining areas in Mpumalanga Province are near the towns of eMalahleni, Middelburg, Ermelo, Standerton and Secunda out of which eMalahleni (formally known as Witbank) is considered the leading coalfield at present (Figure 1). Nevertheless, due to the fast depletion of Mpumalanga coalfields, mining is shifting to the Waterberg coal basin in Limpopo Province (Figure 1; DMR, 2014). Based on the local demand of energy, the local power utility Eskom estimates the necessity of 4 billion tons of coal in the next 40 years out of which 2.5 billion tons will need to come from new sources (DMR, 2014). More recently however, the Integrated Resource Plan 2019-2030 requires the decommissioning of all but two coal-fired power stations in South Africa. The growing role of unexploited coalfields in the South African coal production would not only entail the increased risk of coal-related environmental problems but will also put additional pressure on the mining companies to maintain the natural resources. Besides the use of land and water resources, coal production also contributes to land and water degradation, the increase of waste generation, pollutant and particulate matter emission. As coal mining in the eMalahleni started in 1895, this region well-represents the long-term environmental impacts of the different mining activities related to coal. According to Maree et al. (2004) approximately 50 ML/d mine water discharges into and pollutes the water resources of the upper Olifants River catchment. Efforts were made by the mining industry to decrease the impact of the released mine drainage on the area. The eMalahleni Water Reclamation Plant (EWRP) was installed in 2007 and serves as a good example to represent the management of ARD. The capacity of the plant is 25 ML/d and its operation is based on limestone neutralisation, ultra-filtration and reverse osmosis desalination (Mey et al., 2009). Because of the low capacity and the high costs of installation and operation however, it cannot be used to improve the general condition of the local environment (McCarthy, 2011).

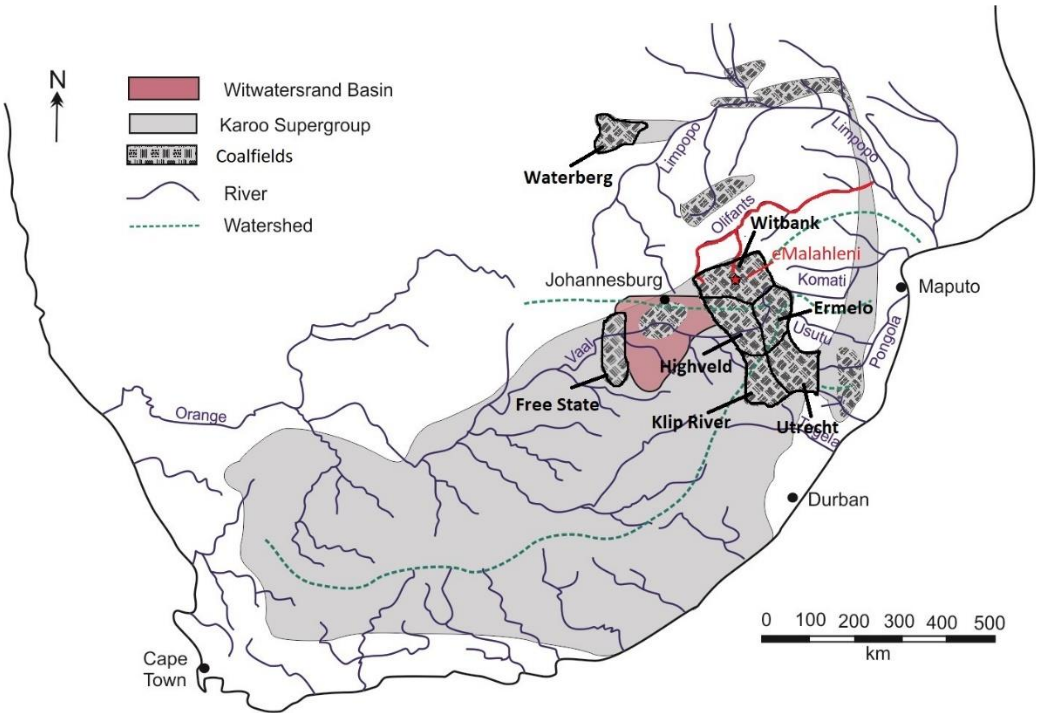

Fig. 1. **Distribution of coal fields of South Africa (modified after McCarthy, 2011)**

This paper provides an overview of the operation of a colliery located in eMalahleni and the impact of the mining activities on the local water regime. In addition, a future project is also outlined that will mainly focus on the source of sulfate and associated ARD using the stable isotope technique.

2.0 GEOLOGICAL SETTING AND MINING ACTIVITIES

2.1 Local Geology

The majority of South Africa`s coal reserves are hosted in the Karoo Supergroup, which underlies approximately 60% of South Africa by area (Figure 1; Cairncross, 2001). The thick sequence of Karoo sediments consists of sandstone, shale, carbonaceous siltstone, conglomerates, coal seams and deposited over the diamictites and tillites of Dwyka Formation between 300 and 180 million years ago (Figure 2). The Karoo sediments show coarsening upwards sequences representing deltaic and fluvial environment. The coal seams are in the Vryheid Formation, of the Ecca Group, of the Karoo Supergroup (Figure 2). Coal was deposited in a post-glacial varying environment from proximal conglomeratic alluvial fans through fluvial, delta-plains, back barrier or lake margins (Hobday, 1987). Most of the commercial seams occur in fluvial and delta sequences. The different depositional environments along with the variable sedimentation rates, local topography, changes in base level affected the coal quality and geometry. Dolerite dykes and sills intruded to both Dwyka and Ecca Formations have resulted in variation in coal rank (Schmidt, 2008) ranging from sub-bituminous, bituminous coal to anthracite. The coal seams at the northern part of eMalahleni coalfield are in a shallow position due to the proximity of the northern margin of Karoo Supergroup below this area (Figure 2). The depth of coal seams increases towards the south with a slight dip. Five bituminous coal seams are present in the eMalahleni coalfield numbered consecutively from the No. 1 seam to No. 5 seam. No. 4 seam is the most important resource of high yield, export quality coal.

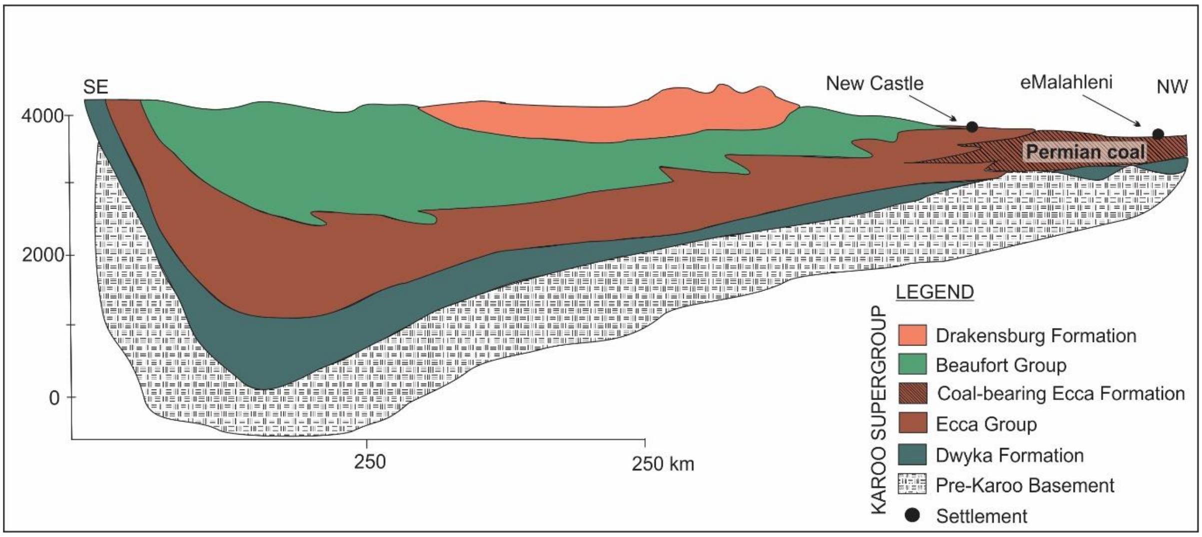

Fig. 2. **Cross section of the Karoo Basin (adapted from Cadle et al., 1993)**

2.2 Mining Operation

The mine primarily was established to supply coal to overseas markets, but it also supplies small quantities of coal for domestic use. Historically the No. 1, 2, 4 and 5 seams have been mined within the mining right area. Recently the bulk of the life of mine (LOM) tonnage is sourced from one seam, which is laterally distributed over the colliery. The mine produces thermal coal that is extracted using the continuous mining method. The estimated remaining in situ coal reserves of the colliery associated with the active seam are above 200 million tons.

It currently produces about 4 million tons of ROM coal per annum. A further million tons of mineable reserves are held in the currently inactive seams. In total, close to 20 vertical and inclined shafts are located within the mining right area, but only two of them are operational. Due to the nature and composition of the active seam, coal beneficiation is needed to upgrade the coal to export quality specification levels. Run of mine (ROM) coal is brought to the surface via conveyors to the beneficiation plant processing coal from this seam (Figure 3). Once at the plant, the coal is crushed and washed using dense media separation, magnetic separation and flotation. The discard and slurry from the washing is sent to the coal discard dump that is continually being upgraded and extended. In this process, the original coal discard dump, compacted dump and slurry dam are consolidated into an integrated residue facility. The supernatant water associated with the slurry is decanted by penstock to the pollution control dams (PCD). The processed coal is then conveyed to the rapid loading terminal (RLT) from which the coal is transported to the markets (Figure 3).

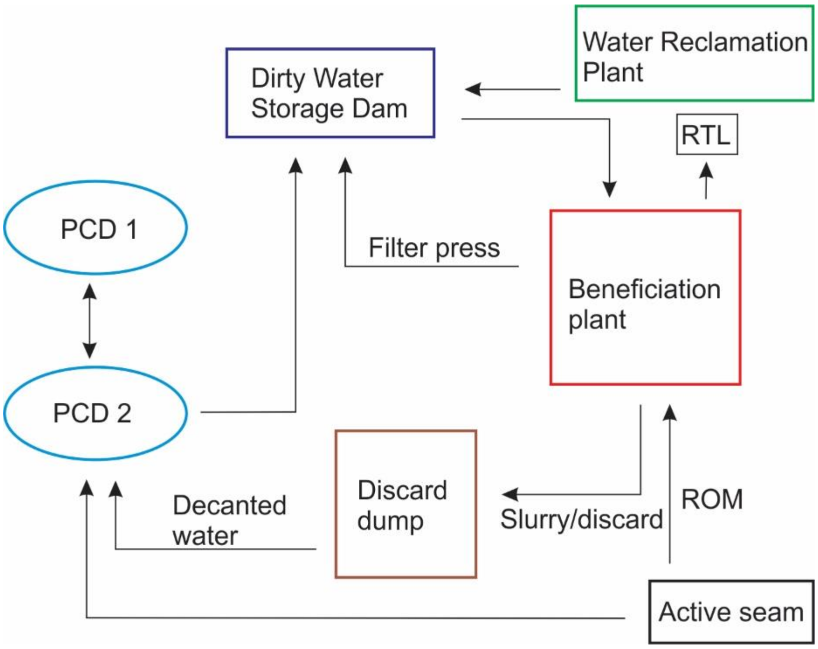

Fig. 3. **Simplified flowsheet of the mining operation (modified after Shangoni, 2015)**

3.0 WATER CHEMISTRY AND REGIONAL ENVIRONMENTAL IMPACTS

Close to ten PCDs are in operation in the mining area. Only one of the dams is plastic-lined as it was constructed after the National Water Act regulation (1998). The operation of non-lined dams raises the risk of the contamination of surface water bodies and groundwater resources. As a result, surface and groundwater qualities in the operation area highlight the impact of coal mining activities. The colliery is located adjacent to te source of a creek that discharges into the eMalahleni dam. This creek is one of the main tributaries of the Olifants River, which is the primary tributary of Limpopo River System. Water from both upstream and downstream of the creek shows neutral pH values and high concentration of SO_4 with elevated Mn and Mg concentrations (Nepid Consultants, 2015). The quality of additional surface water e.g. runoff, dam and groundwater in the operation area are characterised by acidic pH along with high SO_4, Fe, Ca, Mn and Mg concentrations. On the other hand, some water samples show neutral-alkaline pH associated with high/elevated SO_4 and Mg (Shangoni, 2016). Acidic mine effluents mainly relate to underground workings, storage facilities and PCDs indicated by the low pH and high metal concentrations. Long term observation of DWA's (Department of Water Affairs) monitoring stations situated in the Olifants River catchment area showed that the concentration of sulfate in the river consistently exceeded the 200 mg/l threshold value for domestic use and human consumption during the monitoring since 2001 (De Villiers and Mkwelo, 2009). In the upper Olifants River catchment area a large number of dams have been constructed to regulate the surface runoff and their water is mainly used for agricultural purposes. Sulfate concentration at the eMalahleni dam was one of the highest ranging from 34 to 300 mg/l between 2001 and 2009 (De Villiers and Mkwelo, 2009). Whereas, 41% of the surface water in the upper catchment of the river together with the tributaries is under stress, the middle and the lower sections have tolerable and acceptable status. According to Water Research Commission, the threat on the surface water quality caused by coal exploitation ranges from moderate to very high at Olifants River Water Management Area (WRC, 2018). The presence of local surface water pollution significantly affects the condition of the groundwater system besides the direct contamination of mine waste leachates and the agricultural activities. Although, groundwater is a valuable fresh water source, its usage is quite small in the Mpumalanga Province compared to that of the surface water resources. Even if the immediate threat of coal mining on groundwater is ranked from moderately low to high risk (WRC, 2018), it is likely to have a longer-term impact on the environment due to its very long residence time in the aquifer (Cook and Böhlke, 2000).

4.0 CONCLUSION

Elevated sulfate concentrations together with low pH values indicate the presence of ARD reactions at the studied mine site. As land use adjacent to the mining area is predominantly agricultural, in addition the colliery is situated within the primary catchment area of Olifants River, it is important to ensure that the ARD affected water is not released into the environment via plume movement. In order to minimise the potential impacts of ARD on natural water systems it is essential to understand the mechanisms taking place during ARD formation and identify the source of various contaminants along with the processes control their mobility. Based on the assumption that Mg originates from the high saline pore water of the underlying Karoo sediments (Shangoni, 2016), we propose to measure the sulfur isotope composition of dissolved SO_4 in both surface and underground water in order to assess the origin of sulfur (gypsum vs pyrite) at the studied mine site. Sulfate from the oxidation of sulfide minerals typically has negative sulfur isotopic composition (Butler, 2007) as opposed to the positive sulfur isotopic composition of gypsum derived from the evaporite-bearing sedimentary rocks (Lui et al., 2017). The effective differentiation of mining-related sulfate contamination from non-mining-related sulfates by using the above explained dichotomy in their isotopic compositions was proven by number of authors (e.g. Fennel and Bentley, 1998; Knöller et al., 2004; Ren et al., 2017). A secondary aim is to track sulfur conversions and the changes of pyrite oxidation mechanisms based on sulfur and oxygen isotope composition of dissolved sulfate within various unit operations across the mine and plant by sampling water at different stages of its surface cycle and at seepage points. The expected findings of the project can ultimately be used to inform the improvement of geotechnical designs of processing and storage facilities, water management plan or water quality monitoring program that covers the impacts of all the mining activities on the studied area. This isotope study will also be a benchmarking exercise that can provide reference dataset for future isotope projects on the area.

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AN INTEGRATED PROTOCOL FOR THE ASSESSMENT OF MOBILITY AND RISKS OF POTENTIALLY TOXIC ELEMENTS IN MINE TAILINGS

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ABSTRACT

An integrated protocol for the assessment of mobility and derived ecological and human health risks of potentially toxic elements (PTEs) in mine tailings is presented and tested. The proposed methodology comprises four interrelated investigation levels, namely (1) Chemical characterization and contamination degree of tailings by PTEs, (2) Mineralogical characterization: bulk and quantitative automated mineralogy analysis by SEM (QEMSCAN®), (3) Assessment of PTEs potential mobility by sequential extraction procedure (SEP) fractionation coupled with mineralogy analysis and 4) ecological (ERA) and human health risk assessment (HHRA) on the basis of fractionation results. This protocol was applied to study selected diverse Chilean fresh and old tailings from an operative Cu-Mo mine and from an historical impoundment, respectively. According to pollution indices, Cu, Mo, As and Pb are most concerning PTEs in the tailings. SEP shows that major portion of the PTEs is strongly fixed as residual fraction, although the Fe-oxides also play a key role in controlling mobilization of PTEs in the old tailings, while a considerable portion of Cu in the fresh tailings was sulphide-bound. Cu (32-75 %), As (10-50 %) and Mo (1-45 %) were identified as the PTEs most prone to mobilization. ERA suggests that the old tailings poses a very high potential risk for ecological receptors (PERI = 663–3356), mostly due to Cu and As, while the FTs belong to the considerable or very high risk classes. HHRA indicated that the old tailings pose higher potential non-carcinogenic health risks. The cancer risk decreased in the order ingestion > dermal > inhalation for both children and adults and for the three carcinogen PTEs (As, Cr, Ni) in the tailings. Carcinogenic-HHRA signaled As as the main PTE of concern via ingestion pathway. This study illustrates how the proposed methodology can be applied for reliably assessing the whole risks due to PTEs mobilization in mine tailings.

1.0 INTRODUCTION

Tailings, in particular sulfide-containing tailings, are well-known sources of acid and metalliferous drainage causing potentially toxic elements (PTEs) contamination. Tailings seepage may contain hazardous substances from the early stages of tailings deposition into perpetuity, particularly if the tailings are not capped and are subjected to the ingress of oxygen and infiltrating precipitation (Edraki et al. 2014). Relevantly, tailings impacts mainly relate with the PTEs concentrations and chemical forms in water in contact with the solid phase rather than with the total PTEs content in the tailings. Diverse methodologies have been applied to evaluate and/or predict the potential mobilization of PTEs in mine wastes. Among them, leach testing using extracting solutions to mimic diverse environmental and/or disposal scenarios, gives an indication of PTEs mobility and helps to identify constituents that are immediately available for release from a given material type (Brough et al. 2013). In this regard, sequential extraction procedures (SEP) have revealed as a particularly useful method because they provide more detailed information on the associations between PTEs and specific geochemical phases and forms present in the waste matrix (Scheckel et al., 2003; Al-Abed et al. 2006). This allows to infer the fate and mobility of the PTE in the environment, and indirectly its bioavailability, in response to changes in environmental conditions (Hass and Fine, 2010), which then can be linked to potential environmental and human health impacts and consequences (Edraki et al. 2014). Coupling SEP fractionation with mineralogical analysis helps to elucidate the PTEs associations with the different geochemical phases and to identify the minerals dissolved in each step. There is a need and opportunity for developing methodologies aimed to trusty evaluate and predict the geochemical stability and potential risks of tailings. In this work, an integrated protocol for the assessment of mobility and derived ecological and human health risks of potentially toxic elements (PTEs) in mine tailings is presented. The proposed approach considers the potentially mobile fractions of PTEs in the tailings, while it emphasizes the relationship between mineralogy and PTEs mobility and risks. The main objectives of this study were: (i) to develop an integral protocol for assessing mobility and environmental risks due to PTEs in tailings, tailored to the specific characteristics of Cu-tailings and susceptible of being adopted by the mining industry practice, (ii) to apply the methodology for assessing the potential mobility of PTEs from selected fresh and old Cu-tailings from Chile, and (iii) to assess the potential environmental and human health risks due to PTEs in Cu-tailings by linking PTEs partitioning with ecological and human health risk assessment.

2.0 MATERIALS AND METHODS

2.1 Tailings

Six tailing samples, differing in origin, aging and ore processing, were studied: 1) three fresh flotation tailings (FTs) (FT1, FT2 and FT3) from an active porphyry Cu/Mo ore deposit in Central Chile, and 2) three old tailings (OTs) (OT1, OT2 and OT3) obtained from a historical impoundment in North-central Chile storing Cu and polymetallic tailings mixed with slag-tailings. The samples were oven-dried at T<60 °C, disaggregated, sieved (<2 mm), homogenized and milled in a tungsten carbide vibratory mill for their use.

2.2 Assessment protocol methodology

The methodology, named with the acronym CHEMINSPHERA, comprises four interrelated investigation levels: (1) Chemical characterization and contamination degree of tailings by PTEs, (2) Mineralogical characterization: bulk mineralogy and quantitative automated mineralogy analysis by SEM (QEMSCAN®), (3) Partitioning (speciation) of potential mobility of PTEs by SEP aided by mineralogy analysis and 4) ecological (ERA) and human health risk assessment (HHRA) on the basis of partitioning results (Figure 1).

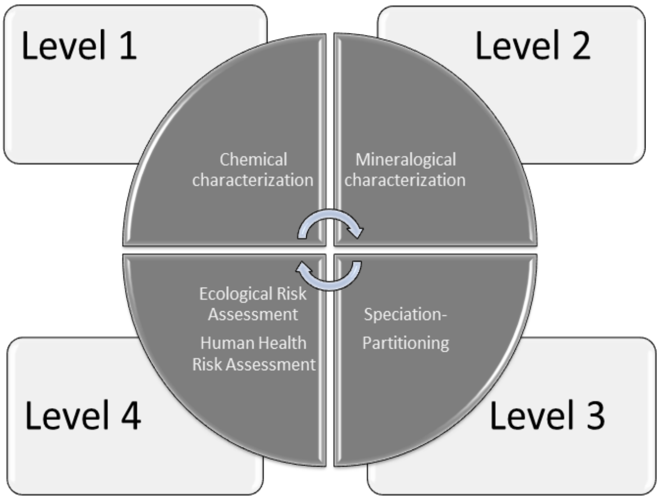


Fig. 1. Methodology (CHEMINSPHERA) used for the assessment of mobility and risks of PTEs in tailings.

2.2.1 Chemical and mineralogical characterization

Chemical composition of the tailings was determined by X-Ray Fluorescence (XRF) (Rigaku ZSX Primus II XRF spectrometer) and by acid digestion (concentrated $HF/HNO_3/HCl$ plus H_3BO_3) for trace elements. PTEs concentrations in extracts and solutions were measured by ICP-OES (Agilent Technologies 5110 instrument with Agilent SPS 4 autosampler).
The bulk mineralogy of the tailings was analysed by powder XRD (Bruker D4 Endeavor diffractometer with Lynxeye detector operated with Cu-radiation and Ni filter for Kß radiation). Quantitative analysis of minerals by SEM was carried out by analyzing samples dispersed in an Epofix resin (Struers) with graphite to ensure grain separation, in a QEMSCAN® system installed on a Quanta 250 SEM equipped with two Bruker XFlash 6130 (Silicon Driff Detector) N2L free detectors measuring 50,000 particles per sample, using a point spacing of 5 µm and an accelerating voltage of 25 kV. Idiscover-Imeasure 5.3 platform was used for data analysis.

2.2.2 Partitioning of PTEs by SEP

A six-step SEP was applied to fractionate PTEs in the tailings (Table 1). Tailings samples (2 g) were successively extracted (orbital shaker, 200 rpm) with 50 mL of the corresponding extracting solution, then they were centrifuged (2500 rpm, 15 min) and the supernatants filtered (Whatman 42 filters). The extracts were stored at -18 °C until elemental analysis by ICP-OES. All extractions were performed in triplicate. In parallel, a series of tailing samples were single extracted by each SEP reagent and the mineralogy of the dried (30 °C) tailing residues were studied by X-ray diffraction (XRD).

Table 1. Sequential extraction procedure for fractionation of PTEs in the tailings

Step	Fraction	Reagent		Reference
1	Exchangeable	0.05M $(NH_4)_2SO_4$	1 hour	Lombi et al. (1999)
2	Specifically sorbed - Carbonate-bound	1M Na-acetate pH 5	2 hours	Tessier et al. (1979)
3	Bound to amorphous or poorly crystalline Fe oxyhydroxides	0.2M NH_4-oxalate, pH 3.3	4 hours (in darkness)	Graupner et al. (2007)
4	Bound to crystalline Fe oxides.	0.2 M NH_4-oxalate + 0.1M ascorbic acid, pH 3.3	30 minutes, (boiling water bath, 96 °C)	Lombi et al. (1999)
5	Organics and secondary sulfides	35% H_2O_2	1 hour (heat in water bath)	Dold (2003)
6	Residual (sulfides enclosed in silicates, aluminosilicates)	Acid digestion (Aqua regia + HF plus H_3BO_3)	-	Graupner et al. (2007)

2.2.3 Ecological Risk Assessment

The Potential ecological risk index (PERI) -a cumulative ecological risk index which reflects the combined effect of toxic elements- was used to assess the environmental risks. PERI was calculated considering the non-residual concentrations of PTEs by Eqns. [1]–[3] (Håkanson 1980):

$$C_f^i = \frac{C_s^i}{C_r^i} \quad [1]$$

$$E_f^i = T_f^i \times C_f^i \quad [2]$$

$$\mathrm{PERI} = \sum E_f^i \quad [3]$$

Where C_f^i is the contamination factor; C_s^i is the concentration of the PTE in the tailing and C_r^i is the reference value for PTEs concentration (Taylor and McLennan, 1995). E_f^i is the potential ecological risk factor for the given PTE and T_f^i is the toxic response factor for each metal (Håkanson, 1980), except for Mo and V (not available in the literature).

2.2.4 Human Health Risk Assessment

Health risks for the PTEs present in the tailings were assessed using the methodology described in Forghani et al. (2019). The chronic non carcinogenic risks were evaluated by estimating the average daily doses (*ADD_s*) (mg $kg^{-1}day^{-1}$) via ingestion (*ADD_{ing}*), inhalation (*ADD_{inh}*) and dermal absorption (*ADD_{derm}*) of each PTE, using Eqns [4]–[6], respectively:

$$\mathrm{ADD_{ing}} = \frac{\mathrm{C \times R_{ing} \times EF \times ED}}{\mathrm{BW \times AT}} \times 10^{-6} \quad [4]$$

$$\mathrm{ADD_{inh}} = \frac{\mathrm{C \times R_{inh} \times EF \times ED}}{\mathrm{PEF \times BW \times AT}} \quad [5]$$

$$\mathrm{ADD_{derm}} = \frac{\mathrm{C \times SA \times SL \times ABS \times EF \times ED}}{\mathrm{BW \times AT}} \times 10^{-6} \quad [6]$$

The sum of the PTEs concentrations extracted in the first three fractions of the SEP were used as a surrogate of potentially bioaccessible concentrations to calculate *ADD*s. Corresponding hazards quotients for each PTE (*HQ_i*) were calculated as the ratio of the *ADD* of each PTE to its reference dose for the same exposure pathway:

$$\mathrm{HQ_i} = \frac{\mathrm{ADD}}{\mathrm{RfD_i}} \tag{7}$$

Where RfD_i is the Reference Dose (mg $kg^{-1}day^{-1}$) expressing the average daily exposure below which no adverse effects are expected. Adverse health effects are unlikely if HQ ≤1, whereas there may be concern for potential non-carcinogenic effects if HQ >1 (Cao et al. 2014). The overall potential for non-carcinogenic adverse effects caused by more than one chemical was expressed by the Hazard Index (HI):

$$\mathrm{HI} = \sum\nolimits_{i=1}^{n} \mathrm{HQ_i} \tag{8}$$

HI >1 suggest potential cumulative non carcinogenic health risks, while HI <1 indicates that adverse health effects are unlikely. The non-carcinogenic cancer risk through different pathways was expressed as the total exposure Hazard Index (THI):

$$\mathrm{THI} = \sum\nolimits_{i=1}^{n} \mathrm{HI} \tag{9}$$

Chronic non-carcinogenic risks are unlikely when THI ≤1 and likely to occur when THI >1.
Carcinogenic risks were assessed as the Incremental Lifetime Cancer Risk (ILCR), which defines the incremental probability of developing cancer of an individual over a lifetime by exposure to a potential carcinogen. ILCRs were calculated by multiplying the *ADD_s* by the corresponding slope factor (SF) of the carcinogenic element:

$$\mathrm{ILCR} = \mathrm{ADD} \times \mathrm{SF} \tag{10}$$

When multiple contaminants occur, the carcinogenic risk for all carcinogens and exposure route are added. $1 \times 10^{-6} \leq \mathrm{ILCR} < 1 \times 10^{-4}$ are considered as acceptable (Cao et al. 2014).

3.0 RESULTS

3.1 Chemical composition and mineralogy of the tailings

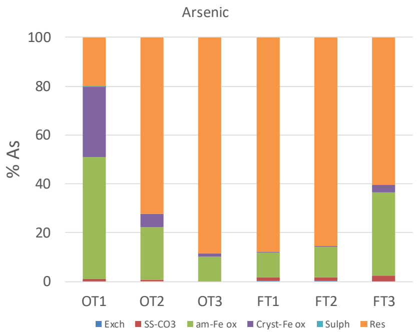
The tailings contain Si (35–55% wt), Fe (9–38% wt) and Al (5–18% wt) as major chemical constituents, and considerable contents of Ca (1–25% wt), Mg (1–4% wt), Na (1–6% wt) and K (2–9% wt). The FTs have higher total S contents (5–8% wt) than the OTs (0.3–1.2% wt). Besides, the tailings contain variable concentrations (at mg/kg level) of an array of PTEs, some of them included the USEPA's lists of toxic and priority pollutants (Table 2). In general, the OTs contain higher PTEs concentrations than the FTs, as typically for tailings from historical mining operations. The degree of contamination by PTEs was assessed on the basis of diverse pollution indices as criteria: geoaccumulation index (I_{geo}), single-factor index (P_i), combined pollution index (CPI) and pollution load index (PLI). I_{geo} classifies the tailings as highly or extremely high polluted with Cu (I_{geo} = 4.0–6.9). OT1 is also classified as highly to extremely high polluted with Pb (I_{geo} = 4.4) and extremely high polluted with Mo (I_{geo} = 5.4). Arsenic levels fall in the moderately to highly polluted or highly polluted classes (I_{geo} = 2.5–4.0). CPI shows the OT1 as the most polluted (CPI = 65; ultra-high pollution degree) tailing. PLIs >>1 indicate that the tailings are polluted with PTEs and further confirm OT1 (PLI~11) and OT2 (PLI~7) as most concerning tailings. QEMSCAN® and XRD results showed that the tailings commonly contain significant proportions (% mineral mass) of quartz (10-45%), plagioclase (5-42%), K-feldspars (2-7%), chlorite (7-30%) and mica (1-16%). OTs contain higher contents of spinel-type Fe oxides from slag-tailings (up to ~30%), carbonates (skarn gangue) (up to ~10%) and Cu-oxides (up to ~2%) than the FTs. Conversely, the FTs contain higher proportions of mica (up to ~16%), biotite (up to ~13%), pyrite (up to ~2%) and anhydrite-gypsum (up to ~2%) than the OTs.

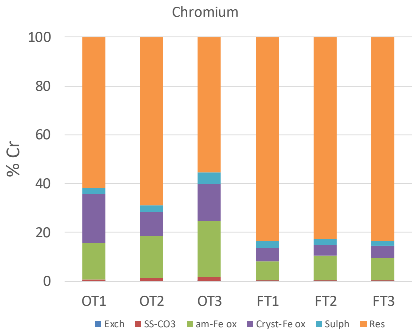
Table 2. Concentrations (mg/kg) of PTEs in the tailings

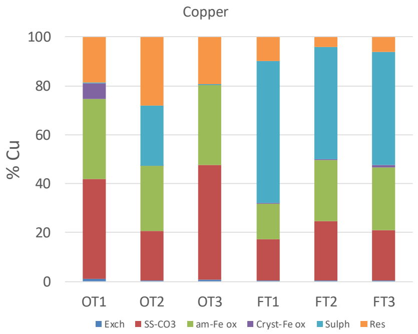
Sample	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
OT1	311	55	8110	380661	716	95	18	651	197	559
OT2	131	57	3375	148673	2678	26	22	138	237	158
OT3	183	22	3734	168155	1212	25	12	13	249	84
FT1	113	47	1091	104724	306	68	25	17	187	66
FT2	152	55	1061	110110	328	41	29	21	227	75
FT3	183	64	1434	123226	308	77	30	14	215	71

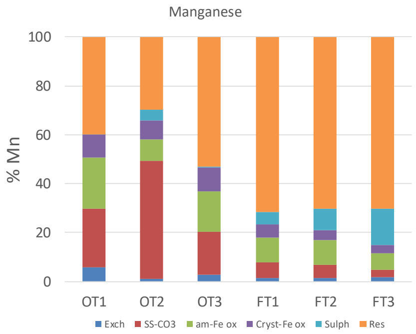
3.2 Partitioning of PTEs by SEP

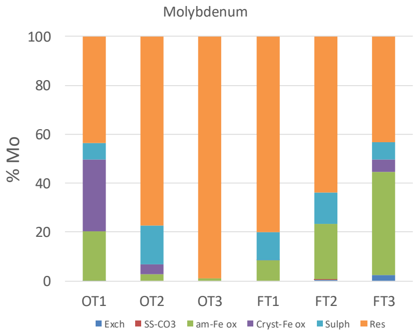
The partitioning of PTEs in the tailings (Figure 2) shows that, in general, greater portion of PTEs remain in the residual fraction, which is the less reactive phase of lowest mobility and bioaccessibility. Most part of As (~60–89% of As_{tot}) was in the residual fraction, although a considerable portion (~10–50 % of As_{tot}) was amorphous and poorly crystalline Fe oxyhydroxydes–bound. This fraction could be potentially mobilizable upon environmental changes, particularly under acidic, reducing and/or chelating conditions, and thus it is considered potentially bioaccessible. The mobility factors (MF) for As ranged between 10% and 51%. QEMSCAN® analyses support Fe-oxides (likely corresponding to slag–tailings phases) as most probable geochemical controls of As in the OTs. QEMSCAN® did not identify any mineral phase of As in the FTs, but traces of arsenopyrite. Noteworthy features of Cu partitioning were: the high contribution (up to 47% in OTs) of the carbonate-bound fraction, which is Cu potentially mobilizable under weak acidic conditions, the considerable amorphous-Fe oxides bound Cu (20–30%) and the high sulphide-bound Cu in the FTs (up to 58% of Cu_{tot}). MF indicates that high portions of Cu_{tot} is potentially mobilizable: up to 80% in the OTs and up to 50% in the FTs. Most Pb (62–76%) was in the residual fraction; nevertheless, considerable amounts of Pb were crystalline–Fe oxides (8–20%) and amorphous–Fe oxides (6–12%) bound. QEMSCAN® identified galena (PbS) in the OTs, which is a poorly soluble ($K_{sp} = 10^{-27.5}$) and low bioavailable form, which restricts the Pb mobility in such tailings. Based on MF, most Pb in the studied tailings is strongly fixed and thus not readily mobile or bioaccessible. However, OT1 has the highest MF ~20% and the highest Pb concentration. Major portion of Mo (43–99%) is in the residual fraction, although considerable Mo was crystalline Fe-oxides-bound (30%) and amorphous Fe-oxides–bound (20%) in the OTs, and up to 43% of Mo_{tot} in FTs. MFs support that considerable Mo may be potentially mobilizable in the FTs (MF=9–45%). Major fraction of Cr (55–84%), Ni (54–83%), V (47–94%) and Zn (50–75%) was residual, whereas for Mn, the adsorbed and carbonate–bound fraction (18–48% of Mn_{tot}) was noteworthy, which suggest that the potential mobility of the metal and transfer to waters from the FTs must be considered.

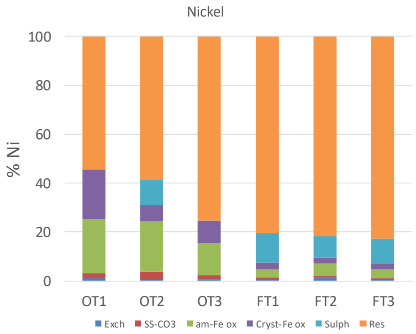

Arsenic
% As
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res

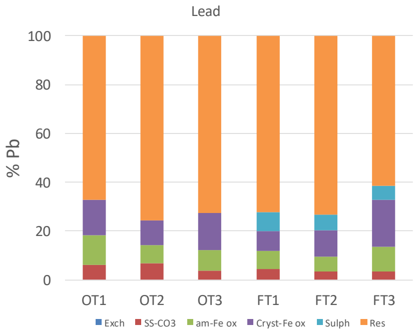

Chromium
% Cr
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res

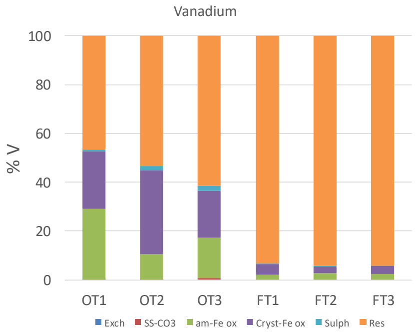

Copper
% Cu
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res


Manganese
% Mn
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res


Molybdenum
% Mo
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res


Nickel
% Ni
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res


Lead
% Pb
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res


Vanadium
% V
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res

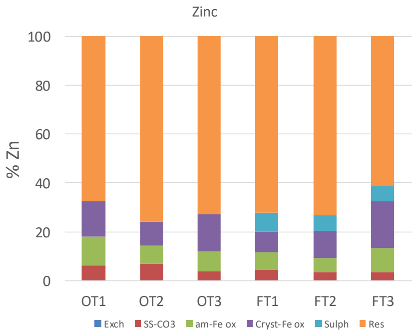

Zinc
% Zn
0
20
40
60
80
100
OT1
OT2
OT3
FT1
FT2
FT3
Exch
SS-CO3
am-Fe ox
Cryst-Fe ox
Sulph
Res

Fig. 2. Partitioning of PTEs by SEP extraction in the tailings

3.3 Ecological risk assessment

E_f^i values indicate that Cu and As are the PTEs of highest ecological risk in the tailings (Table 3). E_f^i for As indicates a very high risk to the environment in OT1 and FT3, a high potential risk in OT2 and a considerable risk in the other tailings. E_f^i values for Cu indicate very high risk or high risk in the OTs and the FTs, respectively. Tailing OT1 has moderate ecological risk due to Pb. Cumulative PERI values correspond with considerable (300 < PERI < 600) and very high risks (PERI >600) for ecological receptors, respectively. PERI suggests that the OTs pose a very high potential risk to the environment, while Cu and As are mostly responsible of this risk. FT3 has the highest PERI (>600, very high risk) amongst the FTs, mostly due to As. These results recommend surveillance of potential ecological risks by PTEs mobilisation, particularly of Cu and As, from the tailings.

Table 3. Results of the environmental risk assessment according to PERI

	E_f^i									PERI
Tailing	*As*	*Cr*	*Cu*	*Mn*	*Mo*	*Ni*	*Pb*	*V*	*Zn*	
OT1	1880.00	1.20	1416.77	0.68	–	2.01	53.08	–	2.62	3356
OT2	275.00	1.01	566.02	3.13	–	2.31	8.31	–	0.79	857
OT3	141.11	0.56	518.48	0.89	–	0.75	0.90	–	0.57	663
FT1	92.78	0.44	229.47	0.13	–	1.24	1.19	–	0.28	326
FT2	148.33	0.54	241.20	0.18	–	1.33	1.42	–	0.26	393
FT3	482.78	0.61	319.35	0.18	–	1.31	1.38	–	0.26	806
T_f^i	10	2	5	1	–	5	5	–	1	

3.4 Human health risk assessment

HQs through different pathways (Table 4) were in most cases <1 for any PTE, age group and exposure pathway, excepting for ingestion of As by children in OT1, OT2 and FT3, and for Cu in OT2. In contrast, the cumulative HIs were >1 for children through ingestion pathway for any tailing but FT1. Similarly, THI were >1 for these tailings, showing a potential non-carcinogenic risk for children if regularly exposed to the tailings (Table 5). Incidental ingestion of tailings was identified as the potential exposure pathway of risk. In contrast to children, both the HIs through ingestion and THIs in adults were slightly >1 for OT1 by ingestion pathway, suggesting that the risks are much lower for this group. Non-cancer risk indices for inhalation and dermal contact were in all cases <1, indicating marginal health risks through both exposure pathways. Tailing OT1 presents the higher potential health risks among the tailings, particularly for children upon incidental ingestion, while As was identified as the PTE of higher human health concern in the tailings.

Regarding cancer risk, ILCR values decrease in the order ingestion > dermal > inhalation for both children and adults and for the three carcinogenic PTEs (As, Cr, Ni) present in the tailings (Table 6). Carcinogenic HHRA identified As as the most concerning PTE in the tailings via ingestion pathway, whose ILCR exceed the maximum acceptable level for children for any tailing and for adults in tailings OT1 and FT3. Conversely, ILCRs for As via dermal and inhalation pathways suggest low risk of As through via these pathways. ILCR for Cr either marginally exceeded 1×10^{-4} only for children through ingestion pathway. Likewise, but in OT1 for children through ingestion, ILCRs for Ni were below or within the acceptable value range, suggesting no carcinogenic risks due to Ni in the studied tailings.

Table 4. Hazard quotients (HQ) for non-carcinogenic risk for children and adults through different pathways

					HQ (ing.,child.)				
Tailing	*Pb*	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	0.4320	0.0035	7.6677	2.0755	0.0486	0.0367	0.0028	0.0313	0.0816
OT2	0.0715	0.0013	1.4135	0.5938	0.0019	0.0451	0.0035	0.1422	0.0352
OT3	0.0058	0.0010	0.7849	0.8241	0.0006	0.0230	0.0012	0.0385	0.0614
FT1	0.0073	0.0003	0.5682	0.1289	0.0147	0.0163	0.0008	0.0045	0.0058
FT2	0.0073	0.0005	0.9234	0.1988	0.0245	0.0250	0.0013	0.0057	0.0085
FT3	0.0070	0.0005	2.8519	0.2526	0.0872	0.0255	0.0009	0.0037	0.0072
					HQ (ing.,adult)				
	Pb	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	4.63E-02	3.74E-04	8.22E-01	2.22E-01	5.21E-03	3.93E-03	3.05E-04	3.36E-03	8.75E-03
OT2	7.66E-03	1.39E-04	1.51E-01	6.36E-02	2.05E-04	4.83E-03	3.74E-04	1.52E-02	3.77E-03
OT3	6.20E-04	1.11E-04	8.41E-02	8.83E-02	6.85E-05	2.46E-03	1.29E-04	4.13E-03	6.57E-03
FT1	7.83E-04	3.30E-05	6.09E-02	1.38E-02	1.58E-03	1.75E-03	8.34E-05	4.87E-04	6.21E-04
FT2	7.83E-04	5.30E-05	9.89E-02	2.13E-02	2.63E-03	2.68E-03	1.40E-04	6.13E-04	9.11E-04
FT3	7.50E-04	4.85E-05	3.06E-01	2.71E-02	9.34E-03	2.74E-03	9.59E-05	4.00E-04	7.74E-04
					HQ (inhal.,child.)				
	Pb	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	1.20E-05	9.76E-08	1.29E-03	5.80E-05	1.36E-06	3.84E-04	7.57E-08	2.45E-03	2.28E-06
OT2	1.99E-06	3.63E-08	2.37E-04	1.66E-05	5.36E-08	4.72E-04	9.29E-08	1.11E-02	9.83E-07
OT3	1.61E-07	2.89E-08	1.32E-04	2.30E-05	1.79E-08	2.41E-04	3.20E-08	3.01E-03	1.71E-06
FT1	2.03E-07	8.61E-09	9.53E-05	3.60E-06	4.11E-07	1.71E-04	2.07E-08	3.55E-04	1.62E-07
FT2	2.03E-07	1.38E-08	1.55E-04	5.55E-06	6.85E-07	2.62E-04	3.47E-08	4.47E-04	2.38E-07
FT3	1.95E-07	1.26E-08	4.78E-04	7.06E-06	2.44E-06	2.68E-04	2.38E-08	2.92E-04	2.02E-07
					HQ (inhal.,adult)				
	Pb	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	*6.77E-06*	*5.50E-08*	*7.25E-04*	*3.27E-05*	*7.66E-07*	*2.17E-04*	*4.27E-08*	*1.38E-03*	*1.29E-06*
OT2	1.12E-06	2.05E-08	1.34E-04	9.36E-06	3.02E-08	2.66E-04	5.24E-08	6.28E-03	5.54E-07
OT3	9.06E-08	1.63E-08	7.42E-05	1.30E-05	1.01E-08	1.36E-04	1.80E-08	1.70E-03	9.67E-07
FT1	1.14E-07	4.86E-09	5.37E-05	2.03E-06	2.32E-07	9.64E-05	1.17E-08	2.00E-04	9.13E-08
FT2	1.14E-07	7.79E-09	8.73E-05	3.13E-06	3.86E-07	1.48E-04	1.96E-08	2.52E-04	1.34E-07
FT3	1.10E-07	7.13E-09	2.70E-04	3.98E-06	1.37E-06	1.51E-04	1.34E-08	1.65E-04	1.14E-07
					HQ (derm.,child.)				
	Pb	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	8.06E-03	4.89E-05	2.15E-02	1.94E-02	1.36E-04	1.03E-04	7.97E-06	5.12E-03	2.29E-04
OT2	1.34E-03	1.82E-05	3.96E-03	5.54E-03	5.37E-06	1.26E-04	9.78E-06	2.32E-02	9.85E-05
OT3	1.08E-04	1.45E-05	2.20E-03	7.69E-03	1.79E-06	6.43E-05	3.37E-06	6.29E-03	1.72E-04
FT1	1.36E-04	4.32E-06	1.59E-03	1.20E-03	4.12E-05	4.57E-05	2.18E-06	7.42E-04	1.62E-05
FT2	1.36E-04	6.92E-06	2.59E-03	1.86E-03	6.86E-05	7.00E-05	3.65E-06	9.34E-04	2.38E-05
FT3	1.31E-04	6.34E-06	7.99E-03	2.36E-03	2.44E-04	7.15E-05	2.51E-06	6.09E-04	2.02E-05
					HQ (derm.,adult)				
	Pb	*Zn*	*As*	*Cu*	*Mo*	*Cr*	*Ni*	*Mn*	*V*
OT1	1.23E-03	7.46E-06	3.28E-03	2.96E-03	2.08E-05	1.57E-05	1.22E-06	7.81E-04	3.49E-05
OT2	2.04E-04	2.78E-06	6.04E-04	8.46E-04	8.20E-07	1.93E-05	1.49E-06	3.55E-03	1.50E-05
OT3	1.65E-05	2.21E-06	3.36E-04	1.17E-03	2.73E-07	9.82E-06	5.14E-07	9.61E-04	2.62E-05
FT1	2.08E-05	6.59E-07	2.43E-04	1.84E-04	6.29E-06	6.97E-06	3.33E-07	1.13E-04	2.48E-06
FT2	2.08E-05	1.06E-06	3.95E-04	2.83E-04	1.05E-05	1.07E-05	5.58E-07	1.43E-04	3.63E-06
FT3	2.00E-05	9.67E-07	1.22E-03	3.60E-04	3.73E-05	1.09E-05	3.83E-07	9.30E-05	3.09E-06

Table 5. Non-carcinogenic Hazard Index (HI) and total exposure Hazard Index (THI) values for children and adults though different pathways

Tailing	HI (ing., chil.)	HI (inhal., child.)	HI (derm., child.)	THI child.	HI (ing., adult)	HI (inhal., adult)	HI (derm., adult)	THI adult
OT1	10.380	0.004	0.055	10.438	1.112	0.002	0.008	1.123
OT2	2.308	0.012	0.034	2.354	0.247	0.007	0.005	0.259
OT3	1.741	0.003	0.017	1.760	0.186	0.002	0.003	0.191
FT1	0.747	0.001	0.004	0.751	0.080	0.000	0.001	0.081
FT2	1.195	0.001	0.006	1.202	0.128	0.000	0.001	0.129
FT3	3.236	0.001	0.011	3.249	0.347	0.001	0.002	0.349

Table 6. Carcinogenic health risks (ILCR) of As, Cr and Ni to children and adults through different exposure pathways

Tailing			Arsenic			
	CR(ing.,child.)	*CR(ing.,adult)*	*CR(inhal.,child.)*	*CR(inhal.,adult)*	*CR(derm.,child.)*	*CR(derm.,adult)*
OT1	3.45E-03	3.70E-04	9.71E-07	5.47E-07	2.36E-05	3.60E-06
OT2	6.36E-04	6.82E-05	1.79E-07	1.01E-07	4.35E-06	6.63E-07
OT3	3.53E-04	3.78E-05	9.93E-08	5.60E-08	2.41E-06	3.68E-07
FT1	2.56E-04	2.74E-05	7.19E-08	4.06E-08	1.75E-06	2.67E-07
FT2	4.16E-04	4.45E-05	1.17E-07	6.59E-08	2.84E-06	4.33E-07
FT3	1.28E-03	1.38E-04	3.61E-07	2.04E-07	8.77E-06	1.34E-06
			Chromium			
	CR(ing.,child.)	*CR(ing.,adult)*	*CR(inhal.,child.)*	*CR(inhal.,adult)*	*CR(derm.,child.)*	*CR(derm.,adult)*
OT1	1.65E-04	1.77E-05	4.64E-08	2.62E-08	1.13E-06	1.72E-07
OT2	2.03E-04	2.17E-05	5.70E-08	3.22E-08	1.39E-06	2.12E-07
OT3	1.03E-04	1.11E-05	2.91E-08	1.64E-08	7.06E-07	1.08E-07
FT1	7.34E-05	7.87E-06	2.06E-08	1.16E-08	5.02E-07	7.66E-08
FT2	1.13E-04	1.21E-05	3.16E-08	1.78E-08	7.69E-07	1.17E-07
FT3	1.15E-04	1.23E-05	3.23E-08	1.82E-08	7.85E-07	1.20E-07
			Nickel			
	CR(ing.,child.)	*CR(ing.,adult)*	*CR(inhal.,child.)*	*CR(inhal.,adult)*	*CR(derm.,child.)*	*CR(derm.,adult)*
OT1	8.54E-05	9.15E-06	2.40E-08	1.35E-08	5.83E-07	8.91E-08
OT2	1.05E-04	1.12E-05	2.95E-08	1.66E-08	7.16E-07	1.09E-07
OT3	3.61E-05	3.86E-06	1.01E-08	5.72E-09	2.46E-07	3.76E-08
FT1	2.34E-05	2.50E-06	6.57E-09	3.70E-09	1.60E-07	2.44E-08
FT2	3.91E-05	4.19E-06	1.10E-08	6.21E-09	2.67E-07	4.08E-08
FT3	2.69E-05	2.88E-06	7.56E-09	4.26E-09	1.84E-07	2.80E-08

4.0 CONCLUSIONS

A methodology for evaluation of the overall risks of tailings from potential mobilization of PTEs to ultimate ecological and human health impact has been developed and applied to assess diverse Cu tailings from Chile. The protocol outcomes allowed for inferring: (i) Presence and degree of contamination of PTEs in the tailings, showing that they contain some priority hazardous PTEs at levels above environmental and health protection guidelines, while pollution indices classify the tailings as polluted with Cu, As, Pb and Mo; (ii) Distribution and mobilization of PTEs, revealing that major fraction of the PTEs is strongly fixed in the tailings, although considerable portion of PTEs is potentially mobilizable and bioaccessible. Cu, As and Mo were identified as most potentially mobile PTEs in the tailings; (iii) Ecological impact through ERA, which indicates that the OTs mean a higher potential environmental risk than the FTs, while As and Cu mostly contribute to this risk; and (iv) Human health risk through HHRA, which categorizes OT1 as the tailing with highest potential non-carcinogenic and carcinogenic health risk, particularly for children upon ingestion pathway, while it identifies As as the PTE of higher human health concern in the tailings. This study shows how the proposed methodology may be reliably applied for assessing the whole risks due to PTEs in mine tailings.

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RESIDUAL RISK CONSIDERATIONS: GEOCHEMCIAL INTERACTIONS ON TAILINGS DAM STABILITY

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ABSTRACT

The long-term storage of mine tailings in above-ground impoundments presents risks that must be managed throughout the life of the facility. As the industry gains better understanding of closure residual risk, we recognize that the decisions made at the design stage of facilities, past and present, affect the social acceptability of the industry in the future. Potential dam safety failure modes must consider initiating events and progressive forces that may affect the physical stability of these structures over the long-term.

The influence of supernatant water and seepage chemistry on the hydrologic and physical properties of dam construction materials, stored tailings, and engineering design is an important component of understanding dam safety residual risk. However, these are not commonly considered in the current state of practice for dam management strategies. In this paper we discuss dam safety residual risk, geochemical processes responsible for potential physio-chemical changes of dam materials, and practices useful when preparing a design basis.

1.0 INTRODUCTION

Construction of a Tailings Storage Facility (TSF) includes the use of various materials that range from local overburden, run-of-mine waste rock, imported native materials, geosynthetics, compacted filtered tailings, and milled-cycloned tailings sand. A design basis that includes material geotechnical properties (i.e. gradation, moisture content, Atterberg Limits, specific gravity, compaction, consolidation, etc.) and constructability is common practice.

However, the chemical and mineralogical nature of the construction materials that may influence the physical properties of the TSFs is not often considered a key factor in a design basis. Changes in the effectiveness of preventative TSF critical engineering controls (e.g., toe drains, material strength assumptions, filter zones, etc) may not be fully known until post-closure. Residual risk closure costs often don't reflect the scale of remaining uncertainty in steady-state conditions and long-term tailings management required.

This paper discusses some of the geochemical processes responsible for the physio-chemical changes of TSF dam materials and summarises measures to adopt when considering a design basis. Information can then be used to inform preventative and contingency control measures and assist Owners understand the range of post-closure monitoring and maintenance.

2.0 RISK ASSESSMENT AND DAM SAFETY

Risk assessment is important in understanding potential dam safety failure modes and designing a TSF that is both robust (i.e., a number of preventative lines of defence, allowing the system to respond well across a wide range of operating conditions) and resilient (i.e., capacity to recover quickly from difficulties and ability to absorb or avoid damage without suffering complete failure).

Throughout the design process, the designer and Owner need to consider the potential risks associated with the entire tailings facility as well as the TSF dam and design controls and measures to limit these risks. Understanding the physio-chemical factors that may initiate or contribute to potential physical stability failure modes is important when informing the range of preventive design controls. There are numerous guidelines and tools available for assessing dam-safety risk. Sanders, et al. (2019) summarizes risk management steps outlined in ISO 3100:2018 as it relates to tailings and closure residual risk.

Dam failures are the result of human factors (i.e., poor engineering judgement and/or construction or operator error). Of importance are the smaller cumulative potential failure modes that when combined with other contributing factors may lead to an unsafe dam condition. Sanders, et. al (2019) identifies some of these potential human elements as they relate to dam safety and closure residual risk. These same elements are applicable to physio-chemical processes that may affect dam safety, summarized below:

- Complacency: familiarity can create a normalisation of deviance (i.e. departures from desirable conditions become expected and accepted, imparting a false sense of security and complacency) over time. Embed risk-based thinking and processes into LoM planning values and culture. Vick (2017) provides an excellent overview of this as it relates to dam safety risk.
- Competency: ensure competent teams facilitate and assess potential dam failure modes to improve quality outcomes. Materials characterization objectives should be confirmed with an experienced geochemist and dam safety engineer. Include external review mechanisms in confirming risk treatment programs.
- Compliance: geochemistry's influence on the physical stability of dams is not well known and not an aspect evaluated in many regulatory or corporate governance requirements. When considering a TSF design basis, ensure objectives are clear and include risk-based thinking in addition to compliance-focussed requirements.
- Capacity: resources may be constrained to adequately characterise changes to the dam material properties over time. A dedicated role must be embedded in the business to assess and implement dam safety risk management measures.
- Change: actively manage planned and unplanned changes over the mine life. Characterization of physio-chemical changes should be captured in the Operations, Maintenance and Surveillance (OMS) manual. See Sanders et al. (2018) for type of change and ideas in managing this.

3.0 GEOCHEMICAL MECHANISMS AND POTENTIAL FAILURE MODES

Tailings dam failures in recent years have shined a spotlight on static liquefaction and strength loss caused by undrained failure (Robertson, et. al, 2019). KCB's forensic investigations into Mount Polley, Fundão and Feijão have highlighted the role of undrained shear strength in the dam failures, where either clay foundation or tailings can become susceptible to failure as in-situ stress increases. As dams increase in height, particularly upstream tailings dams, designers should consider the potential for undrained failure and that the future performance of a dam can change (KCB 2018a).

Physical and chemical changes that occur in TSF structural components can also affect the effectiveness of that design feature over time. Geochemical changes within the dams that can influence dam stability need to be considered in these design basis assumptions. Robertson and Durocher (2017) and Durocher et al. (2017) identify the key issues for consideration in physio-chemical changes in dams that can alter the strength, porosity, and permeability of dam fill materials. These include:

- Degradation of structural fill resulting in a loss of strength or global physical stability;
- Degradation of fill and filter materials resulting in a change in material permeability (increase or decrease) altering the original design parameters; and/or
- Formation of secondary precipitates within the pore spaces of filter materials, drains, and embankment fill. This may result in changes to material permeability and piezometric surface or change the strength behaviour of the tailings, becoming more brittle. As concluded in the Feijão Dam Failure, "*the combination of a steep upstream constructed dam, high water level, weak fine tailings within the dam, and the brittle nature of the tailings created the conditions for failure*" (Robertson, et. al. 2019).

Robertson and Durocher (2017) provide details of the weathering mechanisms for primary sulphides and silicate clay minerals resulting in the formation of secondary minerals within fill materials. These include mineral dissolution through primary sulphide and silicate mineral weathering and secondary phase formation in acidic and neutral drainage tailings environments.

These processes occur over time and may not present as an immediate concern. However, given the nature of dams and their long lifetimes, these present a closure residual risk issue. This effect is more readily illustrated in ageing facilities. Mitigation measures for dam material degradation, once constructed, can be costly and challenging and, as such, preliminary material and seepage characterization and management of these materials at the design stage of construction are critical for long term dam management.

4.0 TSF DESIGN CONSIDERATIONS

ISO 31000:2018 defines risk as the "*effect of uncertainty on objectives*". TSF design, construction and operations is inherently managing risk (i.e., uncertainty in achieving a safe, stable and non-polluting conditions). TSF designers must adequately reflect this range of uncertainty in Factor of Safety (FoS) estimates and limitations in constructability and operations.

FoS is a measure used in engineering design to represent how much greater the resisting capacity of a structure or component is relative to an assumed load. With respect to slope stability, FoS is the ratio of shear resistance to driving force along a potential failure plane. A FoS greater than 1.0 implies the available shear strength to resist failure is greater than the driving force to initiate failure. FoS of a slope is estimated based on industry standard analytical methods with assumed material parameters inferred from various data sources (laboratory, drilling, empirical correlations) under various loading conditions (e.g. static, post-earthquake, construction). FoS analysis depends on the quality of investigations, testing, design and construction (KCB 2018b).

As such, the confidence in dam stability FoS values can vary significantly, depending on the uncertainty of assumed material parameters and the engineers' experience in defining assumptions and interpreting the results. As these factors change, the risk associated with a specific FoS value can vary between sites, dam owners, or even different segments of a single dam or slope. Design parameters should be chosen based on a range of opinions on the most likely design case, reflect the level of uncertainty and be grounded in independent third-party review. Where there remains uncertainty in design parameters, sensitivity assessment is required, and a precautionary design adopted. Assessing changes to potential failure modes requires a life of mine approach to characterize the solids and solutions present, using a precautionary design approach. A precautionary design uses parameters that assume realistic most unfavourable conditions. This approach is more conservative, carries a higher cost and relies less on interpretation and the Observational Method outlined by Peck (1969).

The Observational Method uses performance monitoring to inform design and reduce risk. It involves considering the effects of the possible range of values of the parameters and having in place a plan to deal with occurrences that fall outside of the expected range. Identification and management of potential failure modes, performance review, monitoring triggers and precursors, etc., are essential elements to completing the "observational loop" consistent with the principles of risk management. A pre-approved and permitted contingency design case (i.e., contingency buttress, drainage, etc,) is required to adapt with uncertainty if, through surveillance results, the minimum FoS conditions change. However, the approach is not as effective in situations where the design is not flexible, preventative contingency measures cannot be applied, or the potential failure mode is rapid/brittle with little emergency response time.

Once potential failure modes are identified and design completed (at least to pre-feasibility level which should include an evaluation of seepage, seepage-solid, and rainfall-solid interactions), an appropriate program for testing and evaluation can be developed. Robertson and Durocher (2017) describes evaluation methods to apply to design. These are listed below and summarized in the following sections:

- Laboratory testing;
- Field sub-surface investigations;
- Dam surveillance;
- Benchmarking against similar site conditions; and
- Numerical modelling.

4.1 Laboratory Testing

Key geochemical laboratory testing is summarised below.

4.1.1 Mineralogical Analysis by Electron Microscopy

Electron microscopy (i.e., SEM, EMPA or QEMSCAN) allows for visual microscopic observations at the grain scale from undisturbed to mildly disturbed materials. The chemical composition and visual observations from electron microscopy such as primary and secondary mineral textures, grain size and pore space can be used to understand the extent and nature of important mineral weathering reactions and secondary mineral formation in dams. These methods are extremely beneficial for comparison to indirect measurements at the bulk scale.

4.1.2 Mineralogical Analysis by X-Ray Diffraction

X-Ray diffraction (XRD) coupled with Reitveld refinement methods to quantify mineralogical abundance is a bulk solid phase mineralogical test that uses diffraction patterns to identify major (> 1% by weight) minerals present in a sample. Key minerals identified in XRD important to dam safety include carbonate, silicate and sulphide minerals. Minerals within these groups are typically characterized for their potential for neutralizing or acid generating potential, however, their neutralizing or acid generating reactivity results in physical changes at the micro scale. This test is relatively quick and cost effective, and identifies major minerals present in a sample. Since secondary minerals can occur in relatively low abundance, grain size separation, chemical treatments and separate XRD measurements should be considered depending on the material type.

However, XRD should not be the only method used to assess the mineralogical composition, since targeted secondary phases can be amorphous and therefore do not diffract X-Rays, XRD results may not accurately represent the secondary assemblage.

4.1.3 Mineralogical Analysis by Optical Petrography

Additional qualitative assessments of mineral composition are required to piece together the various scales in understanding from Electron Microscopy methods and semi-quantitative XRD methods. Optical mineralogy allows for better understanding of existing mineral alterations and potential ongoing weathering risks. For example, a mineral identified by XRD as a feldspar could be completely altered and replaced by a weaker mineral (such as sericite or chlorite) that would only be identified through optical methods.

4.1.4 Total Elemental Analysis by Digestion

The chemical composition of mine waste rock, overburden, imported fills, and native materials, geosynthetics, tailings and their secondary reaction products can be determined by digesting a ground sample in a strong acid and measuring the concentration of recoverable (dissolved) major, minor and trace elements with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) or atomic emission spectrometer (ICP-AES). The digestion method is an important aspect to consider when considering which elements are reported and the type of digest should be chosen carefully based on site specific conditions and the goal of the test.

4.1.5 Leachate Extraction Testing

Shake Flask Extraction (SFE) testing provides information on the short-term mineral solubility in de-ionized sub-neutral-pH water. Mineral solubility under acidic conditions is not characterized by this method. These tests do not relate to specific ARD field conditions but provide information on the dissolution of readily soluble phases in water under laboratory conditions.

Soluble phases may include secondary surface coatings or adsorbed species as well as soluble primary or secondary minerals present in the sample. In the test, the sample is placed in a flask with de-ionized water (at a 3:1 water to solid ratio by weight) and shaken (end over end) for 24 hours. Following the agitation, the sample is settled, and the supernatant is removed, filtered, and the pH, electrical conductivity, and the hardness are measured. The chemical composition of the supernatant, which is a direct reflection of the chemical composition of the dissolved phases, is determined by ICP-MS.

Other types of leachate testing can be beneficial in this type of assessment, as certain minerals are more readily liberated under acidic conditions. A modified SFE can be conducted where the pH of the test solution is decreased through the addition of acids (such as nitric acid) and buffered to the desired pH. Other methods with varying solid:liquid ratios or other standard tests such as the meteoric water mobility procedure (MWMP), and the synthetic precipitation leaching procedure (SPLP) can also be repurposed and employed.

Post-leachate residue mineralogical testing also produces very valuable information on weathering reactions incurred throughout the test when compared to pre-leachate mineralogical results. Leach tests should be selected based on the material characteristics and the expected dominant weathering and transformation mechanisms. If the dominant weathering mechanisms are unknown at the time of test, a broad-based approach to testing is recommended.

4. 2 Field Sub-Surface Investigations

Subsurface field investigations can be used to collect samples for laboratory analyses, or measure in-situ properties in the dams and TSFs. Investigation methods which allow for the collection of continuous undisturbed samples are preferred to measure the geotechnical properties and geochemical composition of the materials (e.g. shear strength, porosity, chemical and mineralogical composition etc.).

Changes in material properties are likely to occur in discrete zones based on preferential water flow pathways and differences in water quality with depth. Subsurface investigations should be conducted to a maximum possible depth of the TSF, sampling intervals should be frequent, and locations should cover a broad spatial area. Subsurface investigations are most effective when cross-sections from upstream to downstream of the tailings dams are evaluated so that chemical and physical changes along the seepage flow pathway can be evaluated.

Typical investigation techniques and field-testing methods include:

- Test pitting;
- Drilling;
- Cone penetration testing (CPT) and seismic CPT (SCPT); and,
- Field permeability testing, using methods such as rising head and falling head slug tests in monitoring wells or near surface using a Guelph permeameter (or similar).

CPTs provide real-time in-situ data such as cone tip resistance, sleeve friction, porewater pressure and resistivity. Seismic wave velocity measurements (shear and compressional) using SCPT method can also be conducted in select CPT holes to provide an overall indication of liquefaction conditions.

Remote sensing methods using electromagnetic (EM) survey may be misleading on a global scale for dam safety, however downhole methods may provide useful data in combination with other measurements.

4.3 Dam Surveillance

Dam surveillance is imperative to evaluate changes over time and monitor the potential chemical indicators for further weathering or secondary mineral formation. For existing TSFs, field observations and water monitoring can provide the first indications of issues.

Designing a tailings dam surveillance program is often done without first critically thinking about its objectives or the appropriate input data and may be biased by the desire to implement “leading-edge” technology. An effective tailings dam surveillance program must have specified objectives and must identify and manage selected parameters that can be monitored and will add value by minimizing risk KCB 2019). Depending on the site, field monitoring as part of a dam surveillance program may include:

- Pond, seepage, and pore water sampling;
- Piezometric level monitoring;
- Seepage flow monitoring; and,
- Visual inspection of material weathering or secondary mineral formation.

Samples collected as part of regular field monitoring or during subsurface investigations can be subjected to various geochemical tests. Solids collected, including construction materials, primary minerals, and secondary phases should be subjected to laboratory testing which include, mineralogical analysis, total elemental analysis, and leachate extraction testing. The most common analyses performed on liquid samples include:

- In-situ field parameter measurement, including field pH, redox (oxidation-reduction potential with Eh or ORP), electrical conductivity, temperature, and dissolved oxygen (DO);
- Laboratory analysis for major metal(loid)s, anions, and non-metals including sulphate; and,
- Specialized isotopic or ion speciation (depending on the site) for example, Fe^{2+} and Fe^{3+}.

A key component of dam surveillance is responding to indicators of unusual conditions in a timely manner. Contingency plans and emergency response plans must be based on established thresholds, also known as Trigger Action Response Plans (TARPs). TARPs need to be pre-defined and integrated into the overall surveillance system architecture. It should be noted that not all initiating events and failure modes can be monitored to provide enough advance warning of a potential dam break (e.g., static liquefaction, earthquake).

4.4 Benchmarking

Benchmarking is an extremely useful (and often underutilized) practice of comparing processes and performance data to help inform questions you are trying to answer. Mutually beneficial knowledge sharing is important to learn lessons and improve dialogue throughout the industry (Sanders and Wendtman 2016). Benchmarking provides a window into the future so that the hierarchy of controls (i.e., elimination, substitution, engineering, management) can be effectiveness applied to design elements.

A recent use of benchmarking is the main author's involvement in an alternatives assessment project for a site located in New Mexico, U.S. As part of the options characterisation comparison, we compared lessons from long-term operating and legacy sites with similar ore type, mill process, climate conditions and dam construction methods to new design aspects. The preferred alternative was selected based on technical merit and the range of uncertainty. Forward works programs were developed to advance to feasibility level design that included a range of geochemical test work and further benchmarking that will help inform the dam design.

4.5 Numerical Modelling

Using the data collected in field studies (i.e., field program, surface water, pore water and seepage water as well as the mineralogy), and the results of the laboratory analyses, a conceptual geochemical model can be developed which identifies the key geochemical changes occurring in the materials and allows for the development of mitigation options to slow or inhibit further change.

Numerical geochemical modelling software (such as Geochemists Work Bench (GWB) and PHREEQC) can be used to assess the concentrations of aqueous and solid species and predict solution-solid reactions, kinetic reaction rates, and thermodynamic equilibrium. These software programs can be used to evaluate chemical reactions, species in solution, and mineral solubility which can be used to understand whether minerals are expected to change at a given pH, Eh, temperature and pressure. When combined with numerical models that assess the saturated/unsatured flow in TSF, an understanding of potential chemical changes can be obtained.

The relationship between the chemical change and physical changes can evaluated and design basis assumptions revisited, as required. Revised seepage or stability modelling can be conducted to re-evaluate the factor of safety (FOS) and legacy risk associated with existing structures. These methods can also be used to validate field observations, guide future sampling programs, assess options and evaluate the benefit of engineering mitigation strategies.

5.0 CONCLUSIONS

The influence of the dam seepage chemistry on the hydrologic and physical properties of construction materials and engineering design is not well known and is not commonly considered in dam safety. However, the importance of geochemical processes and understanding these complex systems will likely become increasingly important with a greater focus on closure residual risk. Understanding the physio-chemical processes that may initiate or contribute to potential failure modes is important.

Understanding reaction pathways in design can help predict outcomes and even mitigate issues earlier at less cost. Done well, risk assessment can be a useful tool to facilitate this discussion and identify areas of uncertainty to address in design assumptions.

Laboratory testing and dam surveillance programs are essential to evaluate potential changes in material properties over time and to monitor the potential chemical indicators for further weathering or secondary mineral formation. Numerical modelling in combination with other methods (such as benchmarking) can be used to assess the range of uncertainty in current and potential future conditions. Risk-informed decisions on preventive design controls can then be better informed as it relates to the range of design uncertainty and FoS estimates.

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GEOCHEMICAL AND HYDROLOGICAL LAGS AND EFFECTIVENESS OF COVERS ON PAF MINE WASTES

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ABSTRACT

Sulfidic mine wastes, including waste rock and tailings have, with the passage of time, the potential to generate acid and metalliferous drainage. Acid and metalliferous drainage (AMD) occurs on oxidation of the wastes exposed to the atmosphere, the exhaustion of any acid neutralising capacity present in the wastes or process water, and the transport of the oxidation products by rainfall runoff and/or infiltration, or by groundwater.

Waste rock typically emerges from an open pit relatively dry and, when conventionally end-dumped in a surface waste rock dump, has ready access to atmospheric oxygen, allowing the oxidation of any sulfidic minerals. The geochemical lag before the generation of net acidity is a function of the acid neutralising capacity (ANC) present in the waste rock and the relative rates of production of acidity and alkalinity. The hydrological lag before the emergence of AMD from the dump is a function of the extent to which, and rate at which, it wets up due to rainfall infiltration. This is in turn governed by the climatic setting and the physical and chemical nature of the waste rock. Initially, rainfall infiltration is largely taken up as storage in the void spaces within the dump. Cumulative rainfall infiltration, particularly intense rainfall events, result in seepage eventually reaching the base and perimeter of the dump, potentially carrying with it any net acidity.

Tailings are typically pumped to a surface storage as a slurry. If the surface of the tailings is allowed to desiccate, exposed sulfidic tailings can undergo oxidation. The oxidation products can then be mobilised by the deposition of fresh tailings, or by rainfall runoff and/or infiltration. If the runoff is discharged via a spillway, any acidity can be released to the environment. Seepage laden with oxidation products can eventually reach the foundation and toe of the tailings storage facility.

The purpose of covers over potentially acid forming (PAF) mine wastes is to minimise the ingress of oxygen into the wastes and/or minimise transport of any AMD via the net percolation of rainfall into the wastes. The appropriate choice and effectiveness of covers is a function of the climatic settings, the mine wastes, and the management of the wastes.

1.0 INTRODUCTION

All too often, AMD takes sites by surprise. Initially, it is not present, while some years after the start of mining and processing it appears, both from surface waste rock dumps and from tailings storage facilities. There is a number of reasons for this.

For conventional surface waste rock dumps, formed by end-dumping, there will likely be a period of time before contaminated interstitial water forms within the dump – the "geochemical lag". During this period, any neutralising capacity will ameliorate any acidity production, although neutral metalliferous and sulfate saline drainage may form if sufficient water flux exists. Further, the acidity reaction will tend to continue during the dry season, while the alkalinity reaction may be subdued during this season. Hence, once the dump is producing seepage, the "first flush" at the start of the wet season will be most acidic and contaminated with dissolved metals, and the quality of any seepage will tend to improve as the wet season progresses. The same pattern is followed in subsequent seasonal wetting and drying cycles. The initially relatively dry waste rock must first wet up sufficiently to release water – the "hydrological lag". The initiation of seepage from the dump will initially require a substantial rainfall event, while lesser rainfall events are required to generate seepage once the dump has wet-up.

For conventional surface tailings storage facilities, involving slurry tailings deposition, there will also likely be a period of time before contaminated interstitial water forms, since the near-saturated tailings must first desaturate to allow any oxidation – the "hydrological lag", which comes first. Desaturation of the tailings will commence from the surface once it becomes exposed, and the extent and depth of oxidation will be a function of the composition, reactivity and particle size distribution of the tailings, the climate and season, the water and air permeability of the tailings, and the duration of exposure before fresh tailings slurry is placed or re-wetting due to rainfall occurs. There will also likely be a period of time before contaminated interstitial water forms within the tailings – the "geochemical lag". During this period, any neutralising capacity will ameliorate any acidity production, although neutral drainage may still form.

The geochemical and hydrological processes of surface waste rock dumps and surface tailings storage facilities are discussed in the following sections. This is followed by discussion covers over potentially contaminating mine wastes to minimise the ingress of oxygen and/or the net percolation of rainfall. Then follows a discussion of the effectiveness of covers over mine wastes in addressing the AMD geochemical and hydrological lags.

2.0 SURFACE WASTE ROCK DUMPS

Surface waste rock dumps are typically constructed by end-dumping from a tip-head, which results in the characteristic structure shown schematically in Figure 1 (after Herasymuik *et al.* 1995). The structure comprises a base rubble zone formed by the ravelling of boulders to the base of the dump, and discontinuous, alternating coarse- and fine-grained layers of waste rock at the angle of repose of the material of typically 35^o for weathered rock to 40^o for fresh rock. The top layer of the dump becomes broken down and compacted by haul truck traffic. The base rubble zone allows unhindered ingress of air and readily drains if wet-up. The coarse-grained angle of repose layers serve mainly as oxygen pathways, and the fine-grained layers store both air and water. The traffic-compacted top layer of the dump, which will be up to 1 m thick, inhibits both air flow and rainfall infiltration.

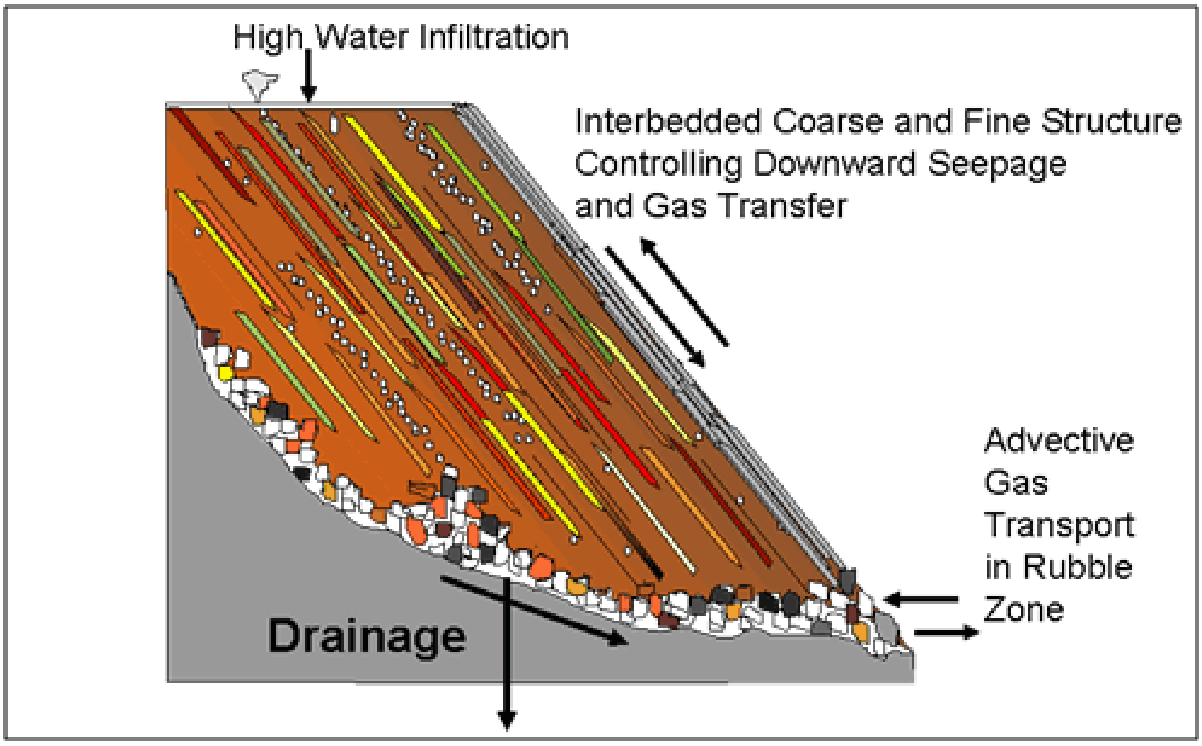

Fig. 1. **Schematic of end-dumped waste rock (after Herasymuik *et al.* 1995)**

2.1 Oxidation Process

The oxidation of an end-dumped waste rock dump comprising sulfidic materials is promoted by the ready supply of oxygen via advection into the base rubble zone shown in Figure 1. Oxygen then readily flows up the coarse-grained angle of repose layers by convection and is available to the adjacent fine-grained angle of repose layers via slower diffusion. Oxygen diffusion can also occur through the traffic-compacted top layer and the face of the dump. The fine-grained waste rock presents the highest surface area per unit volume and hence is responsible for the greatest generation of any acidity in sulfidic waste rock. Being an exothermic reaction, oxidation generates heat, and the fine-grained angle of repose layers become the hottest. Excessive heat generation can lead to spontaneous combustion of very fine-grained pyrite, if there is sufficient pore water and a source of carbon.

2.2 Wetting-Up of Dump

Williams (2006) described the physical characteristics of typical weathered and fresh waste rock in a dump, and the evolution of their moisture state as they are wet-up by rainfall infiltration over time. Weathered waste rock is typically dominated by of the order of 50% gravel-sized particles (2 to 60 mm in size), with smaller proportion of sand-sized particles (0.06 to 2 mm in size), cobble-sized particles (60 to 200 mm in size) and boulders (larger than 200 mm in size, and minor fines (silt and clay-sized particles finer than 0.06 mm). A typical median particle size for weathered waste would be less than 5 mm. As the material weathers further, the gradation becomes finer. Fresh waste rock has perhaps 40% gravel-sized particles, perhaps 40% cobble and boulder-sized particles, and the remainder mainly sand-sized. A typical median particle size for fresh waste rock would be about 50 mm.

In an arid or semi-arid environment, which describes the climate in which many of Australia's mines operate, waste rock emerges from an open pit with a low gravimetric moisture content (mass of water/mass of solids, expressed as a percentage) of typically 2 to 5%, which equates to a volumetric water content (volume of water/total volume, expressed as a decimal) of 0.035 to 0.09. The precise moisture content depends on the degree of weathering of the waste rock and hence its particle size distribution and moisture retention characteristics.

Incident rainfall readily infiltrates a conventional waste rock dump formed by end-dumping, particularly if rainfall runoff is allowed to pond on the dump. A proportion of the rainfall infiltration will go into storage within the voids in the dump, with any excess infiltrating further into the dump, ultimately emerging as seepage at the toe and into the foundation. Due to its very low hydraulic conductivity, the initially dry waste rock will store infiltration from light rainfall events, and a high waste rock dump of relatively dry material may be capable of storing considerable infiltration without significant breakthrough. The wetting front will progress through the dump as the ability of the waste rock pores to store water is exceeded, this occurring well below the fully saturated state, since the waste rock will have achieved a sufficiently high hydraulic conductivity to pass further rainfall infiltration. Wetting-up of a waste rock dump can be reduced by paddock-dumping and if interim compacted layers are placed, particularly prior to the wet season.

Williams (2006) applied unsaturated soil mechanics principles to estimate the wetting-up due to rainfall infiltration of a waste rock dump, leading to seepage reaching the base of the dump. Williams estimated, for a weathered waste rock dump, that once the degree of saturation of the pore space within the dump reached about 60% the rate of seepage would approach the rate of rainfall infiltration. For a fresh waste rock dump, only 25% saturation was required. The time taken to achieve this "continuum breakthrough" of seepage is a function of the height of the dump, the degree of weathering of the waste rock, and the climate.

Williams (2008) produced a chart to estimate the time for the start and fully-developed continuum breakthrough of seepage as a function of dump height and average annual rainfall for a weathered waste rock dump, which is reproduced as Figure 2. For a fresh waste rock dump, continuum breakthrough would occur in about 40% of the time it takes for a weathered waste rock dump.

Rohde *et al.* (2011) monitored the seepage reporting to the base of a 15 m high trial waste rock dump at Cadia Mine, which demonstrated that continuum breakthrough peaked after about 4 years at only 5% of cumulative rainfall (totalling about 3,000 mm) beneath the traffic-compacted top of the dump and at only 10% beneath the angle of repose side slopes of the dump. This implies that the proportion of rainfall that infiltrated into the dump was relatively low at about 22%, with the majority going to storage within the dump. The waste rock wet-up to an estimated 43% beneath the top of the dump and 56% beneath the side slopes over the 4-year monitoring period. The average hydraulic conductivities beneath the top and sides of the dump were calculated to be 3×10^{-6} m/s and 6×10^{-6} m/s, respectively.

Depending on the hydraulic conductivity of the foundation beneath a dump, only a small proportion of the seepage (perhaps as low as 0.1% of rainfall) would emerge at topographic low points around the toe of the dump. If an effective low net percolation cover is achieved over a dump at closure, water stored within the dump would draw down within a similar amount of time to that required to reach full continuum breakthrough. A less effective cover would delay this, and the dump would be subject to re-wetting by extreme rainfall events. Paddock-dumping and the progressive encapsulation and covering of sulfidic waste rock during the mine life could increase both the geochemical and hydrological lags.

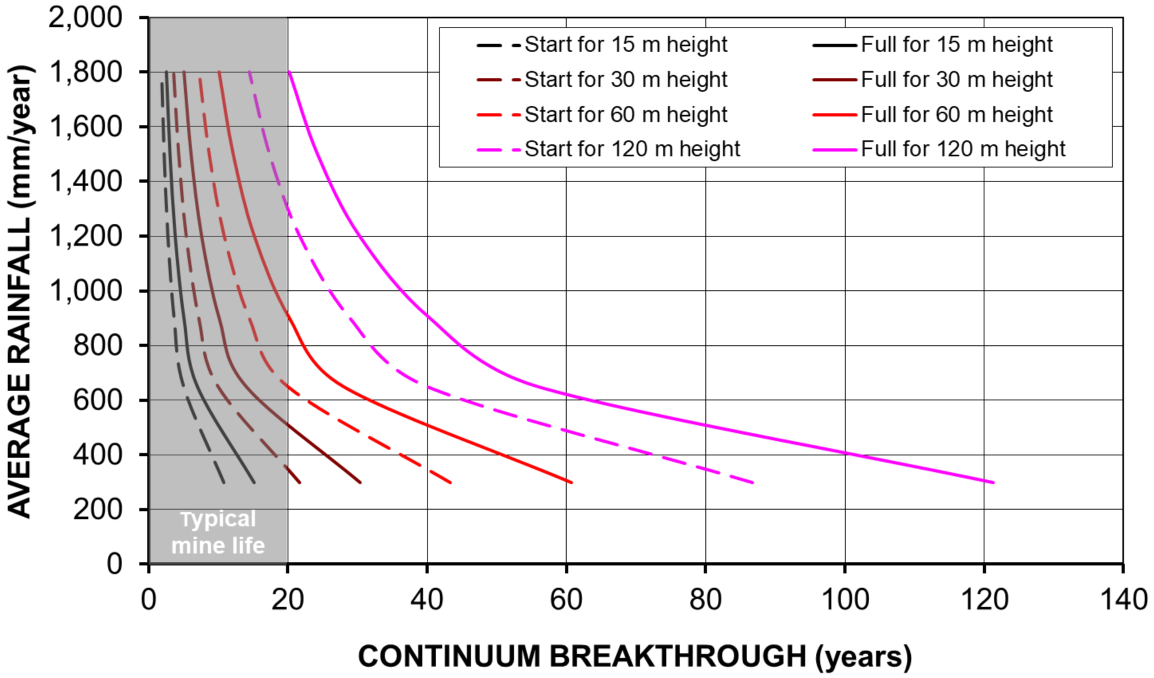

Fig. 2. Estimate time for start of and fully-developed continuum breakthrough of seepage as a function of dump height and average annual rainfall for a weathered waste rock dump (after Williams, 2008)

3.0 SURFACE TAILINGS STORAGE FACILITIES

Tailings are typically deposited in a surface storage facility as a slurry, forming a shallow beach (with a typical average slope of the order of 1%) and a decant pond at the end of the beach, from which process water can be recovered if it is suitable for re-use. On beaching, the tailings will sort hydraulically according to their particle size and specific gravity, with coarser-grained and heavier particles settling on the upper part of the beach and finer-grained and lighter particles flowing towards the pond. Suspended tailings will settle and consolidate under their self-weight, reducing the hydraulic conductivity.

The majority of the water (perhaps 75%) that does not remain entrained within the tailings will drain to the surface as the tailings settle and consolidate. Tailings will also likely generate seepage to the foundation and through the tailings dam, limited by their saturated hydraulic conductivity, which will diminish as the tailings consolidate. Evaporation takes place from the decant pond, and from wet tailings on exposure of the tailings beach to sun and wind, accompanied by desaturation.

3.1 Desaturation of Exposed Tailings

Williams (2007) described the physical characteristics of typical tailings, and the evolution of their moisture state as they may be subjected to periodic desiccation and are wet-up by fresh tailings and rainfall. Tailings are typically dominated by of the order of 50% silt-sized particles, with the remainder sand and clay-sized (finer than 0.002 mm). A typical median particle size for tailings would be less than 0.06 mm.

Williams (2007) applied unsaturated soil mechanics principles to estimate the desiccation of exposed tailings. The formation of a desiccated crust will dramatically reduce the hydraulic conductivity of the tailings and dramatically reduce the continuation of desaturation at depth. The desaturation profile will diminish exponentially with depth and typically be limited to a depth of less than about 600 mm. As the tailings desaturate, seepage rates will reduce, as will evaporation rates from the surface. The deposition of fresh tailings or rainfall will inundate the drying tailings and re-saturate them, commencing from any desiccation cracks that form. Re-wetting will recharge downward seepage and evaporation from the surface.

3.2 Oxidation Process

Oxidation commences when the ore is exposed and trucked to the ROM pad, and continues through the processing plant as the crushed and ground ore is mixed with air and water. By the time it gets to the tailings dam, the oxidation process can be well advanced, although oxidation is slowed by saturation. As exposed tailings desaturate, they will become exposed to atmospheric oxygen via slow diffusion, and sulfidic tailings will start to oxidise. However, since the depth and extent of desiccation is limited by the reducing hydraulic conductivity of the drying tailings, the extent of oxygen ingress and hence oxidation is also limited. If the degree of saturation remains above 80 to 85%, oxidation will be limited. Any oxidation products can be delivered to the foundation and toe of the tailings dam by ongoing seepage, while surface oxidation products and sediments can be transported by fresh tailings and rainfall runoff, potentially overtopping a spillway.

3.3 Hardpan Development

Agnew (1998) investigated the natural formation of tailings hardpans as possible inhibitors of AMD, contaminant release and dusting. Agnew found that the effectiveness of hardpans in inhibiting acid generation is dependent on their reducing oxygen diffusion and rainfall infiltration into the tailings, while maintaining long-term erosional stability. A reduction in rainfall infiltration will diminish the potential seepage of contaminants. The low permeability of the hardpan will also inhibit upward flow and hence the uptake of salts into an overlying growth medium. The mineralogy, morphology, lateral extent, depth (typically less than 10 cm, but diminishing with depth) and rate of formation (typically 6 to 12 months, but at a diminishing rate with time) of hardpans is dictated by the sulfide mineralogy and content of the tailings, their particle size distribution, the method of deposition of the tailings, and the climate. Hardpans can have a hydraulic conductivity 10 to 100 times lower than that of uncemented tailings, and an oxygen diffusion rate up to 1,000 times lower, causing them to maintain a high degree of saturation. However, hardpans may not be continuous across the factility.

Liu *et al.* (2018 and 2019) found that iron-rich cemented hardpans over sulfidic copper-lead-zinc tailings were critical in immobilising zinc and lead via mineral passivation, encapsulation, and supporting native vegetation under semi-arid conditions.

4.0 COVERS ON POTENTIALLY CONTAMINATING MINE WASTES

The need for a cover is dependent on the reactivity of the mine wastes. The choice of cover type on potentially contaminating mine wastes is largely a function of the climate; whether wet, net positive water balance or humid, or net negative water balance or evaporative. Guidance on the choice of cover and cover design are given in the following two sections based on the GARD Guide (2009), with consideration of covers with capillary barrier effects discussed in the following section.

4.1 Choice of Cover Based on Climate

Guidance on the choice of cover type for potentially contaminating mine wastes for different climatic settings is provided by the GARD Guide (2009), as reproduced in Figure 3. The role of covers on potentially contaminating mine wastes is to: (i) limit oxygen ingress, and/or (ii) limit net percolation of rainfall. As soil covers are difficult to construct and be effective on dump slopes, the recommended cover types strictly only apply to the tops or benches of waste rock dumps, implying that no PAF waste rock should be placed beneath the side slopes unless a horizontal seal can be constructed over the PAF waste rock. Tailings beaches, being relatively flat, can readily be covered.

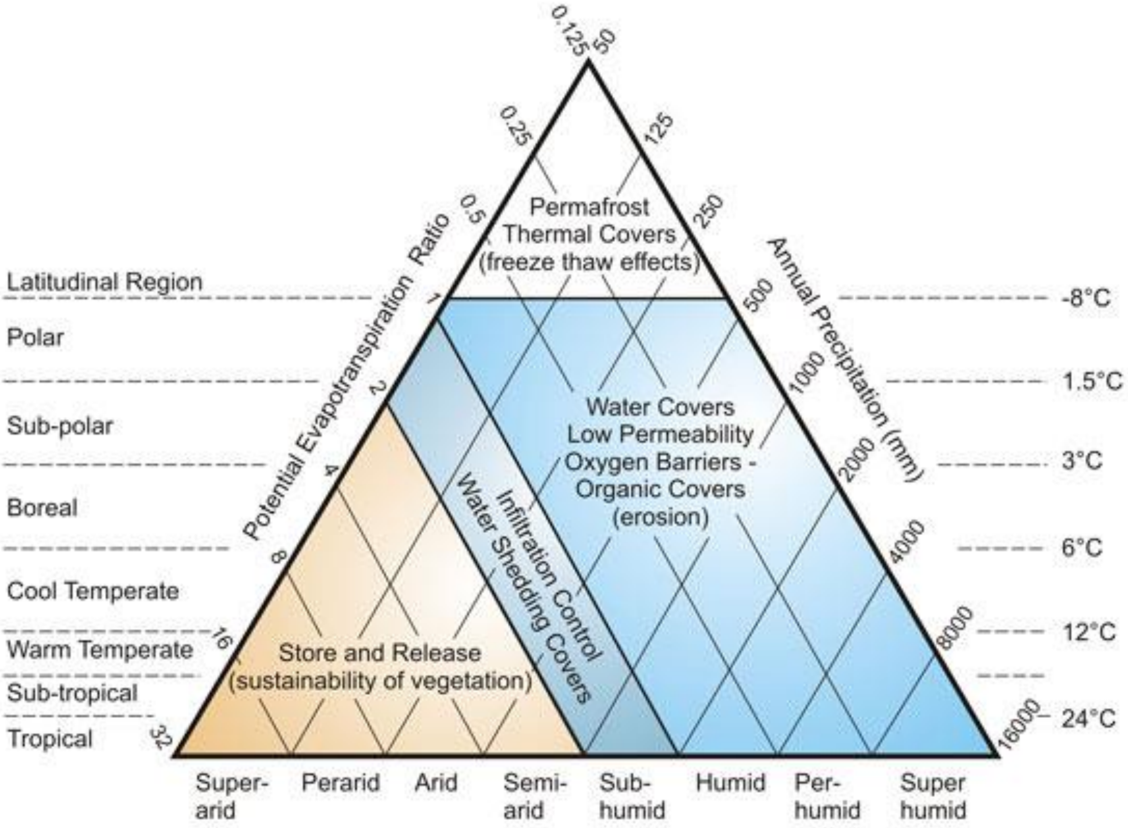

Fig. 3. **Covers and climate types (after GARD Guide, 2009)**

In a wet climate a water cover could be effective in limiting exposure to oxygen, although it should be maintained to limit any oxidation of the mine wastes. For waste rock, this would only be possible by disposal in-pit or in tailings slurry, maintained permanently under water. For tailings, sub-aqueous slurry disposal would be required. A water cover depth of 2 m is recommended, to avoid exposure of the tailings by wind-induced wave-action. Further, there must be sufficient recharge to maintain the water cover and a spillway to discharge excess water and maintain the stability of the dam, which would be required in perpetuity. Even the gentle slope of a tailings beach would likely require a series of terraced ponds, with separating dams. These would be difficult to construct retrospectively on deposited tailings and their stability may not be assured in perpetuity, resulting in water covers over tailings going out of favour, even at sites where the topography and rainfall support them.

In a humid or seasonally wet climate a water-shedding cover is recommended, to limit rainfall infiltration and hence the generation of acidic seepage. In a dry climate, a store and release cover is recommended, to limit net percolation of rainfall and hence the generation of acidic seepage.

4.2 Schematics of Soil Cover Designs

The GARD Guide also shows schematics of soil cover designs, reproduced in Figure 4, which increase in complexity, construction difficulties, potential performance and cost from left to right. These schematics have generated much confusion, particularly in Australia. Cover I, indicating a thicker single-layer of growth medium than the Base Case, is inferred to be "better" than the base case. However, thicker is not necessarily better. A thick "native material or barren waste or oxidised waste" layer intended to serve as a growth medium can lead to the infiltration of rainfall to a depth that makes it inaccessible to revegetation. This can also lead to increased net percolation into the underlying waste rock or tailings, and hence the generation of acidic seepage. The net result may be worse than having no cover at all, since the cover would constitute a "sponge" that would increase rainfall infiltration compared with a traffic-compacted waste rock dump top or a desiccated tailings surface.

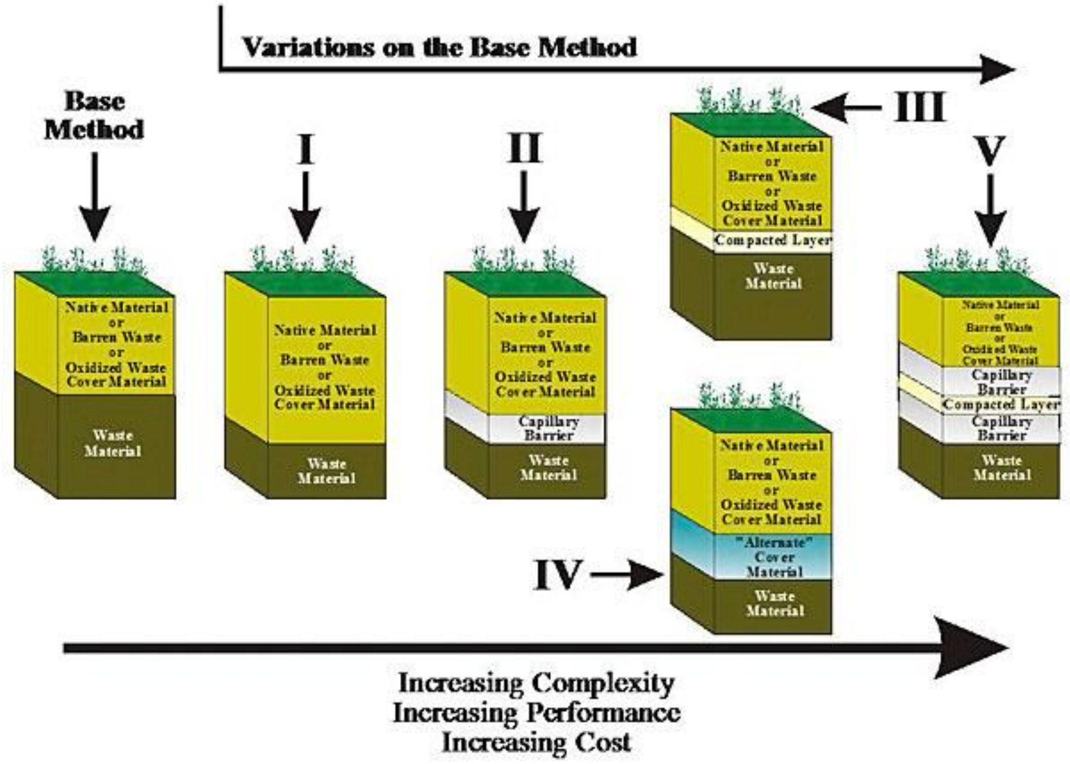

Fig. 4. Sample soil cover designs (after GARD Guide, 2009)

Cover II adds a capillary barrier (or break) beneath the growth medium, which may be desirable to limit the uptake of any salts from the underlying waste rock or tailings into the growth medium. A capillary barrier must be carefully selected and sized to ensure that it is effective and will remain so. Suitable capillary barriers may include clean gravel and clean sand. Run-of-mine waste rock would likely not be suitable for use as a capillary barrier, without crushing of coarse-grained particles and screening to remove fines.

Clean gravel would require a thickness of greater than 300 mm to remain effective as a barrier, while a clean sand would require a thickness in excess of 1 m. The capillary barrier must allow for the possible infiltration of fines from the overlying growth medium, which would render it ineffective over time. The particle size of the capillary barrier must be matched to that of the overlying growth medium, using filter criteria to ensure that the infiltration of fines into the capillary barrier is limited by arching.

Cover III adds a compacted (clayey) layer beneath the growth medium, which is desirable, particularly for a store and release cover to “hold-up” rainfall infiltration within the overlying “rocky soil mulch” layer. Cover IV is a variation on Cover III, in which the compacted layer is replaced by an “alternative” sealing layer, such as a geomembrane, bituminous geomembrane, or geosynthetic clay liner (GCL). A seal could also potentially be achieved by heavily compacting the top of a waste rock dump by loaded haul trucks, or due the development of a hardpan on sulfidic tailings, or by compaction of the tailings surface.

Cover V incorporates three layers separating the growth medium from the waste rock or tailings, comprising a compacted layer sandwiched between two capillary barriers. The intent of such a “double capillary barrier” is difficult to understand. If it were to provide greater surety that a capillary barrier would limit the uptake of salts into the overlying growth medium due to evapotranspiration, a single, thicker capillary barrier would likely be more effective. If a sealing layer is required, this would best be placed between the capillary barrier and the waste rock or tailings, or possibly above the capillary barrier. Cover type V is very uncommon.

The two most common cover types applied to potentially contaminating mine wastes are: (i) rainfall-shedding or barrier covers and, (ii) store and release covers (Williams *et al.* 1997 and 2006), as shown schematically on Figure 5. Rainfall-shedding covers were developed for landfills, partly to limit the net percolation of rainfall into the potentially contaminating landfill, but also to accommodate the inevitable large total and differential settlements of the landfill. The key element of a rainfall-shedding cover is a sealing layer, comprising compacted clayey soil, a geomembrane or GCL, or a composite, which is overlain by a growth medium. Rainfall-shedding covers are applied in wet or humid climates, in which a substantial vegetative cover can be established and sustained to limit erosion. The growth medium has a store and release function, supplied by the wet or humid climate, supporting revegetation.

The key elements of a store and release cover, developed for seasonal, dry climates are: (i) a thick loose “rocky soil mulch” layer with an undulating surface to store the wet season rainfall without inducing runoff, (ii) an effective sealing layer at the base of the cover to “hold-up” rainfall infiltration, and (iii) the appropriate choice of sustainable revegetation to release the stored rainfall during the wet season, through evapotranspiration. The required thickness of rocky soil mulch will depend on the wet season rainfall pattern and the rooting depth of the vegetative cover, and is typically 1 to 2 m. Too thick a growth medium could lead to rainfall infiltration beyond the reach of the revegetation. In a dry climate, store and release covers are more robust than rainfall-shedding covers.

The sealing layer should achieve a saturated hydraulic conductivity of less than 10^{-8} m/s (equivalent to a potential percolation rate of less than 300 mm/year, when water is available), so that in its usual unsaturated state in a dry climate its hydraulic conductivity will be less than perhaps 10^{-10} m/s (a potential percolation rate of less than 3 mm/year). In Australia’s typically dry climate, rainfall occurs on about 30 days/year, so that water may be available on top of the sealing layer for perhaps 10% of the time, reducing the potential percolation rate to less than 30 mm/year, or less than 5% of the typical average annual rainfall, similar to the typical natural percolation rate. High net percolation will be associated mainly with extreme rainfall events. The cover should cycle annually between wet and dry states without a net wetting up (which would lead to net percolation) or drying out (which would cause revegetation die-back and subsequent rainfall-induced erosion). An extreme rainfall event may wet-up the cover, potentially leading to breakthrough into the underlying mine wastes.

In Australia's generally arid to semi-arid climate, a eucalypt tree cover represents the only sustainable means of achieving the required evapotranspiration rates from a store and release cover to handle extreme rainfall events, and be sustainable in the long-term. Since the rocky soil mulch is loose and granular, the trees are unlikely to promote cracking and the development of preferred seepage pathways. The height of trees will be limited by the thickness and water-holding capacity of the rocky soil mulch, while their root patterns will not penetrate the sealing layer. The limited tree height will limit the possibility of wind blowdown and possibly threat to the integrity of the cover.

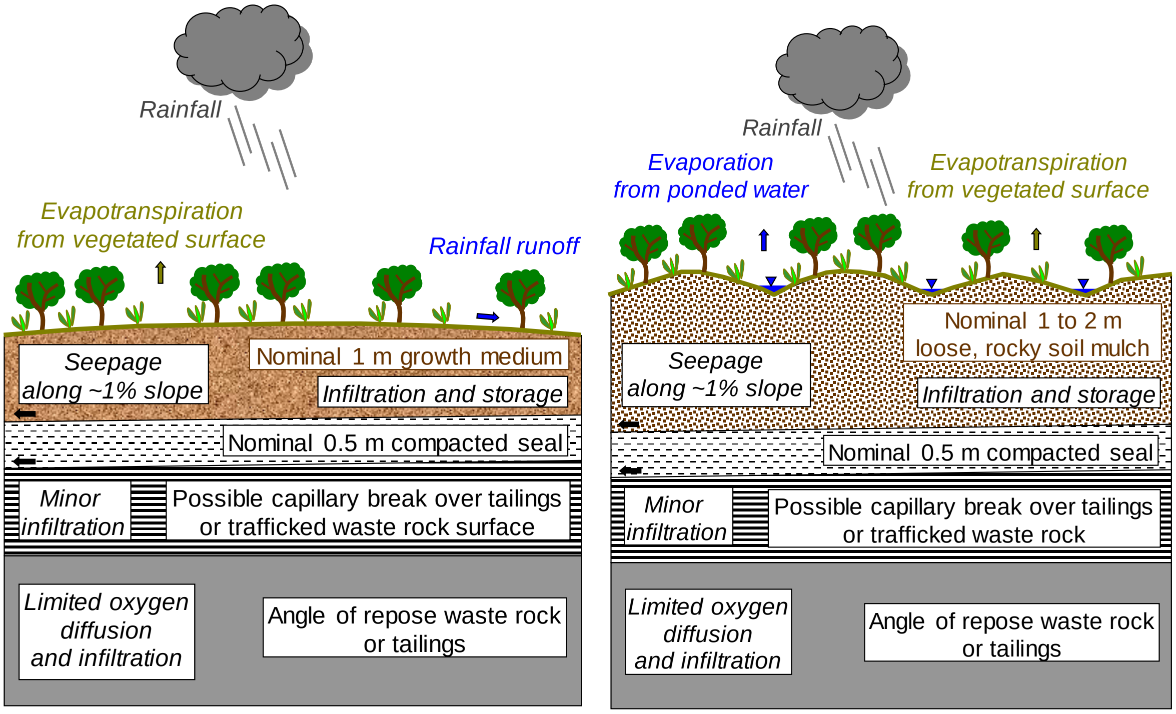

Fig. 5. **Most common cover types applied to mine wastes: (a) rainfall-shedding and, (b) store and release (after Williams, 2012)**

4.3 Covers with Capillary Barrier Effects

Capillary barriers have been considered for limiting the net infiltration of rainfall into underlying mine wastes. However, this relies on the capillary barrier remaining unsaturated to limit its hydraulic conductivity. If extreme rainfall events are possible, they could saturate the capillary barrier, rendering it quite permeable and able to pass rainfall infiltration into the underlying mine wastes.

Covers with capillary barrier effects (CCBE) bear the closest resemblance to the GARD Guide's Cover V. Bussière *et al.* (2006) described a CCBE first employed at the Les Terrains Aurifères (LTA, Figure 6) mine site tailings impoundment, approximately 8 km south-east of Malartic, Abitibi, in Québec, Canada, in a net positive precipitation climate. The LTA tailings impoundment is approximately 60 ha in area and has a height of 12 m. It comprises 7 m of sulfidic (acid-generating) tailings placed over 5 m of non-acid-generating oxide tailings.

Fig. 6. **LTA site, Quebec Canada and proposed CCBE (after Bussière *et al.* 2006)**

The CCBE, purpose-designed for and constructed on the LTA tailings impoundment in 1998, comprises 500 mm of sand (a capillary barrier) placed on the sulfidic tailings, overlain by 800 mm of fine-grained, non-acid-generating tailings (a moisture-retaining layer), in turn overlain by more than 300 mm of sand and gravel (protection and drainage layer). The design objective was to maintain a minimum degree of saturation of 85% in the moisture-retaining layer to effectively reduce the oxygen flux from the atmosphere to the acid-generating tailings. Near-saturation of the moisture-retaining layer was to be maintained by a combination of rainfall infiltration and the suction in the underlying capillary barrier. The intention of the sand and gravel surface layer was to limit revegetation, so as not to reduce rainfall infiltration. The same cover was applied to the side slopes of the tailings impoundment (also comprising sulfidic tailings). The cover initially functioned as intended on the top of the impoundment, which initially remained un-vegetated, but not so well on the side slopes, due to gravity drainage.

Smirnova *et al.* (2011) investigated volunteer revegetation on the LTA CCBE, which commenced the year after construction. Eight functional groups of plants were identified, with herbaceous plants being the most abundant. Of the 11 tree species identified, the four most abundant were poplar, paper birch, black spruce and willow. Root excavation showed that tree roots penetrated the moisture-retaining layer, with an average root depth of 400 mm and a maximum root depth of 1.7 m.

Bussière et al. (2015) reported that after 10 years, the LTA CCBE was effective in reducing the oxygen flux from the atmosphere to the acid-generating tailings. However, the quality of the seepage from the tailings impoundment still did not meet Québec water quality standards, and dolomitic drains were constructed as passive treatment. Views of the LTA tailings impoundment before CCBE construction in 1998, after CCBE construction in 1998, and 10 years later in 2007 are shown in Figure 7.

Fig. 7. **LTA tailings impoundment before CCBE construction in 1998, after CCBE construction in 1998, and 10 years later in 2007 (after Bussière *et al.* 2015)**

The CCBE was designed for a specific purpose, and a specific net positive precipitation climate, and appears to be the only Cover type V double capillary barrier cover applied in practice. It comprised a fine-grained moisture-retaining layer sandwiched between two capillary barrier layers. Its purpose was to maintain a minimum degree of saturation of 85% in the moisture-retaining layer to effectively reduce the oxygen flux from the atmosphere to the acid-generating tailings. It achieved this by a combination of rainfall infiltration and the suction in the underlying capillary barrier. No growth medium or revegetation was added, since revegetation would transpire, reducing the water available to infiltrate.

Double capillary barrier (or break) covers have been promoted by some Regulators in Australia, notably in Queensland. This is perplexing, since the majority of mine sites in Queensland, and elsewhere in Australia, are in semi-arid to arid climates, for which the GARD Guide (2009; Figure 3 herein) recommends a store and release cover. The reason for this may relate more to deficiencies in the design, materials selection and construction of store and release covers over potentially contaminating mine wastes in Australia, and elsewhere. It is suggested that the preferred approach would be to improve the design, materials selection and construction of the appropriate cover type for the potentially contaminating wastes and climatic setting of the mine.

5.0 EFFECTIVENESS OF COVERS IN ADDRESSING AMD LAGS

Apparent deficiencies in the design, materials selection and construction of the appropriate cover type for potentially contaminating mine wastes in a particular climatic setting is compounded by a lack of appreciation of the need to address geochemical and hydrological AMD lags. Surface waste rock dumps and tailings storage facilities experience different geochemical and hydrological AMD lags, which are closely related to the climatic setting.

5.1 Influence of Climate

Climate is the key determinant for the cover types recommended by the GARD Guide (2009, Figure 3 herein). Recommended cover types range from water covers for wet climates (although these have gone somewhat out of favour due to the need for water dams to persist in perpetuity), through rainfall-shedding covers for humid climates, to store and release overs for dry climates. The GARD Guide goes on to suggest a range of soil cover types, and further details of rainfall-shedding and store and release covers are also available in the literature and have been highlighted herein.

5.2 Covers on Sulfidic Waste Rock

The conventional end-dumping of waste rock from a tip-head in a surface dump promotes the oxidation of the initially relatively dry sulfidic waste rock due to the ready supply of oxygen via advection into the base rubble zone, convection up the coarse-grained angle of repose layers, and diffusion into the adjacent fine-grained angle of repose layers. Oxygen diffusion can also occur through the traffic-compacted top layer.

The dump is wet-up by rainfall infiltration, initially going into storage within the dump, until seepage eventually emerges from the base of the dump. The time taken to reach breakthrough is a function of the site rainfall, the degree of weathering and hence particle size distribution of the waste rock, and the height of the dump. For a fresh waste rock dump, breakthrough would occur in about 40% of the time it takes for a weathered waste rock dump, since a lower degree of saturation is required to create continuous water flow paths through the dump. Continuum breakthrough may peak at only about 5% of cumulative rainfall beneath the traffic-compacted top of the dump and at only about 10% beneath the angle of repose side slopes of the dump, implying average hydraulic conductivities beneath the top and sides of the dump of the order of 3×10^{-6} m/s and 6×10^{-6} m/s, respectively. Depending on the hydraulic conductivity of the foundation beneath a dump, only a small proportion of the seepage (perhaps as low as 0.1% of rainfall) would emerge at topographic low points around the toe of the dump. Extreme rainfall events will generate high seepage rates, with a time lag.

For a typical mine life of say 20 years, it is likely that a conventional end-dumped waste rock dump containing sulfidic waste rock will oxidise and generate AMD well within the mine life. Indeed, this is often the case. However, it continues to happen, often to the surprise of the mine operator. A waste rock dump that initially does not generate AMD suddenly does so, some years after the start of construction. In other words, both the geochemical and hydrological lags will have been exceeded. The “AMD horse” has bolted. If an appropriate and effective cover is placed after the end of the mine life, the best that can be achieved is that the dump will continue to drain down, generating AMD, for about as long a period as it remained uncovered, say another 20 years.

The solution to this is fairly obvious, sulfidic waste rock should be identified and paddock-dumped in cells well encapsulated by non-acid forming (NAF) waste rock or, preferably waste rock with ANC, if this is available, as shown in Figure 8 (after Williams, 2019). The cells should be periodically covered with traffic-compacted NAF or ANC waste rock as soon as practicable, and particularly prior to a defined wet season, in much the same way as landfills are encapsulated and regularly covered. By this means the geochemical and/or hydrological lags could be accommodated. A sustainable dump cover at closure should include an appropriate and effective cover on the dump top, and a textured cover on the side slopes of the dump for erosion protection, with no sulfidic waste rock placed beneath slopes unless protected by an appropriate and effective cover on a flat bench above.

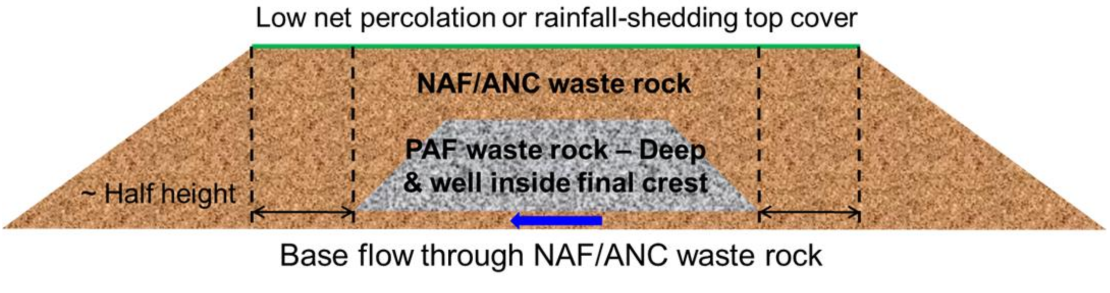

Fig. 8. Encapsulation of PAF waste rock (after Williams, 2019)

5.3 Covers on Sulfidic Tailings

The conventional deposition of tailings as a slurry in a surface tailings storage facility results in desaturation of any exposed tailings, particularly in a dry climate. The formation of a desiccated crust will dramatically reduce the hydraulic conductivity of the tailings and cause the desaturation profile to diminish exponentially with depth and typically be limited to a depth of less than about 600 mm. As tailings desaturate, seepage rates will reduce, as will evaporation rates from the surface. The deposition of fresh tailings or rainfall will inundate the drying tailings and re-saturate them, commencing from any desiccation cracks that form. Re-wetting will recharge downward seepage and evaporation from the surface.

Oxygen will slowly diffuse into sulfidic tailings with degrees of saturation of less than 80 to 85%, promoting oxidation. Any oxidation products can be delivered to the foundation and toe of the tailings dam by ongoing seepage, while surface oxidation products and sediments can be transported by fresh tailings and rainfall runoff, potentially overtopping a spillway.

Tailings that hardpan on desiccation, which is reasonably common for sulfidic tailings, may inhibit oxidation at depth contaminant release and dusting, due to reduced oxygen diffusion and rainfall infiltration into the tailings, while maintaining long-term erosional stability. However, discontinuous hardpans will be less effective in limiting seepage. This can also be achieved by compacting the tailings surface. A tailings hardpan or compacted tailings surface may act as a sealing layer for a cover and will likely inhibit the uptake of salts into the cover. A reduction in rainfall infiltration will diminish the potential seepage of contaminants. The low permeability of the hardpan will also inhibit upward flow and hence the uptake of salts into an overlying growth medium cover.

Relatively few covers have been placed on tailings compared with waste rock dumps. This is likely due to the soft and wet nature of many tailings deposits, compared with readily trafficable waste rock dump tops and benches. The progressive covering of tailings is even more rare, since this is incompatible with their ongoing operation. Hence, covering tailings deposits must await their closure, by which time the geochemical and hydrological lags will have been exceeded for any sulfidic tailings that become desiccated. The generation of AMD could potentially be avoided by careful management of tailings deposition. This could include maintaining sulfide tailings underwater in a wet climate, or managing tailings deposition cycles to maintain sulfidic tailings above the saturation threshold for oxidation. A balance is required between maximising the dry density and physical stability of the tailings, while maximising their chemical stability.

A sustainable tailings storage facility cover at closure should include an appropriate and effective cover on the relatively flat tailings beach, and a textured cover on the side slopes of the tailings dam for erosion protection. A tailings hardpan or compacted tailings surface may act as a sealing layer for a cover, and will likely inhibit the uptake of salts into the cover. Tailings that have achieved a high dry density and high strength will likely be trafficable by appropriately-sized earthmoving equipment for the purposes of placing a cover. Soft and wet tailings can be covered by pushing fill in thin lifts using a low bearing pressure dozer, by displacement of the tailings by end-dumped coarse-grained cover materials, or by placing coarse-grained cover materials hydraulically.

6.0 CONCLUSIONS

Sulfidic waste rock and tailings have the potential to generate AMD over time. Waste rock typically emerges from an open pit relatively dry and is conventionally end-dumped in a surface waste rock dump, giving it ready access to atmospheric oxygen and allowing the oxidation of any sulfidic minerals. The geochemical lag before the generation of net acidity is a function of the ANC present in the waste rock and the relative rates of production of acidity and alkalinity, which are strongly dependent on the particle size distribution of the sulfide minerals.

The hydrological lag before the emergence of AMD from the dump is a function of the extent and rate of wetting-up due to rainfall infiltration. This is in turn governed by the climatic setting and the physical and chemical nature of the waste rock. Initially, rainfall infiltration is largely taken up as storage in the void spaces within the dump. Cumulative rainfall infiltration, particularly intense rainfall events, result in seepage eventually reaching the base and perimeter of the dump, potentially carrying with it any net acidity, dissolved metals and sulfates.

Tailings are typically pumped to a surface storage as a slurry. If the surface of the tailings is allowed to desiccate, exposed sulfidic tailings can undergo oxidation. The oxidation products can then be mobilised by the deposition of fresh tailings, or by rainfall runoff and/or infiltration. If the runoff is discharged via a spillway, any acidity can be released to the environment. Seepage laden with oxidation products can eventually reach the foundation and toe of the tailings storage facility.

The purpose of covers over potentially acid forming (PAF) mine wastes is to minimise the ingress of oxygen into the wastes and/or minimise transport of any AMD via the net percolation of rainfall into the wastes. The appropriate choice and effectiveness of covers is a function of the climatic setting, the mine wastes, and the management of the wastes.

Sulfidic waste rock should be identified and paddock-dumped in cells well encapsulated by non-acid forming (NAF) waste rock or, preferably waste rock with ANC, if this is available. The cells should be periodically covered with NAF or ANC waste rock as soon as practicable, and particularly prior to a defined wet season, in much the same way as landfills are encapsulated and regularly covered. By this means the geochemical and/or hydrological lags could be accommodated. A sustainable dump cover at closure should include an appropriate and effective cover on the dump top, and a textured cover on the side slopes of the dump for erosion protection, with no sulfidic waste rock placed beneath slopes unless protected by an appropriate and effective cover on a flat bench above.

Covering tailings deposits must await their closure, by which time the geochemical and hydrological lags will have been exceeded for any sulfidic tailings that become desiccated. The generation of AMD could potentially be avoided by careful management of tailings deposition. This could include maintaining sulfide tailings underwater in a wet climate, or managing tailings deposition cycles to maintain sulfidic tailings above the saturation threshold for oxidation. A balance is required between maximising the dry density and physical stability of the tailings, while maximising their chemical stability.

A sustainable tailings storage facility cover at closure should include an appropriate and effective cover on the relatively flat tailings beach, and a textured cover on the side slopes of the tailings dam for erosion protection. A tailings hardpan or compacted tailings surface may act as a sealing layer for a cover, if it is continuous, and will likely inhibit the uptake of salts into the cover. Tailings that have achieved a high dry density and high strength can be trafficked using appropriately-sized earthmoving equipment. Soft and wet tailings can be covered by pushing fill in thin lifts using a low bearing pressure dozer, by displacement of the tailings by end-dumped coarse-grained cover materials, or by placing coarse-grained cover materials hydraulically.

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GEOMETALLURGICAL CHARACTERISATION OF MINE TAILINGS: EXAMPLES FROM TASMANIA

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ABSTRACT

Mining of larger, lower grade deposits across several commodities (e.g., Cu, Au, Pb, Zn) in recent decades has led to an increase in the quantities of mine wastes being produced. These materials may contain reactive minerals, including sulfides, and therefore require appropriate management to mitigate against environmental impacts including the formation of acid and metalliferous drainage (AMD). Common AMD remediation strategies involve the application of introducing covers and using chemical or biological techniques to stabilise these wastes, though the long-term success of these strategies is not guaranteed as examples across Australia (e.g., Ranger, Mary Kathleen) have demonstrated. Instead, determining if new economy metals or additional base or precious metals are contained in sulfidic mine waste at economic concentrations presents an opportunity to both reduce AMD risk and recover additional commodities. In this study, geometallurgical characterisation of mine tailings at two mine sites in western Tasmania was performed. Following the logging and sampling of tailings, a geometallurgical investigation program (e.g., XRD, chemical assay, static testing, automated mineralogy, laser-ablation ICPMS) was undertaken. Results confirmed that further investigations to define secondary resources of Co, Cu and magnetite at the Princess Creek Tailings Storage Facility (Copper Mines Tasmania) may add value. In contrast, based on sampling and characterisation of the upper 2m at the Bobadil Tailings Storage Facility, Rosebery mine, reprocessing for Au, Pb, Zn, Cu (and new economy metals) recovery is likely to be sub-economic. A follow-up sampling campaign to target deeper materials is required and, based on these results, should focus on determining the tenor and deportment of Au, Pb and Zn following this geometallurgical characterisation program.

1.0 INTRODUCTION

Whilst the existence (and threat) of global climate change continues to be debated by political leaders many industries are already transitioning to a low-carbon economy to minimise their environmental footprints (Nyambuu and Semmler, 2020). To support this, there has been an increased demand for new economy and critical metals (e.g., Co, REEs, In, V, W) leading to new opportunities for the mining industry to develop projects targeting a broader range of commodities. Exploring in mine waste presents one opportunity to supplement the demand with the advantage of these materials, in the case of mine tailings, having undergone some degree of comminution theoretically reducing overall operational mineral processing plant costs and, in the case of sulfidic tailings, minimising long-term AMD risks. In order to assess such mine waste repositories, a geometallurgical characterisation approach can be adopted as this enables the tenor and deportment of the potential commodities of interest to be determined and, based on this, a suitable mineral processing technology to be selected to maximize recovery. This geometallurgical approach for assessing tailings was presented in Parbhakar-Fox et al. (2018) where the Old Tailings Dam, Savage River mine, Tasmania was investigated and has been adopted in this study characterizing two other tailings storage facilities in Tasmania at Copper Mines Tasmania (Vedanta), and the Rosebery mine (MMG

Ltd.). The aim of the study was to determine the tenor and deportment of new economy, base and precious metals (Co, Pb, Zn, Cu, Au) in these tailings as a first-pass investigation into assessing reprocessing potential.

2.0 MATERIALS AND METHODS

2.1 Site descriptions

Both study sites are located on the Tasmanian west coast an area well-endowed in mineral deposits (Figure 1a; Corbett et al., 2014). In Queenstown, more than 20 sulfide-rich VHMS ore bodies have been worked for Cu at the Mt. Lyell mine since 1883. The mine, now known as Copper Mines Tasmania (CMT), is currently in care and maintenance but the anticipated restart will continue as an underground operations with onsite mineral processing involving flotation to produce a Cu-concentrate. Flotation tailings were deposited into the Princess Creek Tailings Storage Facility (PCTSF) which holds approximately 42 Mt of tailings under a minimum of 1.5 m water cover (Figure 1b). The Rosebery Mine is a polymetallic volcanic massive sulfide (VMS) deposit and is regarded as a world-class base metal (Pb, Zn, Cu, Au, Ag) deposit with a total resource (past and current resources, as of March 2017) of 38.72 Mt @ 13.5% Zn, 4.0% Pb, 0.54% Cu, 127 g/t Ag and 2.0 g/t Au (Corbett et al., 2014). Like CMT, it is an underground operation with mineral processing occurring via 3-stage flotation flowsheet to produce Pb, Zn and Cu concentrates (Au is recovered via gravity separation). Flotation tailings were deposited into the Bobadil Tailings storage facility containing ~18 Mt and is currently sub-aerially exposed (Figure 1c).

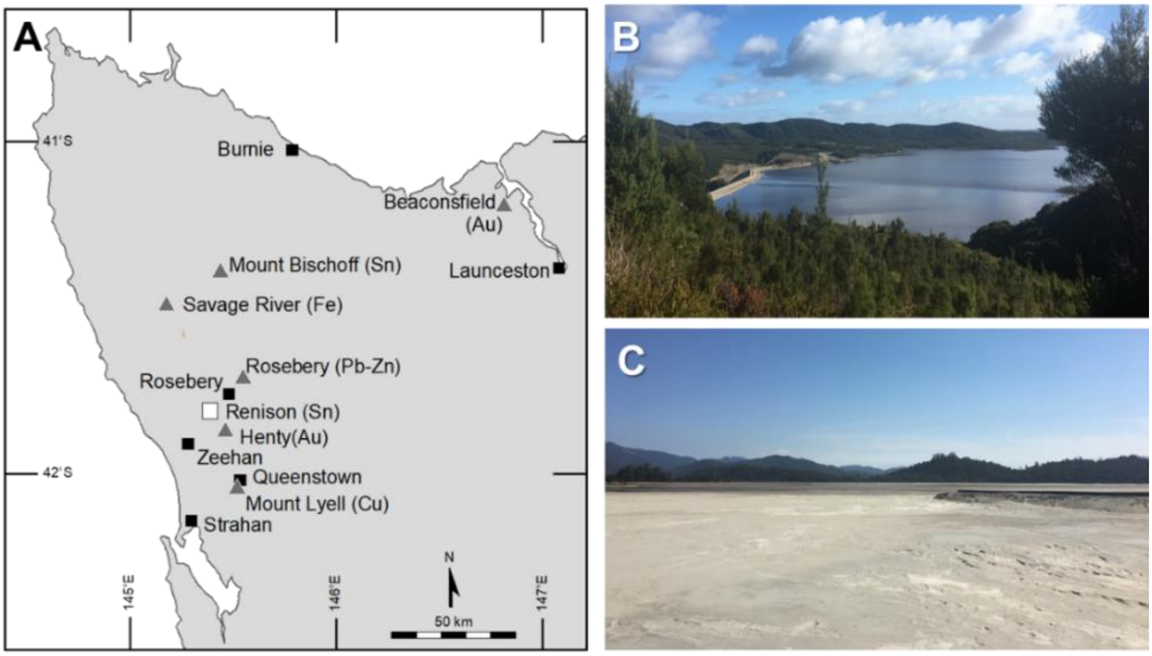

Figure 1: a) Western Tasmania and location of major mines and townships; b) Princess Creek Tailings Storage Facility (Copper Mines Tasmania); c) Bobadil tailings (Rosebery mine).

2.2 Sampling and sample preparation

At the PCTSF, underwater core samples were collected (by Johanna van Balen and team, February and April 2019) along 5 transects (A to D and A’) using a UWITEC weight driven hammer corer by dropping the corer off the side of a boat. The weights on the corer were repeatedly dropped a minimum of 50 times per core collected. Water depth varied across the facility with the shallowest sample taken at 1.2 m (PCTSF_C06, PCTSF_C17 and

PCTSF_test02; Figure 2a) and the deepest at 10.9 m (PCTSF_C16; Figure 2a). In total 21 cores were collected along with 5 bulk samples taken in the northern subaerial portion of the dam (Figure 2a). Cores were transported to Hobart, frozen and subsequently logged and sampled (108 samples taken) at UTAS laboratories. At the Bobadil TSF, 52 tailings sediments were sampled at four 'finger' discharge points (by Lexi K'ng and team, March 2019; Figure 2b) using an excavator arranged by MMG Ltd. The maximum depth of the excavated trenches was ~1.8 metres. Three trenches were also dug from the furthest, the middle and the closest points of a discharge finger from the edge of the tailings dam with approximately five trench samples collected. Where possible, additional samples were collected, for example, from areas with hardpan formation and oxidation. Four additional core samples were obtained by hand using HDPE pipes (5 cm diameter; up to 70 cm depth; Figure 2b) at locations accessible by foot only. Pore water samples were collected at both sites, with infield pH and EC measurements made and samples filtered (0.45 um PES filter), acidified (1% HNO_3) and chilled prior to ICPMS analysis. At both sites, all samples (approximately 200- 500 g) were oven dried (40 °C) and rotary split into 8 representative portions. Unmilled portions were kept for insitu mineralogical analysis whilst others were milled (soft steel and tungsten carbide to < 63 µm) and used for determining bulk mineralogy.

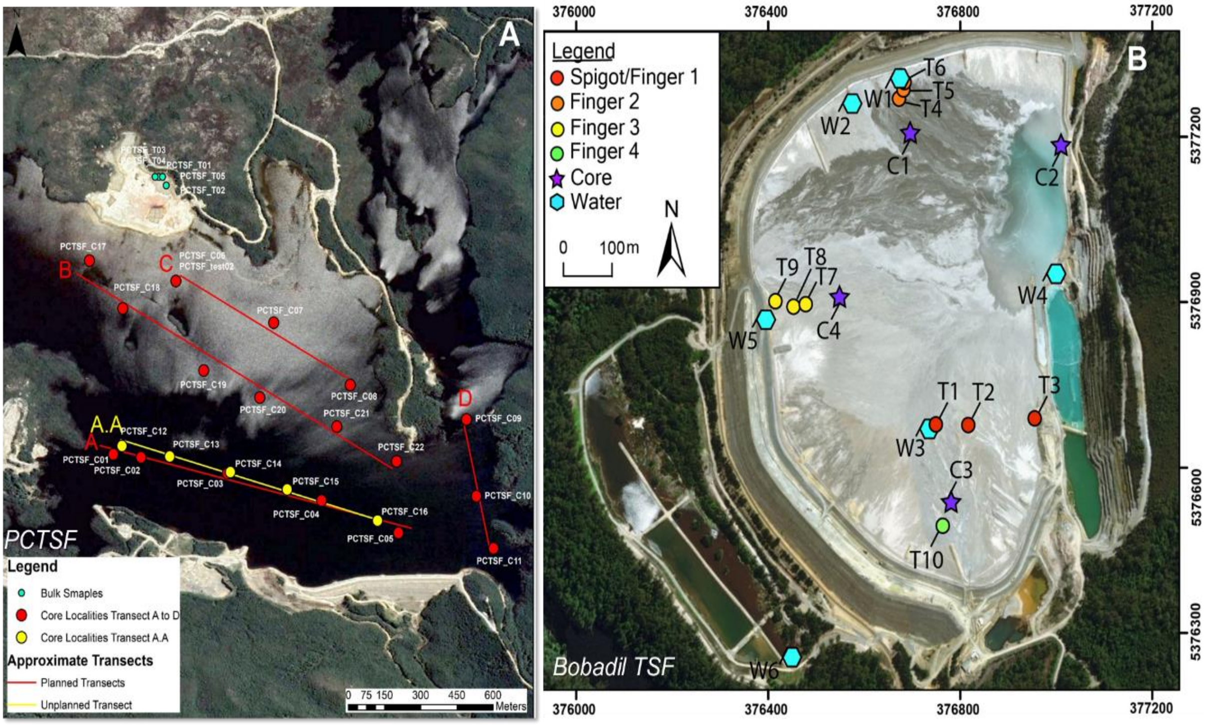

Figure 2: Sample locations at: a) Princess Creek Tailings Storage Facility (Copper Mines Tasmania); b) Bobadil tailings (Rosebery mine).

2.3 Mineralogical and chemical characterisation

A benchtop Bruker D2 Phaser X-Ray diffractometer (UTAS) with a Co X-ray anode, with CoKα radiation was used to determine mineralogy for select samples collected at both sites. Powder samples from the PCTSF (*n* = *55*) were spiked with a corundum standard and combined in an agate pestle and mortar to achieve < 10 µm before loading it into a sample holder prior to entering the analysing chamber. For the Bobadil tailings *(n=85)*, amorphous material was not visually identified during logging (with no well-developed capping oxide seen, as at the PCTSF), so these samples were unspiked. Samples from both sites were analysed for 10 or 30 minutes at 30 kV and 10 mA with each scan range from 5° to 120° 2θ using a 0.020 2θ step size. Minerals present were identified using the Bruker DIFFRAC.EVA software package and PDF-2 (2012) database. Mineral abundances were semi-quantified in the proprietary Bruker software TOPAS (V 4.2) via Rietveld analysis.

To determine bulk chemistry, an Olympus Vanta portable XRF (pXRF) instrument equipped with a rhodium (Rd) X-ray tube anode was used. Pulverised samples (*n=55, PCTSF; n=85, Bobadil TSF*) were loaded into plastic XRF cups covered with 4 μm polypropylene microanalytical film. Calibration of equipment was performed prior to the analyses. Analyses were performed in two modes, geochemistry mode using two beams (40 keV and 10 keV) with 20 seconds of analyses time per beam; and soil mode using three beams (50 keV, 40 keV and 15 keV) with 20 seconds of analyses time per beam. Each sample was measured using both modes. A suite of standard reference materials (i.e., Tasbas, RTS-3, GXR-4, NIST2781) were used before, during and after the analyses to correct data generated from each element of interest. The detection of Co at low levels has traditionally been difficult with pXRF due to inter-element interference between Co and Fe. However, recently Olympus IMA updated their geochemistry model to overcome the interference by deconvoluting the peaks (Wright, 2019). To help refine pXRF correction factors, select samples (*n= 26, PCTSF; n = 5, Bobadil TSF*) were sent to ALS-Global laboratories for chemical analysis (Method codes: ME-MS42, ME-4ACD81, AU-TL43 and ME-EXRF26).

2.4. Mineral liberation analyser (MLA)

An FEI MLA 650 environmental scanning electron microscope (MLA650 ESEM) at the Central Science Laboratory (CSL; UTAS) was used to collect detailed mineralogical and textural information on the sulfides contained in the tailings. Carbon-coated polished grain mounts (*n = 14, PCTSF; n= 26, Bobadil TSF*) were made from select samples chosen based on: i) sulfide alteration index scores (Jambor and Blowes, 1990); ii) geochemical results and iii) their spatial (and depth) location in their respective TSFs. Samples were analysed using MLA application and the XBSE and sparse phase search (SPL-XBSE) modes with, for the Bobadil tailings, a gold search performed (Fandrich et al., 2007). Images were processed in FEI MLA Image Processing (v. 3.1) and Bruker AMICS software to produce detailed mineral maps of ca. 4 μm resolution. Select samples from both sites (*n = 5, PCTSF; n= 14, Bobadil TSF*) were also analysed using a Hitachi SU-70 analytical field emission scanning electron microscope (FE-SEM) to collect detailed BSE images with data processed in Oxford Aztec software (v. 3.3).

2.5. Laser-ablation ICPMS (LA-ICPMS)

LA-ICPMS was used to quantitatively measure trace elements within sulfides. Pyrite was the primary target however sphalerite, chalcopyrite, galena, magnetite and other Fe - oxide or hydroxides were also analysed where permissible. Samples were chosen based on insitu mineralogical investigations with 14 (*n = 550 spot analysis*) and 15 polished grain mounts (*n= 450*) respectively selected for the PCTSF and Bobadil TSF. LA-ICPMS was undertaken at CODES (UTAS) using a Resonetics Resolution 193nm wavelength excimer laser fixed to an Agilent 7700 ICPMS. A spot size of 19 μm and 29 μm, at 5Hz with a fluence of 2.7 J/cm^2 was used. Each spot was pre-ablated for 30 seconds then analysed for 45 seconds. Calibration was performed using in house standards of STDGL3, GSD-1G and PeruPy (Fe) for the sulfides and, BCR-2G and GSD-1G for oxides. Quantification was performed using LADR software (Norris Scientific, Hobart, Tas). Data was screened using signal time and spectra strength as a guide for segregating clean and dirty pyrite and sphalerite. Clean pyrite contains Fe-S only whereas dirty pyrite contains a mix of elements (e.g., Pb, Mn).

3.0 RESULTS

3.1 Bulk properties

At the PCTSF 8 tailings facies were defined ranging from hardpan, 3 sulfide facies, 2 deeper oxide facies, an organic matter facies and a gravel/clastic facies. The presence of deeper oxide facies is representative of paleo-horizons i.e., where the tailings had been sub-aerially exposed during dam wall lifts. At the Bobadil TSF, 11 tailings facies were defined with sulfidic tailings more heterogeneous in terms of their grain size and colour (grey to blue-grey to darker grey). This likely represents greater sulfide variability in the ore lenses. At the PCTSF, the mineralogy was dominated by chlorite, muscovite, quartz, pyrite, chalcopyrite, albite, hematite, magnetite and barite with an average pyrite content of 7.7 wt. %. Similarly, the Bobadil tailings are dominated by quartz, illite/muscovite, chlorite and barite with sulfides dominated by pyrite, followed by sphalerite. Whole rock chemistry identified several elements in excess quantities as per the ISQG Guidelines (McCready et al., 2006) at the PCTSF with Cd and Cu identified as elevated. A maximum Co concentration of 319 ppm was measured (Facies B; fine-grained, unoxidised sulfide tailings) and showed strong positive correlation with Cu (R^2= 0.83). At the Bobadil TSF high concentrations of Pb, Zn, Cu, As and Mn relative to ANZECC (2000) ISQG (low-trigger) values were measured.

3.2 Insitu mineralogy

The majority of pyrite (7.7 wt. %) contained in the PCTSF is liberated with a p80 of 40 µm. Where locked, or partially liberated, pyrite is associated with magnetite or iron hydroxides (Figure 3a), quartz, feldspars, apatite, micas, chalcopyrite (Figures 3b to d), sphalerite (Figure 3e) and galena (Figure 3f). Chalcopyrite present typically occurred in association with medium to coarse grained (ca. 100 to 200 µm) pyrite. At the Bobadil TSF, 17 minerals were identified with a greater diversity of sulfides observed. Approximately 89% of pyrite was liberated with the remainder dominantly associated with muscovite, quartz, barite and sphalerite. Sphalerite were notably oxidised and fractured with 56% liberated and the rest dominantly associated with muscovite, quartz and pyrite. Galena (< 0.5 wt. %) was poorly preserved and found as inclusions or remnants surrounding pyrite. Chalcopyrite was also low in abundance (< 1wt. %) but where present, associated with pyrite or was present as microinclusions in sphalerite as ‘chalcopyrite’ disease. Two tailings samples contained gold particles of <10 µm diameter were identified (Figure 4) and were liberated (Figure 4a) and contained in chalcopyrite (Figure 4b).

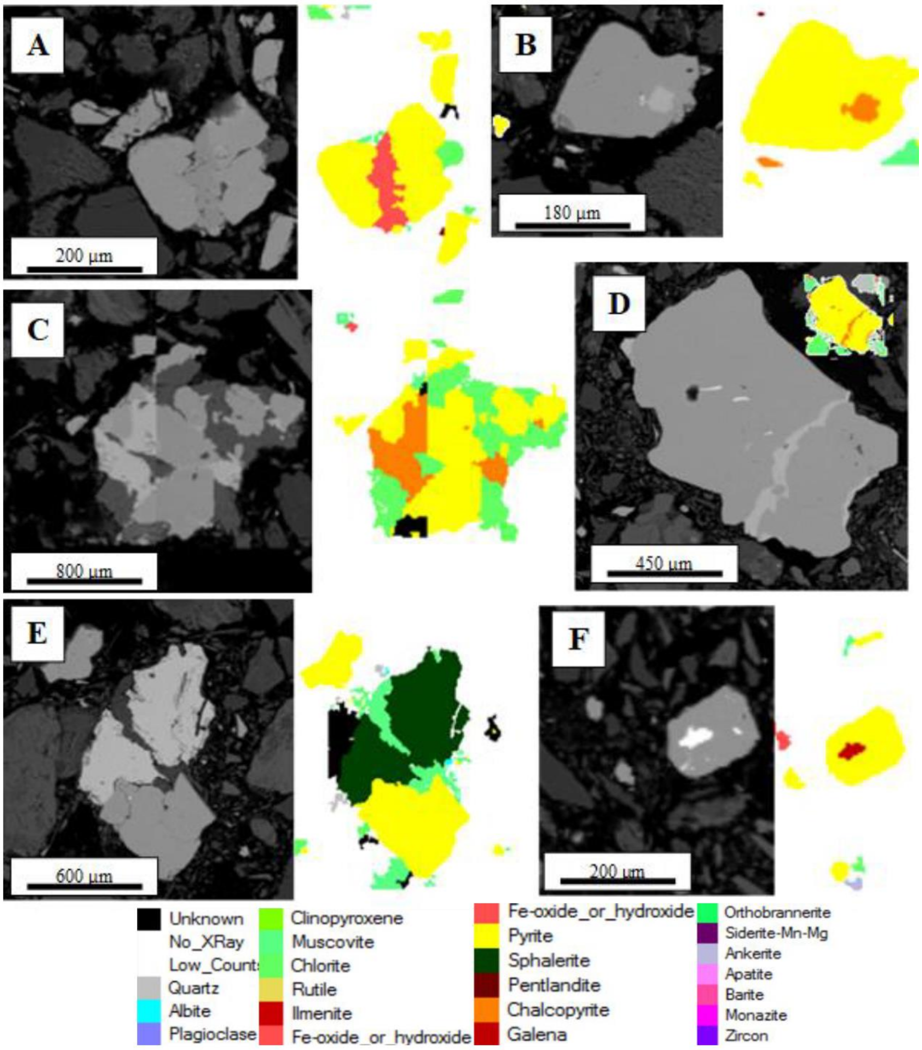

Figure 3: Pyrite grain associations and mineral inclusions in the PCTSF. Examples include: (A) Fe oxide or hydroxide within the pyrite grain (B, C and D) chalcopyrite inclusions and bound up material (E) sphalerite and (F) galena.

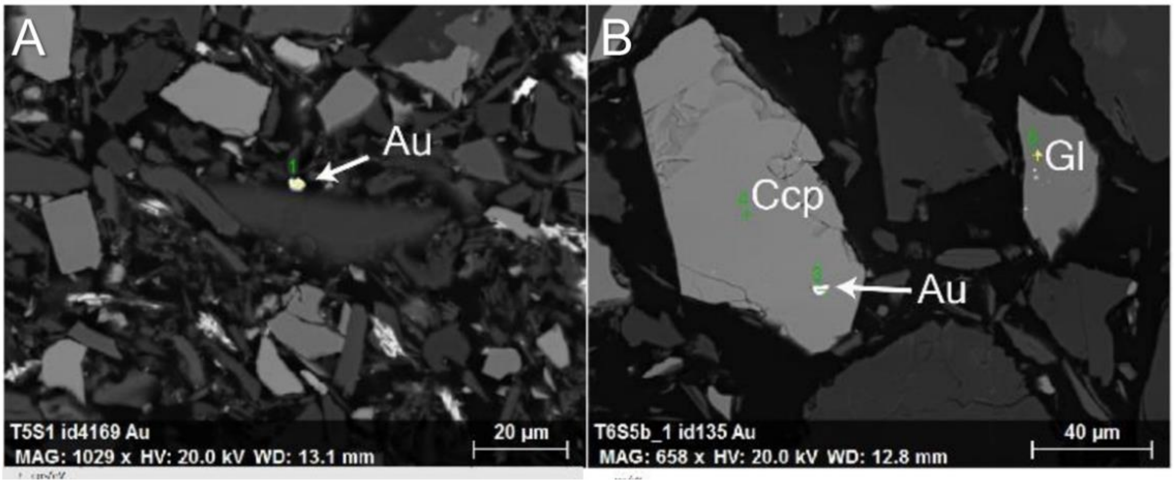

Figure 4: Gold search conducted using SPL-XBSE and XBSE analysis at the Bobadil TSF. (A) T5S1. (B) T6S5b. Abbreviations: Gl, galena, Ccp, chalcopyrite; Au, gold.

3.3 Mineral chemistry

At the PCTSF, LA-ICPMS analysis reported high concentrations of Co in pyrite averaging ~1,805 ppm and ranging from 0.2 ppm to 33,480 ppm. The concentration of Co varied across the transects with the highest average values of 1,744 and 3,022 ppm measured for Transects C and D respectively (Figure 5) and Facies C (medium grained, unoxidised fresh sulfidic tailings) contained the highest Co (average: 2,193 ppm). When segregating pyrite types, clean pyrite was slightly more endowed with 1,946 ppm measured and showed correlation with Ni and had Cu present as (chalcopyrite) microinclusions (Figure 6a). Dirty pyrite (Figure 6b) also contained high Co, Cu, Ni in addition to Zn, Bi, Pb and Au. No discrete Co minerals were found, rather Co is contained in the pyrite lattice (i.e., refractory).

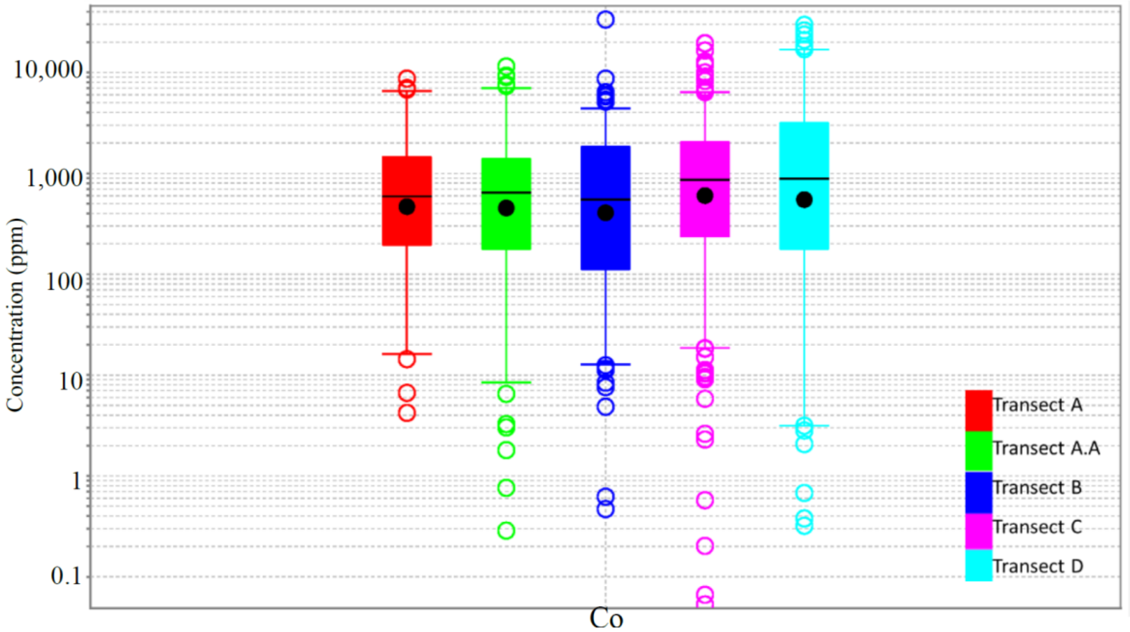

Figure 5: Box and whisker plot of LA-ICPMS Co concentrations in ppm for each transect. The black line represents mean values and the hollow colour circles represent outlier values. The minimum and maximum values are shown by the whisker markers.

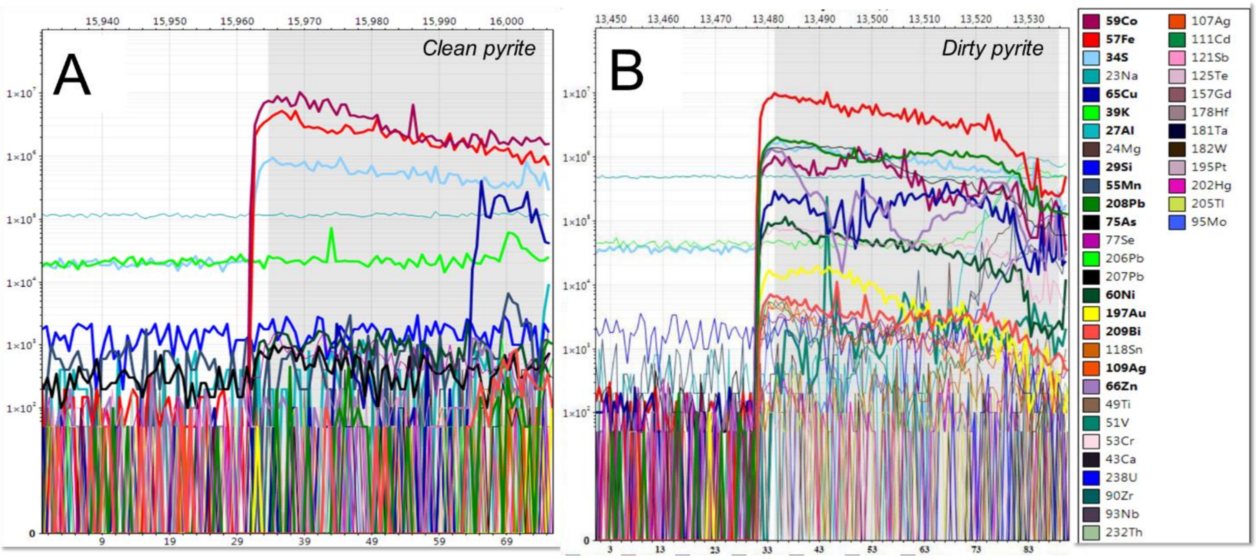

Figure 6: (A) LA-ICPMS spectra image showing a short analysis of a clean pyrite which has high Cowith Cu inclusions; (B) spectra showing a larger grain of 'dirty pyrite containing Cu, Co, As, Pb and higher Au.

At the Bobadil TSF, the same classification of pyrite types was adopted and adapted for sphalerite (clean: higher concentration of Zn and S; dirty: higher concentration of elements other than Zn and S. Dirty pyrite reported the highest concentration of Cu (249,117 ppm) but the highest average Cu was in dirty sphalerite (1,966 ppm) confirming micron-scale chalcopyrite disease. Measured concentrations of Pb were also the highest in dirty sphalerite (max: 742,254 ppm; average: 17,531 ppm) though concentrations were similar in dirty pyrite (max: 7,413 ppm; average: 244,189 ppm). In a spatial context, Au was highest in Finger 2 pyrite, but overall concentrations were low (< 3.62 ppm; Figure 7). In contrast to the PCTSF, Co was much lower (average :< 39 ppm; Figure 7) with the highest values reported for Finger 4. Sphalerite in Finger 3 contained the highest concentrations of several bivalent elements (e.g., Cd, Co, Fe, and Ni) though the highest Pb was reported for Finger 4 (Figure 7) and indicates the presence of galena microinclusions.

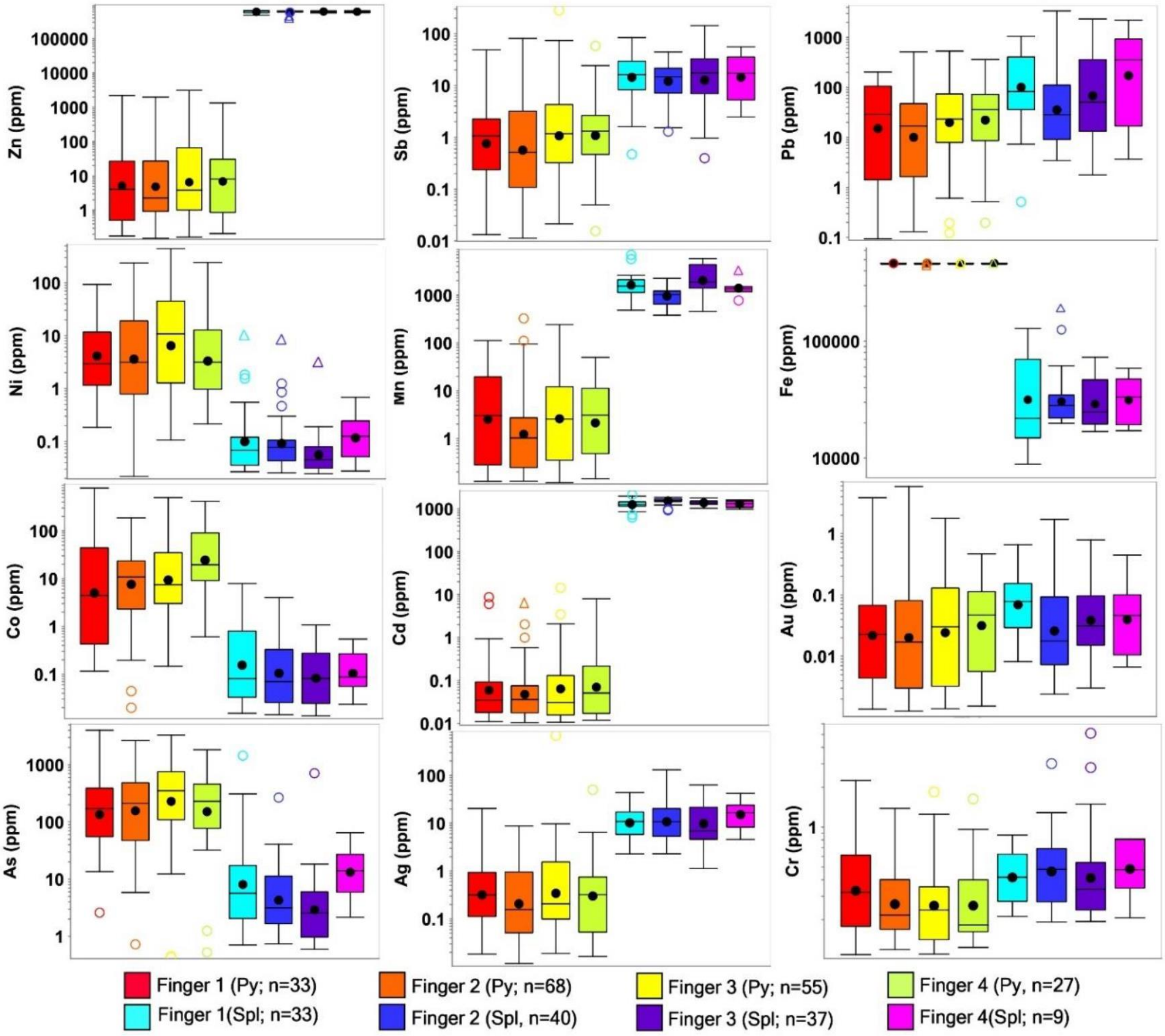

Figure 7: Major and trace element chemistry of Bobadil tailings collected from four discharge fingers (1 to 4). Abbreviations: Py, pyrite; Spl, sphalerite.

4.0 DISCUSSION AND CONCLUSIONS

Mining for essential metals (Cu, Zn and Pb), and new economy metals (Co, In, V, REEs), is a global pursuit necessary to meet the demands of our growing population and low carbon technologies, however, it generates large quantities of waste (Lyu et al., 2019; Naidu et al., 2019). Reducing quantities of stored waste by examining their reprocessing potential represents an opportunity to chemically de-risk sulfidic TSFs whilst generating additional revenue (or at the very least, contribute the CAPEX and OPEX funds required to pursue rehandling and processing TSF material). To determine this, first-pass geometallurgical investigations, as undertaken in this study, are critical for the decision making process as they can assist management teams with deciding if there is value in undertaking detailed drilling to facilitate secondary resource definition. Similar approaches have recently been presented in Alcade et al., (2018), Cenciceros-Gomez et al. (2018), Figueiredo et al. (2019) for a range of commodities.

At the PCTSF, the bulk pyrite content of the PCTSF was determined to be 7.7 wt. % with an average Co content of 1,805 ppm and 1,935 ppm as refractory Cu within pyrite indicating strong reprocessing potential. In pyrite, Cu and Co showed strong positive correlation ($R^2=0.83$) which presents additional options for metallurgical recovery. The PCTSF showed enrichment of magnetite with an average of 1.8 wt. % measured (though LA-ICPMS indicating it not to be a mineralogical host for Co). Gold in the PCTSF was identified to be relatively sparse with LA-ICPMS returning results of a maximum of 17 ppm (average of 0.5 ppm) and whole rock geochemistry showing an average of 0.13 ppm. Whilst the CAPEX/OPEX costs of recovering this value may ultimately prove uneconomic, these results can be used to inform future plant design for the operations when future mining and mineral processing commences enabling new opportunities to recover this highly-sought new economy metal. Further research recommendations include the development of bioleaching test cells to determine optimal metallurgical parameters (i.e., optimal grain size, suited bacteria strain, conditioning time, circuit time, pH and temperature) for metal recovery.

In contrast, based on sampling of the upper 2m, investigations at the Bobadil TSF indicate low reprocessing potential, with low concentrations of critical (Co) and precious metals (sparse free Au < 10 μm otherwise, lattice bound in pyrite) measured in the sulfides, and whilst galena and sphalerite were identified, their bulk content was low (0.39 % and 1.73 % respectively) with respective recovery of Pb and Zn likely to be uneconomic. However, additional sampling and geometallurgical characterisation investigations should be undertaken to the depth of the TSF to confirm this. Instead, reprocessing to desulfurise the Bobadil tailings may provide opportunities for lower risk disposal in new engineered surface structures and/or underground voids, reducing mine closure liability and increasing chances of facility relinquishment by regulators.

5.0 ACKNOWLEDGEMENTS

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GROWTH OF INDIGENOUS BACTERIA FROM MINE TAILINGS: IMPLICATIONS FOR BIOLEACHING FOR COBALT RECOVERY

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ABSTRACT

An alternative approach to improve the management of sulfidic mine tailings is to assess their biohydrometallurgical reprocessing potential thereby reducing AMD risks via desulfurization. However, to recover remaining economic metals, novel mineral processing techniques may be required with bio-processing being one such option for unlocking potential value. The oxidative bioleaching potential and geoenvironmental parameters of five bulk tailings samples collected from the Princess Creek Tailings Storage Facility in Tasmania, including weathered and unweathered sulfide facies, were tested. Indigenous bacteria cultured from the tailings consisted of a diverse consortium of acidophilic Fe- and S-oxidising bacteria. These naturally occurring bacteria were used in a five-week shake-flask bioleaching trial to extract Co from a weathered sample. Several elements, including Al, Cu, S and Fe, were measured in the resulting leachates with their concentrations increasing over time. However, leachate Co dropped after Week 2, intuitively due to its adsorption onto bacterial oxidation reaction products. Therefore, a secondary leach phase to target Co is required to liberate Co. Additional trials to test and optimise the efficiency of these bacteria to leach materials collected from sulfidic facies should be undertaken to evaluate the application of this mineral processing technique to mine tailings deriving from similar ore deposits.

1.0 INTRODUCTION

Mining of critical metals has increasingly become a global pursuit to support the adoption of low-carbon economies (Fankhauser and Jotzo 2018). The increased demand and production rates of these metals (e.g., Co, In, V, Ga, Ge) are associated with the generation of vast amounts of waste material (Izatt et al. 2014). Mine wastes can contain sulfides which are susceptible to oxidation when exposed surficially (Parbhakar-Fox and Lottermoser 2015). Oxidation can liberate potentially deleterious metals which, when released into open water sources, can seriously impact natural ecosystems. It is common practice to dispose of these materials into purpose-built repositories, but this is not without environmental and geotechnical risks. Instead, Pradhan et al. (2008) suggested that by developing new methods for treating tailings it could be possible to instead use them as low-grade ores and reduce the volume of reactive waste being produced. Applications of biotechnology can provide practical and economic alternatives to traditional methods of metal extraction (Tichy et al., 1998, Pradhan et al., 2008, Johnson, 2014). Baldi et al. (1991) explained bacterial leaching as the breakdown of sulfides and iron oxides to recover metals such as Cu, Ni, Co, Zn, Ag and Au. The processing of low-grade ores or mine tailings through biotic means has provided a broad range of alternatives for metal extraction which is feasible, both economically and environmentally. Johnson (2010) explained how using bacteria leads to the production of ferric ions from ferrous promoting the dissolution of pyrite. Using bacteria specific to a mine site, which are well adapted to tailings generated by a particular style of ore deposit (i.e., their feed) as opposed to using commercially available stock bacteria (i.e., adapted to different deposits) may serve to enhance bioleaching and metal recovery. This study sought to identify indigenous bacteria present at the Princess Creek tailings storage facility (PCTSF) in Queenstown, Tasmania and to undertake preliminary testwork into their efficiency at liberating Co from these tailings.

2.0 MATERIALS AND METHODS

2.1 Site Description

Since 1883, the Mt Lyell ore bodies (>20) in Western Tasmania (Figure 1) have been worked for Cu with the system classified as a volcanic-hosted massive sulfide (VHMS; Corbett et al., 2014). Initial open pit mining at the Iron Blow produced 5.6 million tonnes of ore at 1.8% Cu, 1% Zn, 0.2% Pb, 15 g/t Ag and 2 g/t Au. Later, mining activities at North Lyell, Crown Lyell, Cape Horn, Royal Tharsis, Lyell Comstock and Lyell Tharsis were almost entirely underground with mineral processing onsite. Grades in those bodies ranged from 1.4% to 4.3% Cu, 0.4 g/t to 0.7 g/t Au and 2.8 g/t to 33 g/t Ag. When the site was operational (currently in care and maintenance), the mine operators, Copper Mines of Tasmania (CMT) disposed their tailings into the water-covered Princess Creek tailings storage facility (PCTSF; Figure 1b).

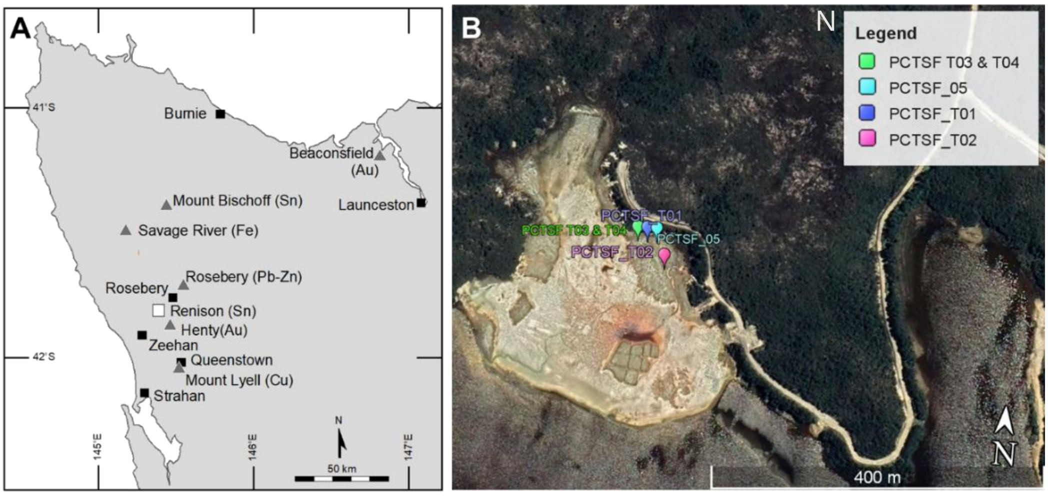

Fig. 1. Princess Creek Tailings Storage Facility (PCTSF). Sample locations are shown as collected from the North of the TSF.

2.2 Sampling

Five bulk tailings samples (*n=5*) were collected from hand-dug trenches from the unsaturated northern part of the PCTSF (Figure 1b) to represent both fresh and oxidised tailings material. Approximately 30 kg of tailings were collected and packed in large air-tight buckets before being transported to the University of Tasmania where they were split and sent to the Sustainable Minerals Institute (SMI), UQ, Brisbane. The samples were stored at room temperature in a large plastic bucket prior to the commencement of the experiments at the School of Earth and Environmental Sciences, UQ. Sub-samples were collected and oven dried for bulk mineralogical and chemical analyses. All samples were photographed and logged.

2.3 Bulk characterisation

A split of the samples were dried and hand ground into a fine powder using an agate pestle and mortar for 5 to 7 minutes for bulk mineralogical analysis using X-ray diffractometry (XRD). Each sample was spiked with corundum (internal standard to allow for amorphous content calculation) and further homogenised. The analyses were performed at the University of Tasmania (UTAS) using a Bruker D2 Phaser X-ray diffractometer. The semi-quantitative mineralogy was determined using a combination of the Bruker Eva (using the crystallographic open database) and Topas (V4.2) softwares and the typical detection limits are reported between 0.1 to 0.5 wt. % modal abundance. For geochemical characterisation a portion of each powdered sample was analysed by the ALS-Global (Brisbane) using a combination of techniques (Method codes:ME-MS61L, MEMS81, ME4ACD81, MEXRF26, Au-TL43). Total sulfur and carbon were measured by a LECO analyser (Method codes: SIR08, CIR07).

2.4 Indigenous bacterial enumerations

Iron- and sulphur-oxidising bacteria were enumerated according to Southam and Beveridge (1992) using the MPN (most probable number) method (Cochran, 1950). The bacterial counts obtained along with the bulk geochemical data was used to select one sample to be used in the subsequent bioleaching trial.

2.5 Bioleaching trial

The bioleaching trial was carried out on sample PCTSF-T01 to liberate Co and other metals of interest (i.e., Ni, Cu). Approximately 100 g of the primary mixed tailings was sub-sampled into a 250 ml beaker using a spatula under normal laboratory conditions. The tailings mix was subsequently used to prepare inoculum for the four-week trial and the residual was recorded as the T= 0 sample. T= 0 sample acts as an important marker for comparison between the initial and the final (bioleached) chemical and mineral compositions. 5 g of the tailings were added to each flask. This was followed by the addition of 100 ml of the freshly prepared M9K media into each flask using 25 ml sterile glass pipette. The final weight of the solution was recorded. This process was continued until all flasks were filled with the sample mixture. Each flask was weighed before and after the preparation of the inoculum. Each flask series labelled ‘A’ and ‘B’ were arranged according to their corresponding weeks and incubated on a rotatory shaker chamber at room temperature (24 ° C) and 120 rpm. Weekly recorded data including: pH, oxidation-reduction potential (ORP), bacterial count and collection of filtered and acidified liquid samples to analyse bulk aqueous chemical data using ICP-OES (inductively coupled plasma optical emission spectroscopy) assays. These data were compared to time zero (T=0) to identify significant chemical changes.

2.6 Bacterial identification

Bacteria from initial (T=0) and the final bioleaching liquor residue, were sub-sampled into small vials and sent to the Australian Centre for Ecogeonomics for molecular analysis of the DNA sequences to identify the primary bacteria responsible for bioleaching. Data extraction and clean-up of excess primers were carried out in mothur software ((https://www.mothur.org/wiki/MiSeq_SOP) required to code base pair repeats and operational taxonomic units) to enable the final identification of the operational taxonomic units (OTU) sequences to be matched on BLAST (Basic Local Alignment Search Tool) via the ncbi website. Bacterial species were identified to genus and species level.

3.0 RESULTS

3.1 Bulk properties

The samples can be grouped phenotypically as representing two facies, namely weathered (PCTSF-01, PCTSF-03 and PCTSF-05) and unweathered (PCTSF-02 and PCTSF-04) sulfides. HFOs (hydrous ferrous oxides) dominate in all samples (31.6 to 65.9 wt. %) reflecting a high hardpan content in this hydrodynamic beach zone whereby the tailings are intermittently wet and dry. The crystalline mineralogy is dominated by chlorite, muscovite, quartz with pyrite identified in both sulfide and oxide facies (Fig. 2). Other iron oxide minerals such as hematite and magnetite were identified (up to 1.8 wt. % and between 0.8 to 2.2 wt. %, respectively; Fig. 2).

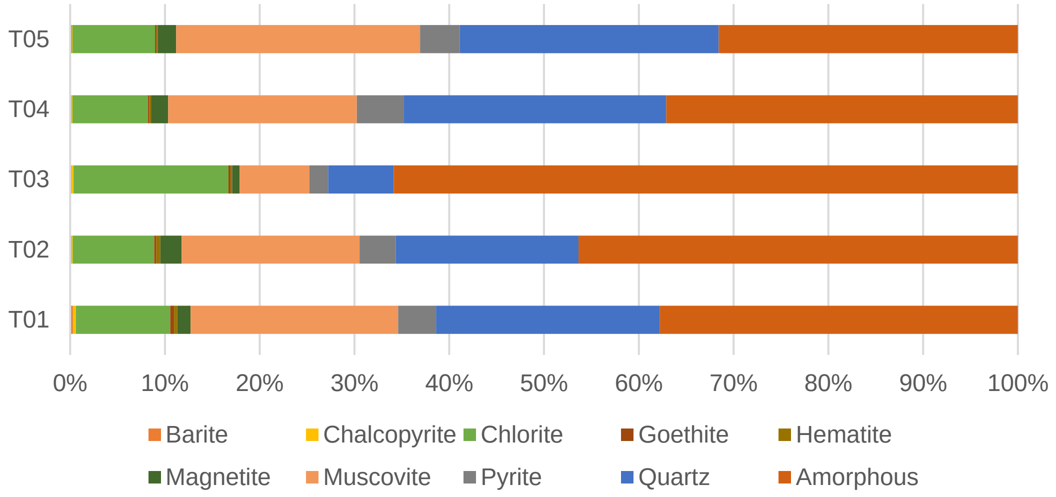

Fig. 2. Stacked bar chart showing bulk mineralogy of TSF01 to TSF05 (wt. %).

SiO_2 and Fe_2O_3 dominate the majors confirming the dominance of quartz and HFOs measured by XRD, followed by Al_2O_3 and MgO (Table 1). The weathered facies are characterised by relatively high concentrations of Co (181 to 307 ppm), Cu (1,415 to 5,070 ppm), Zn (540 to 587 ppm) and Pb (88 to 106 ppm). The unweathered sulfide zone contained between 208 to 229 ppm Co and 1,455 to 1,920 ppm Cu, and slightly elevated concentrations of Au (0.1 to 0.4 ppm; Table 1). Measurements of the interstitial tailings fluids were acidic (pH 1.8 to 2). Generation of H_2SO_4 by AMD processes is likely to have caused Co, Cu, Pb and Zn mobilisation into the pore water fluids and during intermittent drying, these will likely have migrated upwards and concentrated in the oxide facies where they been retained on iron oxide surfaces where they now appear to remain stable.

Table 1. Select bulk geochemical data for PCTSF samples.

Sample Type	PCTSF-T01	PCTSF-T02	PCTSF-T03	PCTSF-T04	PCTSF-T05
Majors					
Al_2O_3 (%)	10.85	12.16	10.34	11.28	11.28
BaO (%)	0.39	0.45	0.37	0.34	0.29
CaO (%)	0.83	0.84	0.88	0.98	0.87
Fe_2O_3 (%)	19.38	18.96	27.04	21.02	23.69
K2O (%)	2.81	3.16	2.41	2.65	2.36
MgO(%)	2.06	2.54	2.6	2.54	2.67
MnO(%)	0.1	0.18	0.17	0.24	0.24

Na_2O (%)	0.04	0.04	0.04	0.04	0.05
P2O5 (%)	0.37	0.34	0.37	0.37	0.35
SiO_2 (%)	52.91	52.85	42.79	50.82	48.01
TiO_2 (%)	0.38	0.41	0.45	0.37	0.41
Traces					
Co (ppm)	181	208	307	229	269
As (ppm)	53	53.3	48.7	83.4	78.6
Cu (ppm)	1415	1455	5070	1920	2730
Zn (ppm)	540	530	559	491	587
Pb (ppm)	88	80	106	85	95
Ag (ppm)	0.9	0.9	1.8	1.5	1.4
Au (ppm)	0.125	0.113	0.266	0.396	0.159

3.2 Bacterial count (MPN method)

MPN counts were high in these tailings confirming this to be a microbiologically active environment with similar values reported in Kock and Schippers (2006) for a pyrite containing tailings in Kristenberg, Sweden. Bacterial growth data showed that the highest microbial count for the Fe-feed series was in PCTSF-01 (Table 2) whilst the highest for the S-feed series was PCTSF-05 (Table 2). In general, the Fe-feed series results were higher than the S-feed with the exception of PCTSF-03 which may be due to the elevated Cu measured (Table 1). The observed trend in the growth suggests the presence of acidophilic iron and sulphur oxidising bacteria.

Table 2. Final microbial count for Fe and S series for PCTSF samples.

Sample	Fe-feed series (MPN/g)	S-feed series (MPN/g)
PCTSF-01 (weathered)	1.6x10^{8}	7.0x10^{3}
PCTSF-02 (unweathered)	2.8x10^{5}	2.2x10^{3}
PCTSF-03 (weathered)	1.7x10^{6}	2.2x10^{3}
PCTSF-04 (unweathered)	1.1 x10^{3}	3.5 x10^{4}
PCTSF-05 (weathered)	2.4 x10^{5}	4.9x10^{4}

3.3. Bacterial DNA extraction and identification

Molecular analysis of the bacterial DNA for PCTSF-T01 at T=0 consisted of 304 taxonomic clusters (or OTUs) with > 80-90% identity match on the ncbi database. For the purpose of this report, we consider the first 10 OTU sequences for reference to ID the indigenous bacterial population in the sample (Table 3). The same bacteria were measured at the end of the trial.

Table 3. Identified bacteria through sequencing alignment on BLAST with their corresponding match identities for the first 10 OTUs.

Sample	Blast identification	DNA sequence (%) identity
OTU-01	*Acidiferrobacter thiooxidans*	100%
OTU-02	*Leptospirillum ferriphilus*	99.60%
OTU-03	*Acidithiobacillus ferrooxidans*	99.20%
OTU-04	*Leptospirillum ferrooxidans*	100%
OTU-05	*Ferroplasma acidarmanus*	99.60%
OTU-06	*Leptospirillum ferriphilum*	98.80%
OTU-07	*unclassified*	Unclassified
OTU-08	*Leptospirillum ferriphilum*	96.80%
OTU-09	*Leptospirillum ferrooxidans*	90.32%
OTU-10	*Leptospirillum ferrooxidans*	97.98%

3.4. Bioleaching trial

Chemical data from the bioleaching trial for select elements is shown in Table 4. Sulfur dominates the overall compositional with high (1,256 ppm) concentrations measured at the end of the trial. This was followed by Fe (364 ppm) and Ca (289 ppm). Concentrations for Cu (0.19 ppm), Ni (0.48) and Zn (15.16 ppm) show a steady increase from their initial concentrations, whilst As is only measured in the final leachate (0.03 ppm). Whilst the head grade for Co was low (181 ppm) Co was poorly leached in the first week (Table 3) with concentrations dropping below detection limit after Week 2. Cobalt has a high affinity to HFOs, a common bacterial oxidation reaction product (~7 wt. % relative increase measured by XRD from T=0 to week 4) at higher pH's as reported by Pontieu et al. (2006). However in these experiments the pH was consistently measured between pH 2.01 to pH 2.17 so it is dubious if Co has been immobilised through adsorption to these phases. Measurements of bacterial counts confirmed the sustained presence of Fe-feed series bacteria with 3.5 x 10^7 MPN per gram measured at Week 4.

Table 4: Geochemical data for T=0 and Weeks 1-4 bioleached as obtained through ICP-OES assay (in ppm).

Sample	**0**	**1**	**2**	**3**	**4**
As	<DL	<DL	<DL	<DL	0.03
Co	0.83	0.74	0.52	<DL	<DL
Cu	12.9	15.9	14	16	17.8
Fe	86.5	125	146	280	364
Ni	0.25	0.29	0.27	0.38	0.48
Pb	0.01	0.02	0.02	0.04	0.06
S	324.3	774.9	807.3	1063.7	1256.1
Zn	12.39	14.06	10.88	13.15	15.16

4.0 Discussion and conclusions

Bacterial ecosystems in tailings, such as that studied here, evolve over time and are influenced by changes in the surface processes and associated elemental-release (as a response to geochemical factors). The applications of biomining have commonly focused on low grade sulfide ores using acidophilic bacteria, which are able to oxidise ferrous iron and reduced elemental sulfur as a result generating lixiviants in the acidic liquor (Kaksonen et al., 2017). In this study, the tailings collected from different locations were identified and segregated into two specific facies–weatherd and unweathered (sulfide). Based on the results, the growth of indigenous microbes is naturally evident with *Acidiferrobacter thiooxidans, Leptospirillum ferriphilus, Ferroplasma acidarmanus, Leptospirillum ferriphilum and Leptospirillum ferrooxidans* identified. Figure 3 presents a schematic representation of the two facies (using data from PCTSF-03 and 04 as these were in the same trench). The weathered facies, as expected, contains greater concentrations of Fe-dominated minerals with the greatest concentration of amorphous (HFO) material. Compositions of individual elements such as Co, Cu, Zn and Pb are noticeably higher in the case of PCTSF-03 (Table 1) consistent with high Fe-oxidising counts for this sample. The bulk chemical concentrations for these elements can be arranged in the following order: Cu > Zn > Co > Pb. Sulfide facies samples report higher concentrations of aluminosilicate minerals but with similar trends in terms of trace metal abundance (with As being higher in sulfide and Ni higher in the weathered facies). If these 'tailings beach' materials remain in this dynamic saturation zone, they will, with the influence of bacteria, continue to generate localized acid conditions increasing the depth of the oxidised horizon (with the sulfides the bacterial feed) with secondary oxide materials likely to adsorb the elements of economic interest (i.e., Co and Cu), particularly as pH values in oxide porewater fluids start to increase post-biotic reaction.

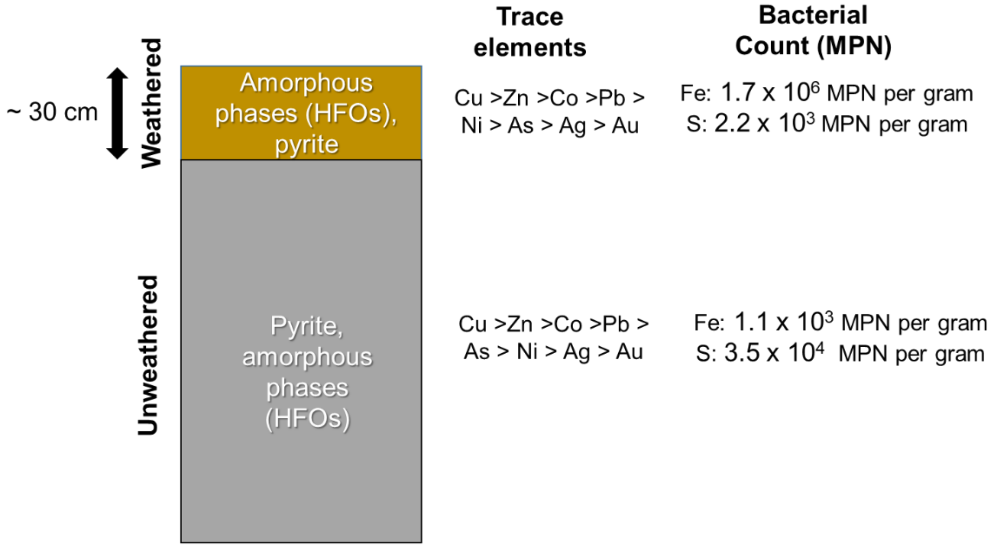

Figure 3: Schematic representation of weathered and unweathered facies (based on field observations) with their corresponding trace elements and bacterial counts (via MPN).

Bioleaching in this experiment was unsuccessful in effectively liberating Co. Whilst pyrite content was high (4.0 wt. %) and the pyrite is Co bearing (van Balen, 2019) this research shows that preconditioning mineral surfaces may be important for enabling successful recovery as a reflected light microscopy study on these pyrites (using a site-specific sulfide alteration index of Blowes and Jambor, 1990; data not given) showed oxidised rims on pyrite. Further experiments which concentrate pyrite (via flotation), clean the surfaces and then bioleach using these indigenous bacteria, suitable for use when treating VHMS tailings, may prove more effective than simply bioleaching using the materials as received in similar continuous stirred tank reactor experiments to those described in Parbhakar-Fox et al. (2018). However, given the Co fertility of the oxide facies, undertaking acid leaching to liberate this as undertaken by Santoro et al. (2019) could also be investigated.

5.0 ACKNOWLEDGEMENTS

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LOOKING BACK: HOW DID PLACING PAF ROCK IN THIS PARTICULAR MINE ROCK STOCKPILE NOT LEAD TO ACIDIC DRAINAGE CONDITIONS

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ABSTRACT

Open cut mines generate large volumes of waste rock and overburden that are typically stored in large waste rock dumps (WRDs). In metalliferous mines located in regions subject to distinctive wet and dry seasons (e.g. Tropical Savannah) reactive sulfidic waste rock must be managed by a waste rock dump designed to avoid and limit acid and metalliferous drainage (AMD) forming. To achieve this goal required a commitment by The Mine management to form an AMD management team and adopt an approach to building the WRD that was different to historical WRD construction methods and different to what they were traditionally familiar with. This commitment extended to senior mine staff taking ownership of the management of reactive waste. Continuity of this commitment persisted through the mine life with AMD management team members replaced as current members moved on, retired or left the mine and ensuring that critical knowledge was passed on to new staff prior to departure of employees. The commitment to change focussed on limiting generation of AMD from the WRD by controlling air entry, limiting rainfall infiltration, limiting water flux through the placed waste rock pile, and minimising surcharging the WRD with rain water during construction. Reactive waste once identified in the pit was selectively mined and selectively placed in dedicated areas within the WRD using paddock dumping. The paddocked dumped reactive waste was then dozed out to form 2-3m high lifts. Prior to the start of the rainy season the flattened tops were sheeted with silty clay and truck compacted using haul trucks. Further all flat surfaces (working surfaces) within the WRD were sheeted with a thin compacted layer of silty clay. Ponding of surface water was limited by grading surfaces to facilitate runoff. Typical result for reactive material within a WRD constructed in climates with distinctive wet and dry seasons is to observe AMD during WRD construction, and then continuation of these conditions following cessation of WRD construction, and indeed exacerbation of AMD as the WRD wets up and drains down. However, this was not observed during construction of the WRD described in this paper. Looking back – why did this WRD perform so well. This paper discusses a number of contributing factors to limiting acid drainage being generated on a dump-wide scale at the Mine. Importantly is the dump design and construction was focussed on minimising reactive rock oxidation by limiting vertical airflow capacity (from the interim cover layers), and lateral airflow capacity (from the paddock dumping), thereby limiting generation of stored acidity and salinity. Equally important was a commitment by mine management to the formation of a waste management team comprising key staff including the Mine Manager, to oversee the management and prevention of acid drainage during the construction life of the waste rock dump and to maintain an AMD management team through the life of the mine.

1.0 INTRODUCTION

The basis for this paper comes from an operating large open cut mining operation (referred herein as "The Mine") which,

- operates in a climatic terrain with distinct rainy and dry seasons (Tropical Savannah);
- had a mix of waste and overburden rock types including:

  - a reactive waste (potentially acid forming; PAF rock) that needed to be managed for AMD control;
  - a barren carbonate altered waste rock with excess acid neutralising capacity;
  - a silty clay overburden suitable for constructing the interim cover layer(s);
- had a large-vehicle mine fleet; and
- had an estimated mine life of 20 plus years.

The presence of the reactive waste rock and proposed large waste landform presented a challenge to limit AMD generation.

The continuing challenge to managing open-cast mining of deposits hosted in rocks that contain metal sulfides is the successful and “correct” disposal of reactive sulfidic and metalliferous waste rock within a landform, which is geotechnically and geochemically stable, is non-polluting, and non-eroding. There are many physical, chemical, geological, social, and mining related factors that must be considered when designing a WRD for managing and containing reactive waste rock material. These include, but not necessarily are limited to:

- the mine plan;
- physiography and geology;
- environmental;
- geotechnical;
- material properties; and
- regulatory and social.

2.0 WASTE ROCK DUMP DESIGN

It was recognised that historically, at many other mine sites around the world limited attempts were made by mining operations to design WRDs for long-term storage of reactive waste materials, and little attempt was made to separate and selectively place reactive waste material within the waste rock emplacement to limit release of metals, acidity and salinity from the oxidation of reactive waste materials. This approach, while seemingly will lower operational cost of a WRD construction, most often results in environmental consequences that could result in significant impacts on downstream communities and ecosystems. In climates with distinctive wet and dry seasons such found in tropical savannah terrains the WRD is allowed to wet-up and become surcharged with rainfall derived water. This surcharge of water generates seepage from the dump that commonly persists long after the completion of WRD construction.

It was agreed with The Mine’s management that traditional WRD design and construction had to be replaced by a better practice of designing and building the WRD; one that looks to manage oxidation while waste was being placed, and limits discharge of acidic and metalliferous drainage in the future.

Overburden in the mine precinct comprised soil and rock that was removed and stockpiled to allow access to the economic resource and the rocks hosting the resource. The overburden did not contain toxic elements present in the underlying economic resource and its host rocks but needed to be characterised for its value as a construction material, particularly for its potential as a growth medium for final cover systems. In addition, it was recognised that the material’s clay content would allow it to serve as an interim cover layer, placed over PAF rock lifts, to reduce net percolation of incident rainfall during dump construction.

Waste rock that comprise the host rock material present when the target deposit was emplaced, was mined to access and extract the economic resource. The waste rock is not mineralised (barren) or contained insufficient concentrations of the target mineral that could be extracted economically and hence is classed as mining waste. The waste rock was characterised for the presence of metal sulfides and potential acid forming capacity, the presence of acid neutralising/consuming minerals, the presence of elements of concern, and physical properties. Importantly, reactive waste and barren waste were mapped, and separately identified in the geological model.

Some of the host rocks (waste rock) to the mineralisation contained sulfide minerals (pyrite) and metals of concern including arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. While metal concentrations in the host rock was not as high as identified in the ore it remained as a potential long-term source of metal that could seep from the WRD and potentially result in adverse impact to waterways and groundwater.

It was identified early in the mine life that some of the designated waste rock contained metal sulfides that when exposed to oxidising conditions start to oxidise and produce more readily soluble oxidation products (acidity, sulfate and metals). Also, these soluble oxidation products potentially could be released from their confining rock mass by meteoric waters. These waste rock materials are referred herein as reactive waste. Managing this reactive waste rock during mining relies on a comprehensive understanding of the chemical and physical properties of the waste and selective placement according to The Mine's adopted waste rock dump design.

The presence of reactive waste necessitated that a set of management procedures be developed to ensure effective waste rock landform design to minimise impacts of AMD.

The procedures adopted at The Mine included:

- Construction of a geological model of the waste, based on the drill hole database;
- Waste chemical and physical properties characterisation using static testing methods for waste rock, soil and subsoil;
- Block modelling of waste rock and merging with the ore resource model, to create the life of mine (LOM) waste mining schedule;
- Design and construction of waste landform for containment and management of reactive waste, including final batter design, final cover system design, and erosion management;
- Design of water management for the waste landform;
- Validating the waste model using in-pit geological mapping;
- Selective handling and placement of waste in designated areas of the waste rock landform;
- Validating placement of waste within the waste rock landform;
- Monitoring for success of placement using piezometers within the waste rock landform, and downstream of this facility;
- Regular technical reviews monthly (internal), three to six monthly (external); and
- Implementing these procedures for Life of The Mine.

3.0 WASTE ROCK DUMP CONSTRUCTION

Critical to the successful implementation of the dump design at the mine site was:

- Characterising the waste rock types for physical and chemical properties prior to dump construction;
- Development of the geological model of the ore and host rocks (waste rock);
- Development of the integrated waste rock and ore block model;
- Daily pit mapping and mark out of waste types using in-pit sampling and field and laboratory testing to validate the geological model;

- Regular updating the waste block model;
- Building the WRD from base up including use of lifts <5m thick in barren waste and 2-3m thick lifts in reactive waste;
- Selective mining and placement of reactive waste in shallow lifts 2-3m using paddock dump dozing and vehicle compaction;
- Not placing reactive waste rock under batter slopes of the waste rock dump;
- Selective mining and placement of non-reactive waste rock in small lifts to encapsulate the constructed reactive waste cell;
- Complete the construction of each reactive waste cell, including placement of an interim cover layer over each completed cell, before the commencement of the rainy season;
- Identify low permeable layer construction material early in mine life and placed in dedicated stockpiles for future dump construction;
- Placement and compaction of silty clay material on all flat surfaces of the WRD that will be trafficked during construction, that formed interim compacted covers;
- Grade dump surfaces and use the compacted surfaces shedding layer to remove water from dump surface and minimise surface ponding within the dump precinct; and
- Establish a waste management team to coordinate, supervise and train mine staff in waste rock identification and management, and ensuring that critical knowledge was passed on to new staff prior to departure of employees. This knowledge included internal management systems: the geological model, the waste block model waste rock management plan for waste rock characterisation, in-pit mapping, WRD surface water management, the WRD design and its purpose, selective mining and placement of reactive sulfidic waste rock, and the need for regular auditing internal and external.

4.0 A COVER SYSTEM DESIGN FOR CLOSURE

4.1 Cover Systems in General

In general, the purpose of a cover system is reclamation of the surface mine waste storage facilities to provide a stable, and sustainable engineered interface between the receiving environment and the mine waste (INAP, 2017). A cover system supports agreed-upon returning land uses, and can be designed to: i) meet regulatory requirements; ii) divert incident meteoric (clean) water and reduce the volume of impacted surface water managed on site; iii) isolate chemically reactive waste material; iv) limit upward movement of process-water constituents and oxidation products; v) limit influx of oxygen and oxidation of certain minerals; vi) limit egress of radiation and radon gas (in the case of uranium mine waste); vii) limit influx of meteoric water to limit oxidation of certain minerals, and limit leaching and dilution of oxidation products; viii) control wind and water erosion of waste material as part of overall landform stability; and ix) provide a growth medium as the "building blocks" for establishing vegetation and ecosystems.

The International Network for Acid Prevention (INAP) classifies cover systems in the following general categories: i) erosion-protection systems; ii) store-and-release systems; iii) enhanced store-and-release system; iv) barrier-type systems; v) cover systems with engineered layers; and vi) saturated soil or rock cover systems.

INAP uses the Köppen-Geiger[6] climate classification system to conceptually characterise site-specific climate conditions because it allows for understanding of the 'first filter' for cover

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[6] https://en.wikipedia.org/wiki/K%C3%B6ppen_climate_classification

system design to be understood at an annual, and more importantly, seasonal basis. The Mine is situated in an Aw/As (tropical savannah) climate as per Köppen-Geiger. There is a relative moisture deficit on an annual basis (i.e. potential evaporation (PE) exceeds rainfall); however, due to strong seasonality of rainfall, during the rainy season there are periods when the PE to rainfall ratio is closer to 1.

4.2 Observations of AMD from the WRD

The typical result for reactive material within a WRD in this sort of climate is observation of AMD during WRD construction, and then continuation of these conditions following cessation of WRD construction, and indeed exacerbation of AMD as the WRD wets up and drains down. However, this was not observed during construction of the WRD described in this paper. In fact, the authors were afforded the opportunity to review the Mine's WRD performance approximately 15 years after the Mine commenced WRD construction and only one WRD seep was observed with elevated salinity and/or metalliferous water quality (sulfate concentration in the 500 mg/L range).

4.3 A Site-Specific Cover System for the Mine's WRD

We concluded from the review that the manner in which the WRD was constructed, and the commitment to a strategy of building the WRD from the ground up to minimise oxidation of reactive waste resulted in a WRD with substantively lower risk of AMD for closure. Typically, a WRD with this sort of reactive waste, and in this type of climate would require quite a complex cover system (e.g. a barrier-type cover system) to manage net percolation of water and oxygen ingress to very low to low ranges, and also collection and treatment of AMD well into closure, and more likely into perpetuity.

Instead, a much simpler cover system design was able to be planned for closure; namely, a store-and-release type cover system that primarily focused on providing sufficient water holding capacity for vegetation required to meet the WRD's returning land use, while also achieving acceptable erosion rates (i.e. a geomorphologically stable cover system / landform). The positive impact to final closure costs was substantial for the Mine,). This manifested in a number of ways, but primarily in lower CAPEX associated with cover system construction, collection and storage of WRD seepage water, and treatment of seepage water, as well as with lower OPEX associated with these same facets.

5.0 LOOKING BACK – WHY DID THIS WRD PERFORM SO WELL

5.1 Typical WRD Conditions

Typical run-of-mine (ROM) waste rock placement planning for a WRD (i.e. WRD construction), is a function of development and extraction of a site's ore resources, while also achieving geotechnical stability criteria for the WRD. Oxidation of sulfides in ROM rock is the primary source of acidity generated within a WRD; hence, availability of oxygen within WRD pore-spaces strongly influences this process. In addition, soluble and sparingly soluble minerals are also generated. Often, release of acidity from soluble minerals is not reflective of oxygen availability; rather, mobilization of these minerals is a function of pore-water movement (i.e. surface infiltration in the case of an uncovered WRD).

The manner in which a WRD is constructed results in differing internal WRD structure, and in turn differing WRD hydraulic performance. The most common WRD construction method is end-dumping given the two key drivers discussed earlier (i.e. lowest cost for extraction of the site's ore resources and attaining geotechnical stability). The height of an end-dump, or the lift height, is highly dependent on a site's location (e.g. open pit mining, ridgeline mining, etc.).

Natural segregation occurs due to end-dumping and typically results in a quite coarser-textured 'rubble zone' at the base of a WRD. In addition, segregation within the mine rock above this rubble zone tends to manifest in a combination of two ways; first, alternating coarser- and finer-textured bedding planes at angle of repose, and second, with a vertical profile of mine rock that is generally coarser-textured at the base of the WRD above the rubble zone, and becoming more finer-textured towards the top of the end-tipped lift. These two facets of mine rock segregation occurring as a result of end dumping, shown conceptually in Figures 1 and 2, coupled with the rubble zones at the base of an WRD lift, as well as relatively low internal WRD water content when the mine rock is placed, allows for relatively high airflow capacity within a typical WRD.

In the context of this paper, delineation of finer- and coarser-textured material is based on the percentage of material passing 4.75mm (#4 sieve), as shown in Figure 3; material is considered 'finer-textured' if more than 40% passes 4.75mm.

Figure 4 is a photograph of a cut through WRD revealing two end-dumped lifts of approximately 30m each, clearly shows the conceptual model for internal WRD structure shown in Figure 1. Also shown in Figure 4 are sonic drill core photographs and textural data from the sonic drill cores, both of which illustrate the second conceptual model for internal WRD structure shown in Figure 2. There is a gradual trend of material becoming coarser-textured towards the base of the lift, and then a finer-textured layer is encountered, which is the haul-truck compacted layer.

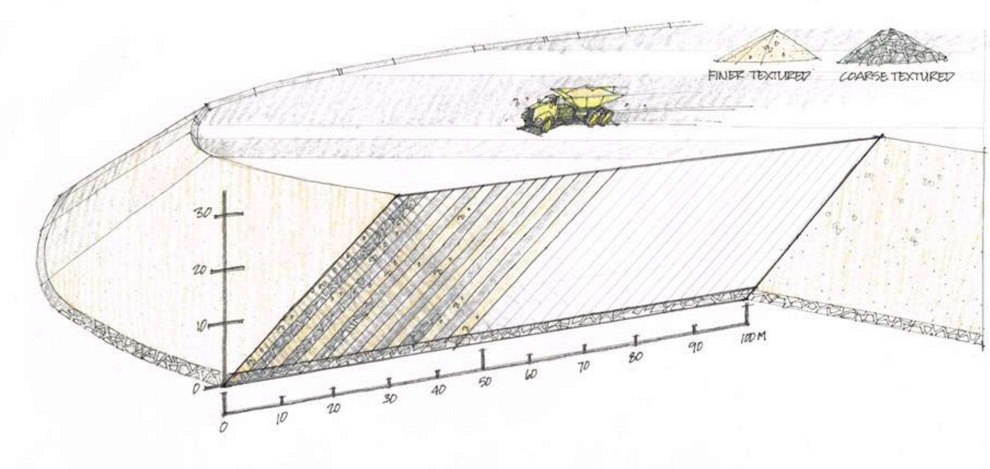

Figure 1: **Illustration of conceptual structure within an end-dumped WRD showing coarser- and finer-textured segregation at angle of repose (O'Kane 2018).**

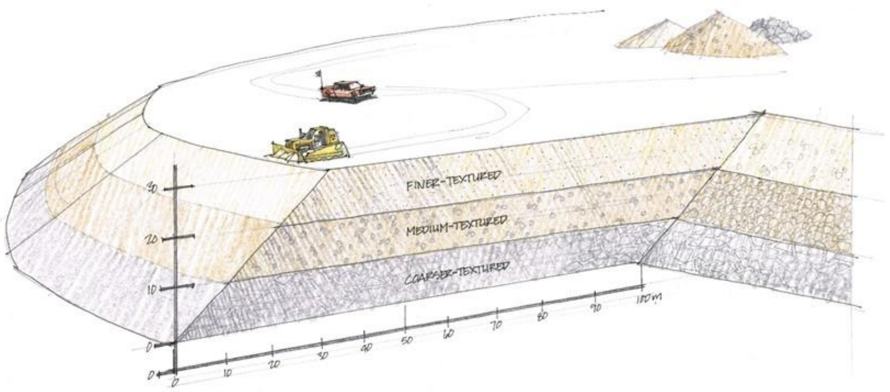

Figure 2: Illustration of conceptual structure within a WRD showing vertical gradation from coarser- to medium, to finer-textured segregation as a result of end-dumping (O'Kane 2018).

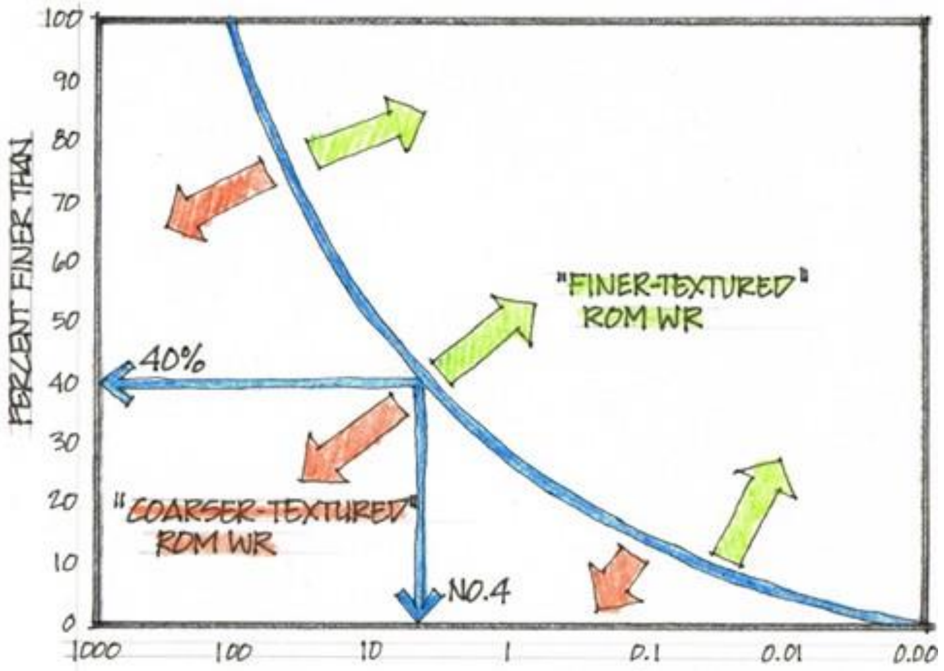

Figure 3: Definition of coarser- and finer-textured ROM rock material (O'Kane 2018).

Figure 4: Photograph of an end-dumped MRS showing finer- and coarser-textured layers at angle of repose, with sonic drill core photographs and percent passing the #4 sieve size (4.75mm); field data adapted from Pearce and O'Kane (2016).

In general, airflow capacity within a WRD is a function of bulk air permeability, which in turn is influenced by porosity (material texture), degree of saturation and continuity of the dominant texture. End-dumped WRDs typically result in material within the WRD having higher air permeability, which can change with time as the WRD 'wets up'[7]. Figure 5 conceptually illustrates wetting up for a WRD; in the example, initial volumetric water content (VWC) of the ROM rock is 0.05, and for the surface infiltration rate and hydraulic material properties assumed, the mine rock wets up to a VWC of 0.11.

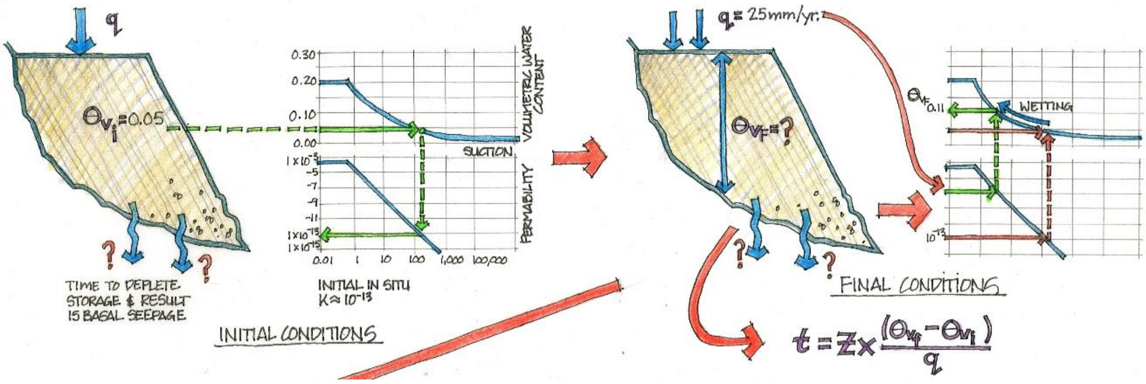

Figure 5: Conceptual illustration for wetting up of a WRD (O'Kane 2012).

Gas, and hence oxygen, moves within a WRD through diffusion and advection. However, given the WRD structural and hydraulic characteristics described, advection is generally more dominant; particularly while a WRD is being constructed and before any cover system is placed. Advection can transport oxygen deep into a WRD such that despite oxygen in pore-space that was at atmospheric conditions when placed, when this oxygen is consumed, there is sufficient airflow capacity to re-supply oxygen, provided the appropriate pressure gradient to drive this advective transport is present. This is shown conceptually in Figure 6.

Pressure gradients due to changes in barometric pressure and convective flows arising from thermal gradients influencing partial pore-air pressure, and thus gas density, result in advection (the movement of a gas as a result of the bulk motion of a fluid). In the context of WRDs temperature-driven convection is a dominant mechanism (Phillip et al. 2012). Therefore, establishing the potential for developing temperature-driven convection is a key facet for enhancing understanding for internal WRD sulfide oxidation, and therefore AMD risk on a site-specific basis.

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[7] Wetted up (and time to wet up): defined in this context as the condition where a 'drop of water at the surface of an MRS results in a pressure response at the base of the MRSF to 'push a drop of water' out the base. This does not represent pore-water velocity (the time for the 'drop of water' to move through the full height of an MRS). In addition, different areas of an MRS 'wet up' faster / slower due to material thickness, all other facets controlling wetting being the same; also, the material will drain due to gravity before the system is 'fully wetted up'. Hence, seepage from the base of an MRS will occur before an entire MRS is 'fully wetted up'. Finally, a 'wetted up condition' does not necessarily imply 'saturated conditions'; it simply describes the steady state volumetric water content of the material for the given surface infiltration (or net percolation) rate, depth of material, texture of material, etc.

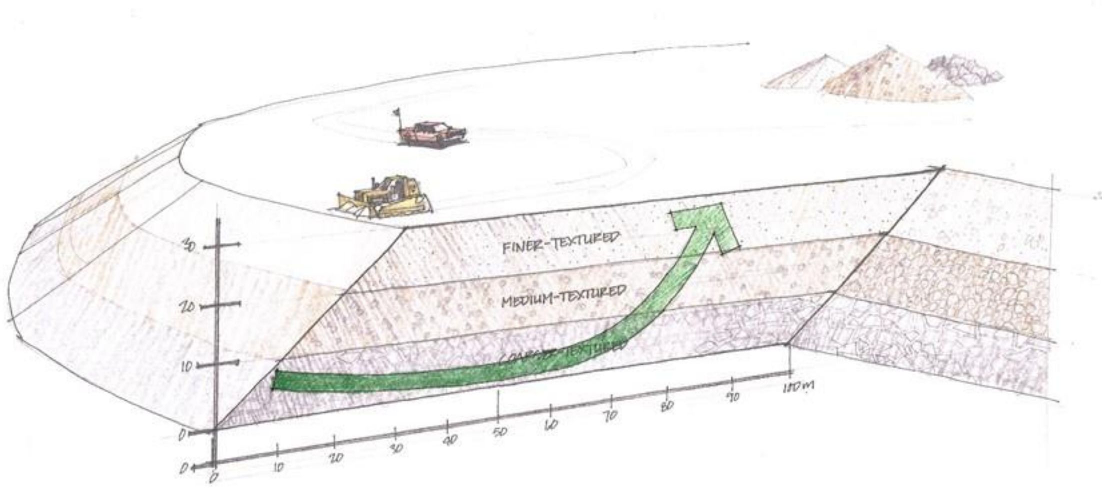

Figure 6: Conceptual illustration for gas transport into an MRS when sufficient airflow capacity exists within the MRS and there is an appropriate pressure gradient (O'Kane 2018).

To develop a conceptual understanding on a site-specific basis for the potential of temperature-driven convection at a site one can determine its Köppen-Geiger classification, and then relate potential seasonal temperature variations to likely internal WRD temperature conditions. For example, a site situated in a 'Dfa' region (hot summer, humid continental) will experience substantive changes in temperature during the year. In contrast, a site in an 'Af' region (tropical rainforest) will experience very little difference in temperature during the year. As a result, assuming each site had a WRD that was constructed similarly with a similar resulting structure (i.e. with high airflow capacity), the site in a Dfa region would have substantively greater potential for temperature-driven convection, and therefore sulfide oxidation within the WRD. Diurnal temperature changes will also strongly influence temperature-driven convection within a WRD and has the potential to re-supply substantive oxygen to internal WRD pore-space.

The key is to appreciate the importance of internal WRD temperature in relation to external ambient temperature, all within the context of internal WRD airflow capacity and WRD geometry.

Diffusion as an oxygen transport mechanism should not be discounted. In the context of a WRD, oxygen concentration gradients are formed by consumption or generation of a gas through processes such as oxidation or microbial activity. Gas diffusion rates depend on the degree of saturation of the near surface mine rock material (a function of mine rock material texture and density), as well as site-specific climate. Consideration should be given to the influence of exposed surface area for diffusive transport of oxygen into WRD; WRDs with plateau and slope areas that have sulfide bearing mine rock near the surface can result in substantive generation of acidity, depending on exposed surface area.

5.2 A Paradigm Shift – The Mine's WRD Performance

The essence of the discussion above in regard to typical WRD performance is that inherently a "typical" WRD constructed via end dumping will have potential for continuous re-supply of oxygen.

For the Mine, the Aw/As climate condition result in similar potential for temperature driven advective gas transport potential as the Dfs climate conditions described above. Hence, why was there no evidence, or observations, of AMD from the Mine's WRD, despite:

- The presence of reactive waste rock;
- Climate conditions that are essentially ideal for flushing of saline and metalliferous WRD pore water; and
- Temperature conditions ideal for temperature driven advective gas transport.

The reason is because of the manner in which the WRD was constructed; just as with typical WRD construction methods (end-dumping from high lifts, etc.), strongly influenced the Mine's WRD hydraulic behaviour, because of the different WRD construction methods (i.e. short lifts and layers on top of these lifts, the interim cover layers for managing rainy season infiltration). These short lifts minimised waste rock segregation and allowed for maximum potential for any neutralisation capacity that is present to be available to pore waters influenced by any sulfide oxidation. In addition, while the interim cover layers are very effective at extending out, and making for more homogeneous, wetting up, these layers also resulted in the intermittent, but consistent, presence of lower air permeability layers. Hence, bulk airflow capacity within the WRD as a whole was substantively reduced. And the result was substantive reduction in re-supply of any oxygen; this is shown conceptually in Figure 7. Ultimately, this resulted in less stored acidity, and therefore dramatic reduction in generation of saline and metalliferous pore waters.

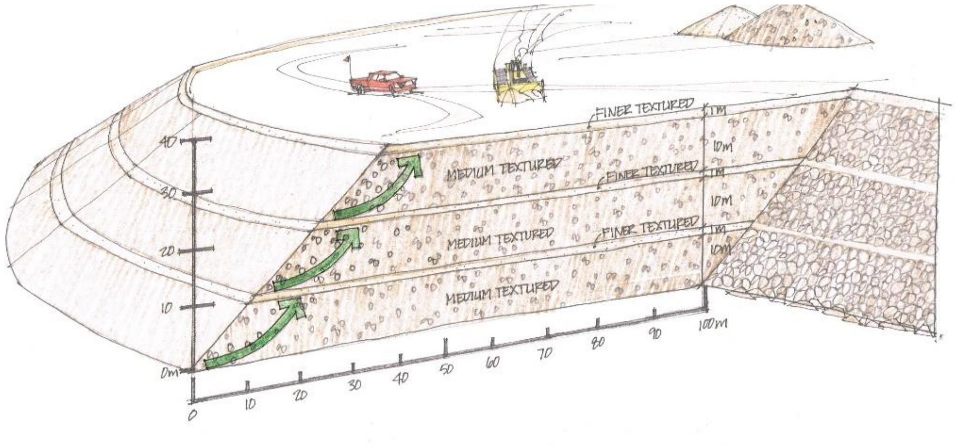

Figure 7: Conceptual illustration for gas transport for a WRD when vertical airflow capacity is limited within a WRD (O'Kane 2018).

The Mine's WRD was also constructed with paddock-dumped haul truckloads of non-acid forming (NAF) material, conceptually illustrated in Figure 8. The NAF material had quite low sulfide content, and this was able to consume any oxygen moving laterally before it was able to be present in pore gas within the PAF material.

The combination of paddock-dumped NAF material and the interim cover layers also substantively reduced the exposed surface area of PAF material for any extended time frame. Hence, acidity generation as a result of oxygen diffusion to near surface PAF material was minimised.

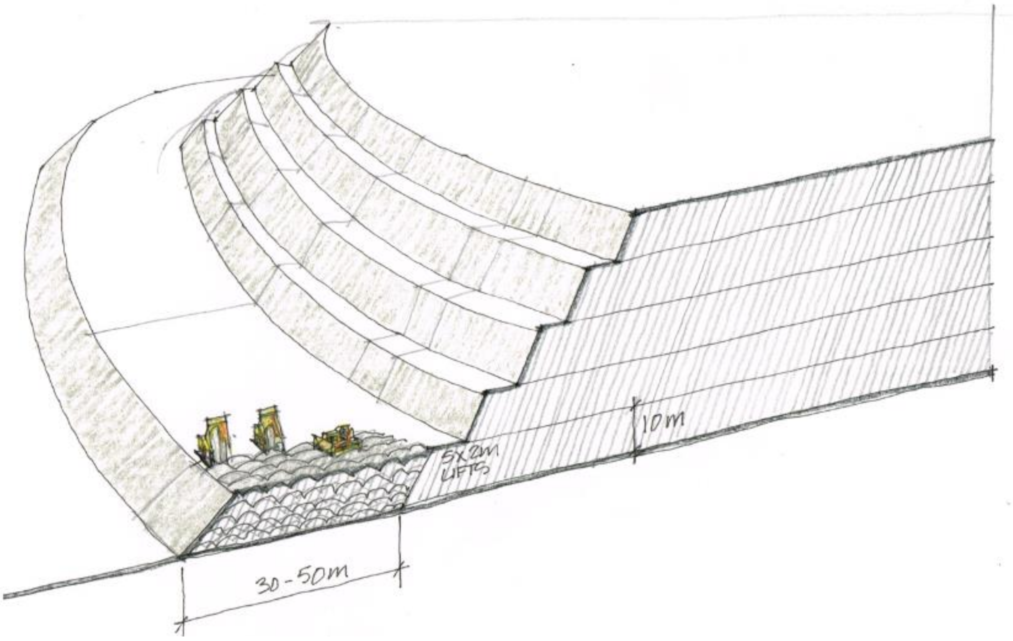

Figure 8: **Conceptual illustration for gas transport for a WRD when vertical airflow capacity is limited within a WRD (O'Kane 2018).**

6.0 CONCLUDING DISCUSSION

There were a number of contributing factors to limiting acid drainage being generated on a dump-wide scale at the Mine, including:

- Recognition early in mine life that reactive waste, potentially acid forming and metal leaching, was present in the host rocks to the ore and that this needed to be managed proactively throughout the mine life;
- The use of paddock dumping of PAF waste in dedicated cells within the WRD and avoiding end tipping, as well as avoiding placement under outer batter slopes, where surface infiltration from rainfall could not be controlled during WRD construction;
- The selective placement of low sulfide NAF waste to encapsulate the PAF waste;
- Construction of interim cover layers to limit incident rainfall and infiltration during waste rock placement;
- Minimising reactive rock oxidation by limiting vertical airflow capacity (from the interim cover layers), and lateral airflow capacity (from the paddock dumping), thereby limiting generation of stored acidity and salinity;
- Waste rock types were routinely mapped to reconcile the waste block model; and
- The formation of a waste management team comprising key staff including the Mine Manager, to oversee the management and prevention of acid drainage during the construction life of the waste rock dump.

Through better knowledge of materials characteristics and using this knowledge to selectively place mined waste in a waste rock storage landform (WRD), considered in the context of the climate and environmental setting allowed the objectives of design adopted by The Mine to be met.

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PREDICTION OF SPOIL SALINITY

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EXTENDED ABSTRACT

1.0 INTRODUCTION

The release of salts from spoil piles can potentially affect surface and groundwater quality and the quality of water in final voids. Current hydrogeochemical salt balance models often assume that the total amount of inherent salts in spoils will be released over time or predict that water salinity will increase into the future based on site monitoring data from electrical conductivity measurements. The closure and rehabilitation of spoil piles and final voids based on such model outputs is uncertain and may be overly conservative, expensive, and uncertain.

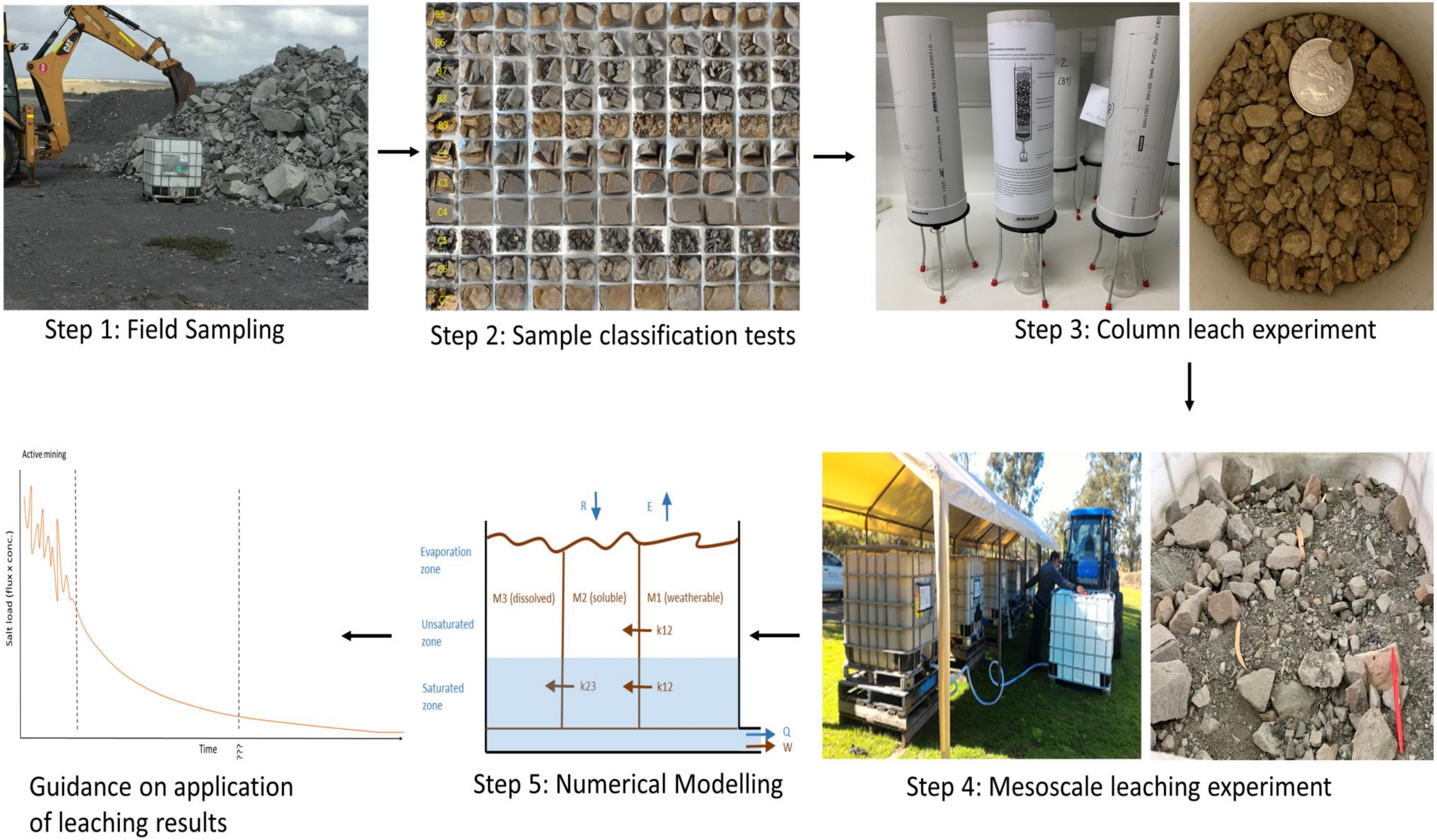
The overall aim of this project was to develop a process for estimating long-term salinity generation rates from different classes of mine spoil.

2.0 RESEARCH APPROACH

Figure 1 provides insights into the research approach adopted by the project. In the previous project (ACARP 25039-Prediction of long-term salt generation from coal spoils; Edraki et al, 2019) which was a precursor to current study, three sites in Bowen Basin were sampled. The focus was on Rangal and German Creek formations. In the current study, additional samples were collected from three new sites where spoils were sourced from Moranbah Formation and Tertiary rocks. Representative samples from two projects were selected for column and mesocosm experiments.

Two types of columns were designed: columns under unsaturated (wet-dry) conditions; and columns under saturation, to simulate intermittently saturated (middle zone) or completely saturated (lower zone) moisture regimes of spoil piles on a small scale. The unsaturated columns were leached fortnightly (over 68 weeks), weekly (over 34 weeks) and bi-weekly (over 17 weeks) to assess the effect of moisture regime on salt release. To better understand the role of pyrite oxidation in salt release, one saturated column was purged with nitrogen gas to create anoxic conditions, and results were compared with those of unsaturated columns.

With support from ACARP and in-kind contributions from The University of Queensland, a mesoscale (1-1.5 tonnes) spoil leaching test facility was set up at UQ’s property in Pinjarra Hills to bridge the gap between small scale laboratory tests and field monitoring of spoil piles. The aim of the mesoscale experiments was to simulate the leaching process closer to field conditions of spoil piles. In the absence of useful field data (saline seepages continuously monitored at the base of spoil piles), comparison of the mesoscale data with bench-top laboratory leaching data helped to understand the role of scale-up effects on the long-term salt release from spoils. The “as received” spoils were subjected to three different moisture conditions that spoils would normally experience in the upper, and middle, and the lower zones of the spoil piles (Simmons et al., 2015).



Step 1: Field Sampling

Step 2: Sample classification tests

Step 3: Column leach experiment

Step 4: Mesoscale leaching experiment

Step 5: Numerical Modelling

Guidance on application of leaching results

Fig. 1 ACARP C28043 General approach

The three different conditions of moisture or irrigation regime were: 1) Wet-dry, 2) Saturated, 3) Close to field or "natural' leaching using a rainfall simulator. The salt release rates and mechanisms were investigated by comparing two ends of the spectrum of spoil classes, i.e., soil-like and rock-like samples.

A simple numerical model that is applicable across two scales (column and mesocosm) was developed to investigate scaling of the kinetic parameters for fast leaching processes (nominally, the dissolution of salts exposed to flowing water in spoil macropores), and slow leaching processes (nominally encompassing the weathering of spoil particles, dissolution of the soluble fraction and diffusion of the solutes from the spoil matrix to macropores).

3.0 RESULTS AND DISCUSSION

The column experiment results showed release of salts depends on pre-disposal state of spoils with regards to weathering. The initial pulse depends on the physical and geochemical characteristics and degree of weathering and pre-disposal alterations. Rocks may have experienced geologic alterations and weathering prior to mining. The initial mineralogy and "geogenic" salt, volcanic lithic fragments and authigenic minerals content is important. The oxidation of pyrite can also contribute to the dissolution of salts from spoils even at very low concentrations.

The drainage volumes and duration of water-rock interaction are also important. Overall, saturated leaching released the highest salt concentration and longer cycles (fortnightly cycle rather than weekly) in cases produced more salts showing the role of interaction time. Despite the above variations, under the column set up most spoils released saline leachates early and reached the quasi-steady state at 10-12 cycles (equivalent to cumulative depth of 700 mm-840 mm drainage). Beyond that, to the end of the experiment at 34 cycles, there was not a significant change in the salinity of leachates. This is important from the perspective of predicting the time to reach a quasi-steady state which seems to be relatively short. The results showed that it may not be necessary to run the column leaching test for a long time to predict spoil salinity. 3-4 months could be enough time. Initial EC, mineralogy, and total salt content and degradation tests can complement column leaching results, but cannot be used as proxies. For example, degradation tests on a piece of rock may predict resistance to breakdown and physical weathering, but not chemical weathering which can be assessed through column leaching tests.

The trends of salt release from spoils in the mesocosm experiments were investigated considering the potential influence of 1) the volumes of rainfall infiltration, 2) the spoil properties in particular the initial mineralogy and salt content, 3) the water/rock interactions and water residence time. Irrespective of the amount and rate of rainfall or irrigation of samples (in this case; wet-dry, saturated or simulated rainfall) the rock-like spoils showed an initial relatively short-lived rise of salinity followed by a gradual, long-term and apparently stable level of salt release per cycle. Comparison of calculated decay rates at early stages with those at late stages showed that the release of less soluble minerals (e.g. carbonates) was more sustained. The salt release rates were higher in the case of saturated mesocosms. In the case of soil-like spoils, the irrigation regime played an important role. Under wet-dry or saturated leaching conditions, samples lost a greater amount of salts particularly in the initial leaching cycles. When samples were leached at rainfall rates closer to field conditions the response of salt release was steady or even increasing for the duration of the experiments. This showed the importance of hydrology in driving the chemistry of salinity of seepage. The mesocosm tests showed that spoils generate increased concentrations of salt as they breakdown over time. However, in some cases that breakdown reduces hydraulic conductivity to such an extent that drainage and salt loads are minimal.

From the perspective of spoil characterisation and predicting potential salt release. The (1 Soil: 5 water) electrical conductivity measurements may under-represent the salinity generating capacity of a spoil. Even though these tests are performed on <2mm size fraction, salts may not be leached that will be leached following spoil weathering. Changes in spoil mineralogy due to weathering, in particular the release of geogenic sources of salinity, are important. In the characterisation of spoils for prediction of salinity, the definitions of rock-like and soil-like are important. A spoil that may seem rock-like due to the presence of larger fragments may breakdown fast and may lose most of its geogenic salts early because of high rate of degradation. For this reason, degradation tests can be useful to estimate the degradable fraction as part of spoil classification (Figure 1, step 2).

The comparison of calculated salt decay rates for columns and mesocosms showed that samples tested in mesocosm release salts at a lower rates which are likely more similar to those in real spoil piles.

The kinetic parameters were principally dependent on drainage rates per unit area. After removing the effect of drainage rate, the scale factors moving from column to mesocosm for three pairs of samples, each pair having similar moisture conditions and spoil types, were 0.13, 0.05, 0.29 for the slow-process parameter and 0.91, 0.23, 0.14 for the fast process parameter.

The inter-dependencies between particle size, drainage rate, spoil moisture and pore volumes in the experiment create ambiguity regarding their degree of influence on these scale factors. Modelling showed the long leaching half-lives of hundreds to tens to thousands of years under the meso-scale experimental conditions. Simple, quasi-steady leach rate models superimposed on spoil hydrology models, which sufficiently represent the flow and moisture distribution in the spoil pile, may be used to provide estimates of long-term salt loads to the environment after appropriate spoil characterisation and scale factor application.

Under field conditions the rates and volumes of water and the chemistry of rainwater is different. Column leaching tests over-estimate salt release due to the increased reactivity of de-ionised water and due to the increased flow rates per unit spoil. It is intuitive that medium scale (mesocosms) are closer to field conditions with respect to spoil salinity predictions. But the “natural” mesocosms showed that saline water may not appear at the base of spoil piles because spoils could degrade to a state that they become non-conductive to infiltration.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Laboratory column leaching experiments showed 3-phases of salt release. 1) leaching of readily available salts, over the first one-three wetting-drying cycles; 2) Phase 2 – recession from the peak to quasi-steady conditions during next 2-10 cycles; 3) Phase 3- quasi-steady leaching where slow weathering processes limit salt concentrations. The mesocosm data showed that the half-life of salt decay would be at least 1,300 years if it is assumed that a realistic drainage rate for a spoil pile is 0.1 m/year. The long time-frame justifies assuming a quasi-steady value (that varies from year to year with drainage rates driven mainly by climate). The results indicate that the leaching rates derived from the mesocosm experiments in units g/kg/day would be conservative for real spoil piles mainly because of high mesocosm flow rates and the assumption that full volume of mesocosms was contributing to the salt leach process. The salt decay parameter which expresses leaching rates in g/kg/m (i.e. decay per meter of drainage) are potentially more transferrable to real spoil dumps. The primary factors affecting salt leaching rates were flow rates (positive correlation), particle size (negative correlation), and degree of saturation (positive correlation).

Considering the limitations of the column and mesocosm experiments, the next logical step would be to validate models through field monitoring of spoil piles to better understand the spatial and temporal distribution of moisture (and water tables) inside the piles. A field approach could benefit from advanced field-based tools such as geophysical and isotope tracer methods.

5.0 REFERENCES

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